PFC Emissions from Detected Versus Nondetected Anode Effects in the Aluminum Industry

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Perfluorinated carbon compounds (PFCs) CF_4 and C_2F_6 are potent greenhouse gases that are generated in aluminum reduction cells during events known as anode effects (AEs). Since the 1990s, the aluminum industry has made considerable progress in reducing PFCs from conventionally defined and detected AEs. However in recent years, the industry has noted the presence of unaccounted PFCs that are generated outside the conventional AE definition. Two additional AE categories have been proposed, namely low-voltage, propagating AEs (LVP-AEs) and nonpropagating AEs (NP-AEs) that relate to continuous, background levels of PFC emissions. These unaccounted PFC phenomena may help explain the recent discrepancy between industry accounting and atmospheric measurements of global PFC emissions. Estimates from AGAGE, a global network of atmospheric observatories, suggest as much as 50% underaccounting of PFCs by the aluminum industry in the 2006–2010 period. The following work reviews this discrepancy and the potential role played by LVP-AEs and NP-AEs.

INTRODUCTION

Anode effects (AEs) are detrimental process events that have long been a topic of study and research in the primary aluminum industry. In the Hall-Héroult process, AEs are responsible for the generation of potent perfluorocarbon (PFC) greenhouse gases tetrafluoromethane (CF_4 or PFC-14) and hexafluoroethane (C_2F_6 or PFC-116). CF_4 and C_2F_6 each have respective global warming potentials (GWPs) of 6,630 and 11,100 times equivalent of carbon dioxide (CO_2), with extremely long atmospheric lifetimes of 50,000 and 10,000 years, respectively.[1] 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.[2]

PFC generation from AEs has traditionally been associated with a rapid, exponential increase in total voltage measured across a reduction cell. Therefore, AEs are typically detected by 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 for more than 3 consecutive seconds.[3] However, the trigger voltage used to declare an AE can vary from as low as 6 V to as high 10 V across the industry.[2] Similarly, trigger durations used to confirm an AE can range from 1 to 3 s to as much as 90 s (as noted by the authors in some Chinese smelters). These definitions form the basis for AE performance statistics—namely the frequency and duration—which are used in the global aluminum smelting industry to account for total PFC emissions for a smelter.[4,5] In this article, AEs defined by this method are termed "conventional" AEs.

In recent years, the discovery of PFC emissions in absence of any "detected" or officially declared AEs by control systems has sparked considerable interest in the aluminum smelting community, evidenced by numerous studies on the subject in the past years.[2,6–10] PFCs generated in such scenarios are not declared by smelter control systems as "anode effects" as they are either:

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(I) *Low-voltage anode effects* that have discrete 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.

(II) *Continuous background emissions of PFCs* that do *not* appear to have the same discrete voltage and PFC emission characteristics as conventional (>8 V) and low-voltage (<8 V) AEs.

While these two scenarios are sometimes referred to as non-anode effect (NAE) emissions,[2,6–10] mounting evidence suggests that PFC generation in both scenarios is initiated by the same fundamental mechanisms as conventional anode effects. However, the major difference is likely to be how and whether these anode effects are propagated within the cell. As such, in this article the authors refer to (I) the first scenario as low-voltage propagating anode effects (LVP-AEs) and (II) the second scenario as nonpropagating anode effects (NP-AEs).[11]

While background PFC emissions are described here on an individual cell basis, unaccounted PFCs are often measured in gas ducts or stacks from an entire potline or section of cells (e.g., 100 cells). At this level, the measured background PFC levels might be partly due to the cumulative impact of nondetected LVP-AEs from a large population of cells rather than NP-AEs occurring on individual cells.

The discrepancy between detected and undetected AEs might, at least in part, explain the growing discrepancy between the industry's accounting of global PFC emissions (referred to here as bottom-up estimates) and global atmospheric measurements of PFCs (referred as top-down estimates).[12] This article sets out to discuss the differences between detected and nondetected AEs and points to the potential impact of nondetected AEs on global PFC accounting.

INDUSTRY ACCOUNTING AND ESTIMATES OF GLOBAL PFC INVENTORY

Intergovernmental Panel on Climate Change (IPCC) Methodology for PFC Accounting

Accounting of PFC emissions from aluminum smelters is carried out with a three tiered methodology as set out by the IPCC.[5] The IPCC Tier 1 method involves estimating the smelter's PFC emissions by multiplying a smelter's annual metal production with a given coefficient based on the technology class used.[5] Because no AE process data are employed in this methodology, it is deemed less accurate than the more detailed methods Tier 2 and Tier 3.[5,13]

IPCC Tier 2 and Tier 3 methods involve multiplying two performance statistics for conventional AEs—average anode effect frequency (AEF, number of anode effects per cell day) and anode effect duration (AED, in minutes)—by the facility's annual aluminum production (MP) and emission coefficients (slope coefficient, S_{CF_4} and weight frac-

tion of C_2F_6 to CF_4 emissions, $F_{C_2F_6/CF_4}$). Calculations are generally carried out on monthly average data and then summed to obtain annual emission outputs. Emission coefficients S_{CF_4} and $F_{C_2F_6/CF_4}$ are based either on the smelting technology class employed (Tier 2, shown in Fig. 1) or from specific coefficients obtained by direct measurements at that smelter (Tier 3):[5]

$$EF_{CF_4} = S_{CF_4} \cdot (AEF \cdot AED) \cdot MP$$
$$EF_{C_2F_6} = EF_{CF_4} \cdot F_{C_2F_6/CF_4}$$

