

NON ANODE EFFECT PFCs: MEASUREMENT CONSIDERATIONS AND POTENTIAL IMPACTS

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Keywords: PFC, perfluorocarbon, tetrafluoromethane, hexafluoroethane, emission monitoring

Abstract

Perfluorocarbons (PFCs) evolved from aluminum electrolysis pots during periods when pot voltage is below eight volts are considered non-anode effect (NAE) PFC emissions, consistent with current PFC measurement protocols. NAE-PFC emissions occur from all commercial smelters, regardless of plant size or technology type. This work uses historical estimations to illustrate the potential impact of including NAE-PFC emissions across a portfolio of location and technology specific PFC inventories and discusses technical considerations regarding the current measurement protocol and potential modifications to include NAE-PFC emissions.

Introduction

Perfluorocarbons (PFCs) are known greenhouse gases with exceptionally long atmospheric lifetimes that are linked to global warming due to their ability to efficiently absorb infrared radiation.¹ Two PFC gases, tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆), are emitted from aluminum smelters during anode effects (AEs). An anode effect occurs when the alumina (Al₂O₃) concentration in the electrolytic bath drops below ~1.5%, the cell voltage rises, and the bath and carbon anodes begin to react.² Aluminum smelters are considered to be one of the largest anthropogenic source of PFC emissions worldwide.³

The United States Environmental Protection Agency (USEPA) and the Intergovernmental Panel on Climate Change (IPCC) have provided good practice approaches for measuring and inventorying PFC emissions from aluminum production.⁴ The Tier 3 method is the most accurate approach and requires an on-site PFC measurement during normal potline operation.⁴⁻⁶ These plant-specific PFC emission coefficients can be used to estimate production normalized plant-specific PFC emissions based upon anode effect minute per pot-day performance.

Most aluminum companies have initiated voluntary programs for actively reducing PFC emissions⁴ and all modern pre-bake smelters have implemented automated methods for terminating anode effects. These methods vary by cell technology; however all have the same goal of minimizing the cumulative anode effect minutes per cell-day at the operating location. Perhaps more importantly, smelter pot feeding and monitoring programs are continually optimized to minimize the frequency of anode effects and the durations of these events. These efforts have reduced anode effect related PFC emissions by almost 90% since 1990.⁷

As reported previously, reductions in anode effect frequency can offer a linear route to CO_{2e} reductions, while a focus on fast anode effect kills (to minimize duration) can reach a point of diminishing returns, given that PFC emission rates (per second of anode effect) are highest during the initial AE onset.⁸⁻¹⁰

A focus on reducing anode effect duration via aggressive kill programs can also have the undesirable effect of increasing pot noise and thereby increasing the likelihood of near term operating periods where localized anode voltages are above normal (> 4.25 V) but overall pot voltage does not reach 8V. Under these conditions, localized PFC emissions can be generated; however the potroom computer system will not register any anode effect time. This is but one example of a root cause of non anode effect (NAE) PFC emissions, which have been observed during in-plant studies since 2000.¹¹

Any situation that causes a localized increase in pot voltage can induce PFC emissions from the cell. These include planned work activities or operational controls, such as anode changes, taps, aggressive anode effect kill programs, low alumina targets and high pot noise. Unplanned root causes for NAE-PFC emissions can include pot starts, recovery from power outages or fluctuations, interruptions to ore supply or transport lines and improper operation of individual pot feeders.¹¹⁻¹⁶

The current Tier 3 method for measuring and reporting PFC emissions does not account for NAE-PFC emission.⁵ Perhaps more importantly, regional PFC or CO_{2e} emission permit limits for aluminum smelters were negotiated based on pre-existing knowledge of AE-based PFC performance and do not include provisions for including NAE-PFC emissions in a non-punitive manner, assuming they could be capably measured or estimated.

The purpose of this work is to use estimations from historical PFC measurement campaigns to illustrate the potential impact of including NAE-PFC emissions across a portfolio of location and technology specific PFC inventories and discusses technical considerations regarding the current measurement protocol and potential modifications to include NAE-PFC emissions.

Experimental

Alcoa has been performing plant-specific PFC emission testing at operating smelters for over 15 years and has the largest data base of Tier 3 coefficients in the aluminum industry.¹⁷ Most of this plant PFC database (and all data discussed herein) employed the use of FTIR spectrometers for generating continuous, real-time PFC emission measurements over operating periods ranging from several days to a month in duration.