For facilities with a control system not recording AEF and AED statistics, the overvoltage method is used, where OVC is the overvoltage coefficient for the technology class (Fig. 1), AEO is the anode effect overvoltage recorded by the system, and CE is the current efficiency of the facility:[5]

$$EF_{CF_4} = OVC \cdot \frac{AEO}{CE/100} \cdot MP$$
$$EF_{C_2F_6} = EF_{CF_4} \cdot F_{C_2F_6/CF_4}$$

Note that AE performance statistics used in the Tier 2 and Tier 3 IPCC methods are collated by the smelter's control system based on continuously recorded cell voltages. These conventional AEs are detected by control systems only after cell voltages exceed a predefined threshold limit and duration. Therefore, the PFCs emitted while a cell is below AE voltage thresholds are not accounted for with the current IPCC methodology.

International Aluminium Institute (IAI) Anode Effect Surveys

Global accounting of PFCs emissions in the aluminum smelting industry is conducted by the IAI through voluntary participation of smelters to an annual anode effect survey.[13] Participating smelters are asked to disclose AE performance statistics, principally annual average AE frequency and duration (AEF and AED), along with information on the number of operating cells and the smelting technology class employed.[13] The IPCC methodology is then applied to estimate total PFC emissions for each smelter. Seventy-eight percent of aluminum production outside China was covered in this manner for the most recent 2013 annual survey.[13] As Chinese smelters do not directly participate in the survey, the global participation rate was equivalent to 40% of the annual world production for this period.[13]

Emissions from nonparticipating smelters are estimated from different sources. For many of these nonparticipating smelters, median emission coefficients of similar technology classes are applied. In the 2013 annual survey, IAI used median emission coefficients from direct measurements of 27 Chinese

TABLE 4.16
TECHNOLOGY SPECIFIC SLOPE AND OVERVOLTAGE COEFFICIENTS FOR THE CALCULATION OF PFC EMISSIONS FROM
ALUMINIUM PRODUCTION (TIER 2 METHOD)

Technology[a]	Slope Coefficient[b,c] [(kg $_{PFC}$/t$_{Al}$) / (AE-Mins/cell-day)]		Overvoltage Coefficient[b,c,d] [(kg $_{CF4}$/t$_{Al}$) / (mV)]		Weight Fraction C_2F_6 / CF_4	
	CF_4	Uncertainty (+/-%)	CF_4	Uncertainty (+/-%)	C_2F_6/CF_4	Uncertainty (+/-%)
CWPB	0.143	6	1.16	24	0.121	11
SWPB	0.272	15	3.65	43	0.252	23
VSS	0.092	17	NR	NR	0.053	15
HSS	0.099	44	NR	NR	0.085	48

[a] Centre Worked Prebake (CWPB), Side Worked Prebake (SWPB), Vertical Stud Søderberg (VSS), Horizontal Stud Søderberg (HSS).

[b] Source: Measurements reported to IAI, US EPA sponsored measurements and multiple site measurements (U.S. EPA and IAI, 2003).

[c] Embedded in each Slope and Overvoltage coefficient is an assumed emissions collection efficiency as follows: CWPB 98%, SWPB 90%, VSS 85%, HSS 90%. These collection efficiencies have been assumed based on measured PFC collection fractions, measured fluoride gas collection efficiencies and expert opinion.

[d] The noted coefficients reflect measurements made at some facilities recording positive overvoltage and others recording algebraic overvoltage. No robust relationship has yet been established between positive and algebraic overvoltage. Positive overvoltage should provide a better correlation with PFC emissions than algebraic overvoltage. Overvoltage coefficients are not relevant (NR) to VSS and HSS technologies.

Fig. 1. Slope and overvoltage coefficients (including uncertainty) for the IPCC Tier 2 method, grouped by smelting technology class (reproduced from the 2006 IPCC Guidelines for National Greenhouse Gas Inventories).[5]
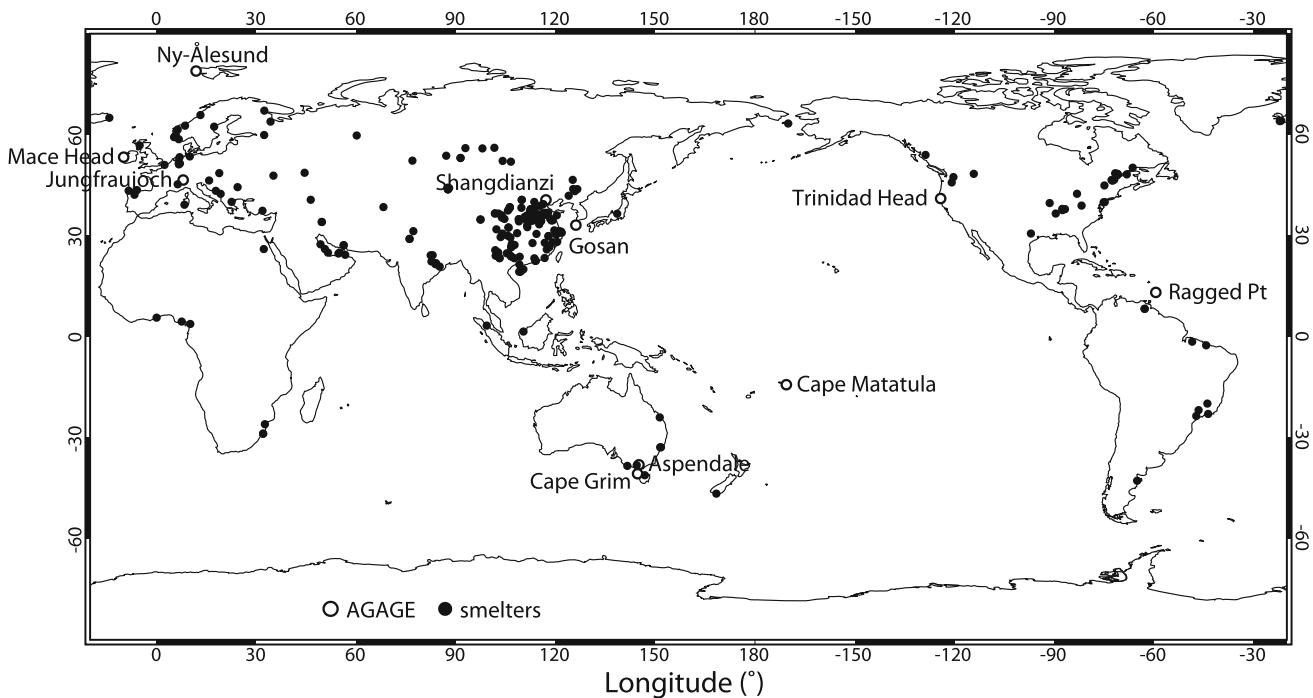

Fig. 2. Locations of AGAGE PFC atmospheric observatories (○) (Mühle et al.[20]) and global aluminum smelters (●).[31]

smelters (2008–2013 period) to infer total PFC emissions for the rest of the nonreporting Chinese industry;[13] this was for the point-fed prebaked (PFPB) technology class that is now the exclusive technology in China. The emission coefficient found in these Chinese smelters (0.80 tonnes CO_2-equivalent per tonne of aluminum produced) was roughly four times higher than similar technology used

outside China (0.20 t CO_2-eq/t Al).[13] Because Chinese emission coefficients were obtained via direct ratios of total PFC emissions measured divided by metal production rates (i.e., rather than using AE performance statistics that do not capture nondetected AEs), the coefficients do encompass PFC emissions from both detected and nondetected AEs.[14] However, as it is similar to a Tier 1 accounting approach (but tailored specifically to the Chinese sector), there are still inherent levels of uncertainty when using such an estimate. Finally, although usage of median coefficients (rather than averages) removes the effect of measurement outliers and abnormal situations encountered, it can result in underestimation of emissions where the statistical distribution of data is skewed toward lower emission coefficients. Subsequent measurement and surveys of the Chinese industry is required for a more accurate assessment.[14]

In light of these uncertainties, a comparison has been made between the industry's bottom-up approach for accounting of PFC emissions versus a top-down approach using atmospheric measurements.

ESTIMATING PFC EMISSIONS FROM GLOBAL ALUMINUM PRODUCTION: INDUSTRY ACCOUNTING (BOTTOM-UP) VERSUS ATMOSPHERIC OBSERVATIONS (TOP-DOWN)

AGAGE Network for Global Atmospheric PFC Estimates

Primary aluminum production is one major anthropogenic source of perfluorocarbons CF_4 (PFC-14) and C_2F_6 (PFC-116). However, both PFCs are also released to the atmosphere by the microchip manufacturing component of the semiconductor industry and, to a minor extent, by the refrigeration[12,15–21] and the rare-earths industries.[22,23] Although trace amounts of octafluoropropane (C_3F_8, PFC-218) have also been found in aluminum smelter exhaust stacks, these are not in sufficient quantities to impact significantly on total PFC emissions.[17,24] As with the aluminum industry, the semiconductor industry has undertaken voluntary mitigation activities to reduce their PFC emissions.

In the production of rare-earth metals by electrolysis, PFC generation is possible where fluoride-based melts (an alternative being chloride-based melts) and carbon anodes are used.[22,23] Despite a rapid growth in the industry after the 1990s (particularly in China), the scale of global rare-earth metal production is minor compared with global aluminum production (roughly 0.1% of aluminum in 2013, based on global rare-earth oxide versus metallurgical-grade alumina output[25,26]). Although there is a lack of information on emission factors, current production figures suggest that the rare-earths industry is unlikely to be a major contributor to global PFCs.
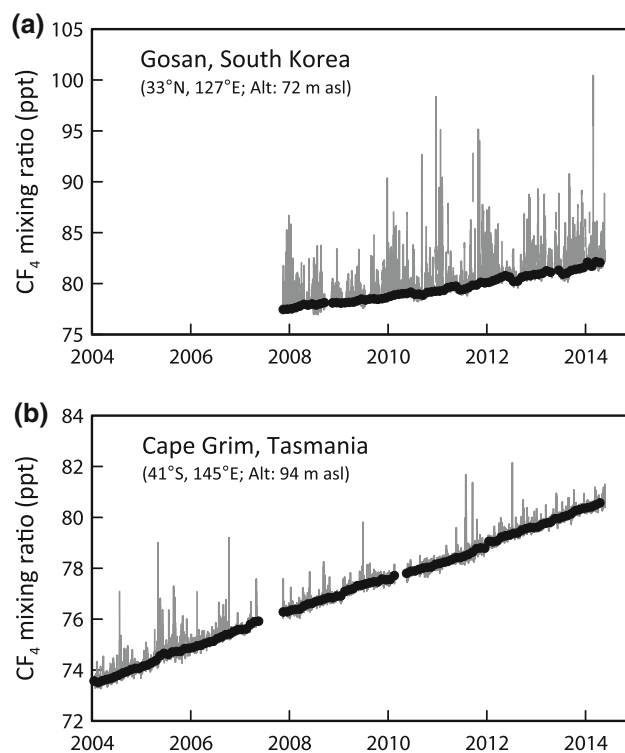

Fig. 3. CF_4 (PFC-14) observations (ppt: parts per 10^{12} molar) at (a) Gosan, S. Korea, and (b) Cape Grim, Australia; gray total data (every 2 h), black background monthly means.[12,20,28,30]

The advanced global atmospheric gases experiment (AGAGE) is an international network (Fig. 2) of state-of-the-art atmospheric observatories designed to measure continuously the global and regional atmospheric concentrations of non–carbon dioxide greenhouse gases, such as hydrofluorocarbons and PFCs. AGAGE commenced PFC measurements in 2004 at Cape Grim, Australia, and in 2007 at Gosan, South Korea (Fig. 3), deploying virtually identical gas chromatography–mass spectrometry instruments[27] throughout the network using common analytical methods, trace gas calibration, and data processing protocols.[28] Global PFC measurements back to the 1970s have been obtained from atmospheric and ice core measurements[15,16,19,29] and from measurements on northern hemisphere and southern hemisphere air archives.[20,30] The resultant data have been used by atmospheric modeling teams to derive global and national emissions of PFCs.[12,18–21,29,30] These atmospheric measurements have shown that significant fractions of the global emissions of these two PFCs remain unaccounted for in emissions reported by the aluminum and semiconductor industries.[12,20]

Characteristic C_2F_6/CF_4 Emission Ratios for Aluminum and Semiconductor Industries

CF_4 and C_2F_6 are both emitted in significant quantities during aluminum production and semiconductor manufacturing, but in different propor-
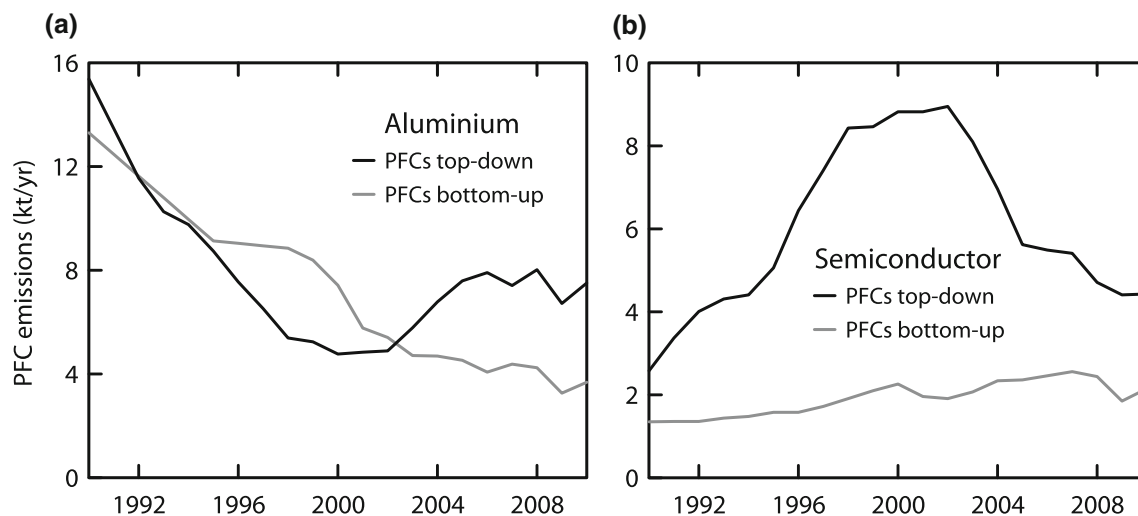
Fig. 4. Total PFC emissions (kt, sum of CF_4 and C_2F_6 emissions) from the (a) global aluminum and (b) semiconductor industries, estimated from atmospheric observations (top-down) and as reported by the respective industries (bottom-up) (from data reported by Kim et al.[12]).

tions. Characteristic C_2F_6/CF_4 emission ratios for the aluminum production and semiconductor industries have been measured at AGAGE stations where the emissions from each industry can be clearly isolated and defined.

For the aluminum industry, more than 100 PFC plumes from the Portland, Point Henry, and Bell Bay smelters have been identified in the AGAGE measurements at Cape Grim (Tasmania, Australia, Figs. 2, 3) and Aspendale (Victoria, Australia) using air mass back trajectories.[12,20,30] Australia does not have a semiconductor manufacturing industry, and there are no significant imports into or production of PFCs in Australia. These Australian PFC plumes result almost entirely from emissions from aluminum smelters. A resulting mean C_2F_6/CF_4 mass emission ratio of 0.10 ± 0.01 kg/kg was obtained based on the fit to the Cape Grim and Aspendale data (2004–2010) from the Australian smelters.[12] This PFC emission ratio for the aluminum industry is in very good agreement with previous estimates, including: (I) measurements of smelter-impacted air samples from the early 1970s that consistently suggest a mass emission ratio of 0.1 kg/kg (as reported by Mühle et al.[20] and references therein), (II) global aluminum industry reported emission ratios from the IAI[32] for 2006–2012 (0.11 ± 0.01 kg/kg) and 2012 (0.10 ± 0.01 kg/kg), as well as (III) an emission ratio of 0.11 ± 0.02 kg/kg measured at another Australian aluminum smelter (Kurri Kurri) by stack sampling of smelter exhaust gases in 2008 and 2009.[30]

For the semiconductor industry, AGAGE measurements at Gosan Station (Jeju Island, South Korea, Figs. 2, 3) have been used to characterize PFC emission plumes from South Korea, Japan, and Taiwan from January 2008 to December 2010, using air mass back trajectories, where only very limited aluminum production occurs.[12,21,33] The semiconductor

production capacity in these three countries comprised about 60% of global production in 2011, and PFC emissions in these countries are almost entirely from the semiconductor industry.[12] The mean PFC emission ratio for the semiconductor industry (0.40 ± 0.19 kg/kg) is based on the averaged emission ratios for South Korea (0.35 ± 0.01 kg/kg), Japan (0.51 ± 0.05 kg/kg), and Taiwan (0.34 ± 0.05 kg/kg); each country's factor is weighted by its reported semiconductor manufacturing capacity.[12]

These industry-specific PFC emission ratios (0.10 ± 0.01 kg/kg for aluminum and 0.40 ± 0.19 kg/kg for semiconductor industries, respectively) are assumed to be time invariant and apply across the global aluminum and semiconductor industries. These values are used to characterize the mix of PFC sources that generates PFC plumes from regions that contain both aluminum production and semiconductor manufacturing industries, for example, China. With this approach, for the first time, atmospheric PFC measurements have been used to separately estimate these two major global PFC sources from 1990 to 2010. This is shown in Fig. 4 (Kim et al.[12]).

Atmospheric Versus Industry PFC Estimates for Aluminum and Semiconductor Industries

Atmospheric data show that annual PFC emissions from aluminum production declined from more than 15 kt in 1990 to less than 5 kt in 2000–2002, representing a 67% reduction in emissions compared with 1990 (Fig. 4). Atmospheric measurements confirm the significant progress made by the aluminum industry in its voluntary response to reducing PFCs. However, from 2002 onward, annual PFC emissions increased again, to nearly 8 kt by 2010 (Fig. 4).

Over the entire period 1990–2010, the estimates of total PFC emissions from aluminum production,
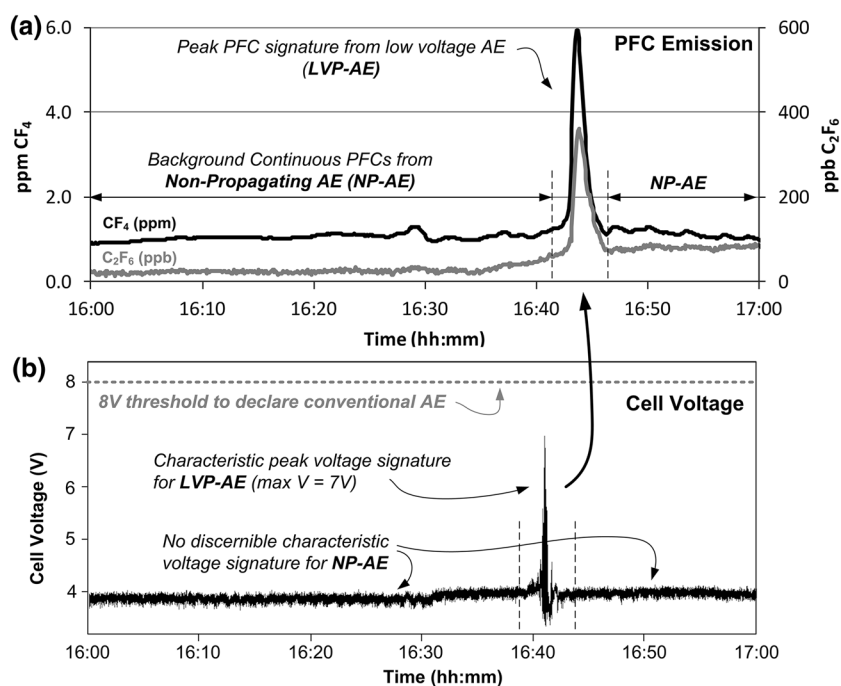
Fig. 5. (a) PFC emissions (ppm CF_4 and ppb C_2F_6) and (b) cell voltage from a single 400-kA cell during a 1-h monitoring period with LVP-AE and NP-AEs (adapted from Ref. 11).

based on atmospheric data (166 kt) and as estimated by the aluminum industry (155 kt), agree very well (within 7%). However from 1996 to 2002, the aluminum industry overestimated their PFC emissions by nearly 40%, and from 2003 to 2010 PFC emissions were underestimated by about 40%.

In the semiconductor industry, annual PFC emissions increased from less than 3 kt in 1990 to nearly 9 kt in 2002, declining to just over 4 kt in 2010 (Fig. 4). The semiconductor industry has consistently underestimated their PFC emissions over the entire period 1990–2010 by nearly 70%: 126 kt from atmospheric data compared with 40 kt estimated by the industry.

During the period 1990–2010, the underreporting of PFC emissions by the semiconductor industry has driven the global imbalance between PFC emissions estimated from atmospheric observations (top-down estimates) and by industry (bottom-up estimates). However, for the 5-year period 2006–2010, both industries appear to have underestimated their PFC emissions by roughly 50%, with aluminum production emitting 38 kt compared with an industry estimate of 20 kt, and semiconductor production emitting 24 kt compared with an industry estimate of 11 kt.

Sources of Discrepancy in the Aluminum Industry

For the aluminum industry, overestimates by the industry in the 1992–2002 period might be due to a higher proportion of smelter emissions being accounted for with less accurate methods. For instance, IPCC Tier 1 accounting methods (with very high uncertainties, not best practice[5,13]) could have been used more predominantly until more accurate Tier 2 (still with uncertainties up to $\pm50\%$[13]) or facility-specific Tier 3 methods (up to $\pm15\%$ uncertainties[13]) became available in later years.

From 2002 onward, however, atmospheric measurements show a significant underaccounting of global PFCs by the industry. Kim et al.[12] have suggested that this coincides with the very rapid growth of aluminum production in China, increasing from 11% of global production in 2000 to 43% of global production by 2013.[34] As outlined previously, one source of discrepancy is the lack of participation from Chinese facilities in the IAI's industry AE surveys. This results in a significant gap in the industry's ability to accurately account for global PFC production.[13] However, it is acknowledged that efforts have been made to account for Chinese non-reporting facilities, using median emission coefficients (0.80 kg CO_2-eq/t Al) and Chinese metal production figures.[13]

A second significant source of discrepancy is the presence of nondetected anode effects in aluminum smelters—namely, LVP-AEs and NP-AEs, associated with background, continuous levels of PFC emissions. Both these events have been measured in Chinese and non-Chinese facilities, with some correlation with facilities operating higher amperage (>300 kA) and large PFPB reduction cell technologies.[9,11] These technologies now make up the entirety of newly installed production capacity, not

only in China but also in other parts of the world. It should also be noted that nondetected AEs have also been measured on lower amperage (<300 kA), smaller cell technologies.[35,36] While indications are that nondetected AEs have lower or at least similar C_2F_6/CF_4 emission ratios as conventional AEs,[7,8] further work may be required to confirm this.

Both categories of nondetected AEs are not accounted for in current IPCC Tier 2 and 3 methods because both types of AEs are not detected by smelter control systems. This therefore represents a significant area of uncertainty for industry accounting of PFCs, not only for the Chinese sector but also abroad. Nondetected AEs are examined further in the remainder of this article.

Discrepancies From Inconsistent Trigger Durations for Conventional AEs

It should be noted that in some smelters (particularly those in China), the trigger duration used by the control system to automatically declare, or alarm smelter operators of, an AE can differ from that used to record an official AE in the smelter's performance statistics. In these facilities, a similar cell voltage >8 V for >3 s trigger definition might be used to alarm smelter operators to terminate an AE on a reduction cell (or for the control system to terminate the AE automatically). However, a *longer* trigger duration might be used to register an official AE, for example, cell voltage >8 V for durations ranging from >15 s up to as much as >90 s. AEs that are shorter than these official reporting durations are regarded as "twinkle" AEs and are not recorded in official AE performance statistics (i.e., AE frequency and duration). This undoubtedly results in underaccounting of PFCs from conventional AEs if such data are used in accordance with IPCC Tier 2 or 3 methods. In this work, the authors refer to any AE that is first declared or alarmed by the control system (>8 V for >3 s or similar) a conventional AE.

UNACCOUNTED PFCS FROM NONDETECTED ANODE EFFECTS

PFCs not attributed to conventional AEs (detected by smelter control systems using a cell voltage trigger threshold) have been reported in operating smelters as early as 2003.[37] At the time, these were predominantly due to measurement artefacts caused by leakage of PFCs from cells outside those targeted.[37] From 2011 onward, however, systematic reductions in AEs and growing awareness of PFCs from nondetected AEs have led to multiple smelter-based studies of unaccounted PFCs being published, as summarized in Table I. Several aspects can be gathered from this table.

First, it is clear that unaccounted PFCs occur not only in Chinese smelters but also in facilities outside of China. For instance, Marks and Bayliss' recent survey of Chinese and non-Chinese facilities[2]

reported 70% and 22% median contributions from unaccounted PFCs to total PFCs, respectively. Nonetheless, the Chinese aluminum sector is likely to be a major contributor to total unaccounted PFCs globally, simply due to its sheer size (43% of global production in 2013[34]). It is again noted that the median emission coefficients used by the industry to account for China do account for some of these unaccounted PFCs.[13,14]

Second, unaccounted PFCs have been found in a range of cell technologies (both Chinese and non-Chinese) operating at a range of line amperages (also corresponds to cell dimensions), from 200 kA to 400 kA and beyond. Studies of non-Chinese facilities by Zarouni et al.[9] support the hypothesis that larger, higher amperage cell technologies are more susceptible to unaccounted PFCs (Table I). In lower amperage cells (<250 kA), 4% to 33% of measured PFCs were not related to conventional AEs, rising up to 63% to 72% for higher amperage cells (>300 kA).[9] While a 2012 study by Li et al.[7] also appears to support this trend, an earlier 2011 study by the same authors[35] does not. It is apparent therefore that line amperage and cell dimensions are not the only factors contributing to the presence of unaccounted PFCs.

CATEGORIES OF AEs REDEFINED

Three categories of anode effects, namely conventional AEs, LVP-AEs and NP-AEs, can be used to describe all types of PFC emissions from industrial aluminum-reduction cells (Table II). Each category can be defined by means of distinct cell voltage and PFC emission signatures, as well as the level of AE propagation (if any) from one anode to another within a reduction cell. Despite these differences, Wong et al.[8,11] and other past works[9,10,39–42] provided strong evidence that the fundamental mechanisms that generate LVP-AEs and NP-AEs are the same as those for conventional AEs.

Conventional AEs are typically initiated on one or two individual anodes in a cell. Electrolysis of fluorides occurs when the local anode potential exceeds the threshold required to co-deposit PFC gases at the anode.[39] On an industrial cell, this can be caused by a combination of (I) insufficient levels of dissolved alumina locally in the bath and/or (II) an increase in local current density on anodes. An anode effect results when the current density exceeds the critical current density (CCD) locally,[43] forming a nonwetting film of PFC gases on anode surfaces, which severely increases the anode resistance and shifts electrical current to adjacent anodes. Adjacent anodes can also increase in current density until they too exceed the CCD locally and go on AE. In a stepwise fashion, the AE quickly propagates within seconds to all (or most) of the anodes across the cell. This propagation results in a rapid rise and peak in both cell voltage (above 8 V) and PFC

Table I. Survey of recent studies estimating the contribution of unaccounted PFCs or NAE emissions to total PFCs from different smelters, as a function of region and line current

Author and source	Year	Number of cells	Line kA	Region in world	Estimation of "NAE" or unaccounted emissions	Comments
Dando*[37]	2003	30	–	Ex-China	Fifty to 190 ppb CF_4 background levels	Background PFCs assumed artefacts
Al Zarouni and Zarouni*[10]	2011	4	–	Ex-China	Background levels of CF_4 and C_2F_6 to 0.10% and 30% of maximum levels	
Li et al.*[35]	2011	Multiple	~180	China	9% and 46% of total CF_4, two smelters	
		Multiple	200–240		9%, 17%, and 36% of total CF_4, three smelters	
		45	295		80% of total CF_4	
		13	335		19% of total CF_4	
Marks and Bayliss*[2]	2012	Multiple	–	China	Median of 70% total CF_4	
		Multiple	–	Ex-China	Median 22% total CF_4	
Li et al.*[7]	2012	Multiple	200	China	34% and 76% of total CF_4, two smelters	
			300		46% of total CF_4	
			350		86% and 93% of total CF_4 in two smelters, respectively	
Wong and Marks*[8]	2012	1	400	China	Background levels on single cells up to 1,000 ppb CF_4 and 40 ppb C_2F_6	
Zarouni et al.**[9]	2013	124	<250	Ex-China	10% total PFCs	D18 technology
		120	<250		4% total PFCs	CD20 technology
		120	<250		33% total PFCs	D20 technology
		40	>300		63% total PFCs	DX technology
		5	>400		72% total PFCs	DX + technology
Åsheim et al.*[36]	2014	28	~200	Ex-China	CF_4 emissions not attributed to AE measured, but not quantified	Small-to-medium sized cells
Gaboury et al.**[38]	2014	Multiple	~350	Ex-China	12% of observed PFCs	AP35 technology

* Definition of "NAE" or unaccounted emissions considers only background PFCs.
** Definition of "NAE" or unaccounted emissions considers both low-voltage AEs and background PFCs.

Table II. Comparison of the three categories of AEs, highlighting the differences in voltage and emission signatures, their expected mechanisms of initiation and propagation, and current accounting methods[11]

	AE Category		
	I Conventional AE	II LVP-AE Low-voltage propagating	III NP-AE Nonpropagating
AE voltage signature	>8 V (or similar voltage threshold)	Between 4 V and 8 V	~4 V (no obvious voltage signature)
PFC emission signature	Sharp emission peak, but drops to background levels after AE termination		Slow-moving, continuous background
AE initiation	Initial PFC generation on one or two anodes due to localized anode polarization, from a combination of low alumina concentration and high current density		
	→	→	→
AE propagation	Rapidly propagates to entire cell; often does not self-terminate, requiring automatic or manual AET	Rapidly propagates but only to a limited section of the cell, e.g., 1/3 or 1/2 of cell; self-terminates after propagation	Does not propagate, but remains on several localized anodes
	→	→	→
Industry accounting method for PFCs?	Yes — Using AE statistical data and IPCC/IAI methodology	None	No standard on measurement and accounting currently available

emissions until the AE is terminated, typically within minutes or seconds.

LVP-AEs differ from conventional AEs in that the AE only propagates to a limited section of the reduction cell, for instance one-third or one half of anodes within the cell.[8,11] Such AEs exhibit similar voltage signatures as conventional AEs, with voltage rising rapidly to a peak at the onset of a LVP-AE but remaining below threshold voltage levels used by control systems (<8 V or similar).[11] Similarly, PFC emissions rise to a sharp peak during the LVP-AE but reduce after the AE terminates. Figure 5 illustrates both voltage and PFC emission signatures for one LVP-AE, measured during a 1-h period on a single 400-kA Chinese technology cell (for measurement details, refer to Ref. 8).

NP-AEs refer to slow-moving background levels of PFCs. Although emissions are low in magnitude compared to peak PFC levels in the other two AE categories, NP-AEs can continue over a time scale of hours and days (rather than minutes or seconds, Fig. 5).[8–11,42] Therefore, this AE category has the potential to completely dominate conventional AEs as the major contributor to total PFCs from a smelter (as much as 92% of total PFCs).[7] This PFC-generating event has been shown to have the same fundamental mechanisms as conventional AEs, being linked to low alumina concentrations in a localized region in a cell.[8–10,40,42] and individual anodes with high current densities, particularly after the changing of anodes in a cell.[8,10,38] Unlike the other two categories, NP-AEs do not appear to propagate to other anodes in a reduction cell; rather, it is likely that the AE remains limited to several localized anodes.[11] Due to the very minor impact on total cell resistance, it is important to note that there is no discernible impact on cell voltage (Fig. 5).[11]

While unaccounted PFCs have certainly been found in smaller, lower amperage (<300 kA) reduction cells,[35,36] evidence suggests that larger, higher amperage (300–500+ kA) cells are more susceptible to generation of unaccounted PFCs.[9,11] High-amperage cells are associated with very large cell dimensions (>18 m), large numbers of anodes (40–48), and often operate with relatively low cell voltages and anode–cathode distances (interelectrode distances).[11]

In high-amperage cells, the transport and distribution of dissolved alumina (from point feeders to anode surfaces) can become more restricted as cell dimensions (and anode dimensions) increase.[11] Similarly, alumina transport is inhibited in cells operated at lower voltage and narrower anode–cathode distances. These cells are therefore more likely to have significant alumina concentration differences. Anodes in lean zones would be more susceptible to localized PFC generation, whereas anodes in high concentration zones would be less likely to generate PFCs.[11] Such conditions limit propagation of AEs and therefore make LVP-AEs and NP-AEs more likely on high-amperage cells.

In cells with large numbers of anodes, the propagation of any AEs across a cell becomes less likely (if at all). Wong et al.[11] demonstrated that when an AE is initiated on any single anode, the impact of shifting electrical current onto remaining anodes is very much reduced for a 400-kA cell with 48 installed anodes, compared with a smaller 200-kA cell with 24 anodes. This again increases the likelihood of LVP-AEs and NP-AEs occurring on high-amperage cells.

IMPLICATIONS AND FUTURE DIRECTION FOR THE ALUMINUM INDUSTRY

Before focusing on the implications of nonaccounted AEs, it is first important to commend the aluminum industry for its significant efforts and successes toward eliminating PFC emissions from conventional AEs. Through the industry's own voluntary regulation and reporting, emissions from conventional AEs have been reduced by as much as 88% from 1990 to 2013.[13]

However, the awareness of PFC emissions outside conventional AEs will undoubtedly continue to grow and the next challenge for the industry will be to properly quantify these emission categories. Detection and accounting of LVP-AEs is likely to be technically feasible with existing smelter control systems and sensors. Detection of these AEs could be achieved by using lower cell voltage triggers (between normal statistical envelope of operating cell voltage and 8 V conventional AE trigger thresholds) or by developing pattern recognition of cell voltage signals at higher data frequencies. Some examples are already under investigation.[9] These would provide frequency and duration statistics that could be combined with specific LVP-AE emission factors to account for this PFC category.

In contrast, detection and accounting for NP-AEs poses a greater challenge as cell voltage signals do not change significantly during such an event. Individual anode current monitoring systems can be used to capture these events. Implementing such systems is, however, a capital-intensive proposition given the number of cells at each facility.

Periodic sampling protocol methods for PFCs and subsequent offline gas analysis such as the integrated sampling and analysis procedures developed by CSIRO[24] and Gaboury et al.[38] have the advantage of being very accurate, inclusive of all PFCs generated by AEs and relatively inexpensive (particularly if multiple gas stacks need to be sampled). However, they give limited information of timing and location of emissions, making it difficult to differentiate and attribute emissions to the three AE categories. Furthermore, the method does not allow for real-time detection of measurement artefacts (such as those reported in Ref. 37) to assure representative sampling has taken place.

Direct real-time measurement of PFCs has the advantage of being able to account for NP-AEs by differentiating between discrete emission events (from conventional AEs and LVP-AEs) and background PFCs. However, the ability to distinguish background PFCs versus discrete PFC events from individual cells degrades when sampling large gas stacks or ducts (from a potline or large pot section). An added advantage of real-time measurement is that it provides the means for smelters to test strategies to mitigate and manage PFCs from nonaccounted AEs as evidenced in past studies.[40,42] Similar measurements are commonly used in smelters to manage HF emissions.

Reducing PFC emissions from nonconventional AEs requires prevention of the initiation mechanism. In all cases, proper feeding, dissolution, and distribution of alumina throughout the cells at all times are key. This represents an increasing challenge as aluminum reduction cells become larger. The probability of feeding process failures and localized AE events multiplies, while at the same time the detectability of such failures decreases (refer to the sections "Unaccounted PFCs from Nondetected Anode Effects" and "Categories of AEs Redefined"). Therefore, development of advanced detection techniques for nonconventional AEs or management of the preconditions leading to these AEs via smarter feed and dissolution control is likely the best prevention method.

Finally, it is important to highlight that in PFC emissions from nonconventional AEs represent not only an environmental cost but also a process cost to aluminum smelters. LVP-AEs and NP-AEs represent localized disturbances to the normal electrolysis process. In particular, the long time-scale nature of NP-AEs gives it not only the potential to dominate total PFCs but also the potential to impact on the long-term efficiency of operating cells.

CONCLUSION

The aluminum industry has made significant strides in reducing PFCs from conventional AEs since 1990. From 2002 onward, however, a significant gap between industry and atmospheric accounting of PFCs from the aluminum industry has been noted. Causes of this discrepancy include a rapid rise in nonreporting facilities (predominantly new production in China) and the contribution of nonconventional and nonaccounted AEs. Nonaccounted AEs can be defined as either LVP-AEs or NP-AE, and they can range from being minor to significant contributors of total PFC emissions. As the awareness of the accounting gap continues to grow, the industry needs first to develop better detection and accounting methods. The next PFC reduction challenge that awaits the industry is prevention of nonconventional AEs.

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