Where possible, these measurements were acquired by monitoring pot exhaust ducts after the dry scrubber system. In many cases, however, the plant exhaust duct configuration or access limitations required sampling prior to the dry scrubbers. The sampling procedures employed have been described previously.^{6,18}

FTIR-based real-time PFC concentration data from monitoring campaigns across Alcoa's production portfolio over the 2008-

2011 timeframe were re-analyzed to estimate the potential contribution from NAE-PFC emissions.

Normal Tier 3 data analysis practice involved collecting temporal plant AE records from the process control computer and matching these records of AE onset and duration to FTIR based measurements of PFC emissions during these periods.

In the present study, NAE-PFC emission estimates were calculated from the original FTIR data records by assuming all observations of non-zero PFC baseline data, when no AE were recorded by the plant computer, were due to NAE-PFC emissions.

It is important to note that a key assumption inherent to all data presented herein is that the historical FTIR data is referenced to a true zero. In other words, we have assumed that the limit of quantitation (LOQ) is 1 ppb. This is a very conservative assumption given the potential for and limited corrections to prevent bias or interference from known or unknown gases present in the sampling stream.^{6,18}

Results and Discussion

During the data evaluation period discussed above, Alcoa's aluminum smelting portfolio consisted of twenty two smelters. The smelting technologies represented in this portfolio included fifteen point-feed prebake (PB) smelters, six Söderberg (S) smelters (both side worked and point feed) and one side worked prebake (SWPB) smelter. The 2010 AE-only PFC emissions for these locations are shown in Figure 1. The technology type of each smelter is indicated by the letters shown in the X-axis. As expected, PB locations exhibit lower AE-base PFC emissions than non point feed SB and SWPB locations. The order of the plants listed on the x-axis of Figure 1 is identical to those shown in Figure 2.

The impact of estimated NAE-PFC emissions on the total PFC emission profile of each smelting location is shown as a percentage of the sum total (AE + NAE-PFC) for each location, as shown in Figure 2. The data shown in Figure 2 is ranked by % NAE-PFC. As noted above, the order of x-axis plant listing is identical to Figure 1.

The most obvious message from the data shown in Figure 2 is that all smelters, regardless of technology type or operating capacity, can generate NAE-PFC emissions.

As evident from the data in Figure 2, the impact of including NAE-PFC emissions is dependent on technology type. Large pot, point feed prebake smelters operating with low AE minutes will be the most impacted relative to their current Tier 3 (AE-PFC only) performance (at left side of Figure2). Correspondingly, those locations with elevated AE-PFC emission performance will be less affected by any future change to include NAE-PFCs their emission inventory. As a result, plants that employ manual feeding (i.e. non point-feed Söderberg and SWPB) are evident on the right side of Figure 2.

As shown in Figure 2, inclusion of NAE-PFCs in emission inventories at plants with very low AE-PFC emissions could increase the total PFCs at a specific location by five-fold (i.e. 80% NAE-PFC), or higher, depending on technology type and plant

AE performance. In other words, large pot point feed prebake locations that have most aggressively driven down AE-PFC emissions will likely see the biggest relative change in their overall PFC emission performance.

The impact of including NAE-PFC emissions on the overall production weighted smelting technology portfolio shown in Figure 1 would be to increase total mass-based PFC emissions by 12%. As noted earlier, this is due to the fact that the highest PFC emission intensity plants in the portfolio shown in Figure 1 employ SWPB and Söderberg technology. NAE-PFC emissions will comprise a greater percentage of the total PFC emissions in future years as the smelting portfolio continues to shift away from Söderbergs to low AE PFC prebake smelters.

If, or when, the PFC protocol is revised to include NAE-PFC emissions, a key concern will be the impact on local or regional operating permits, which may include a only single plant or a limited number of plants and were negotiated prior to any knowledge regarding as-yet unmeasured NAE-PFC emissions. Clearly this issue will need to be addressed to allow non-punitive modification of PFC inventories to include NAE-PFC emissions and allow revision of existing operating permits.

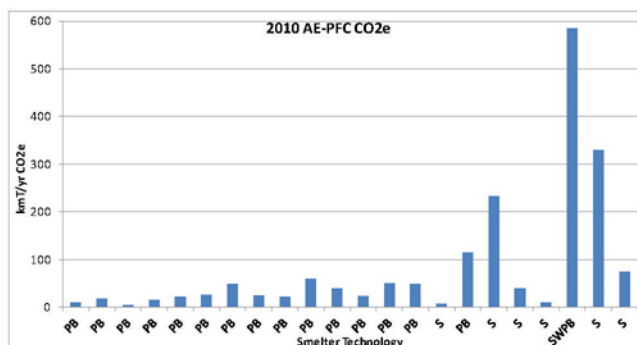


Figure 1. AE-PFC plant emission inventories.

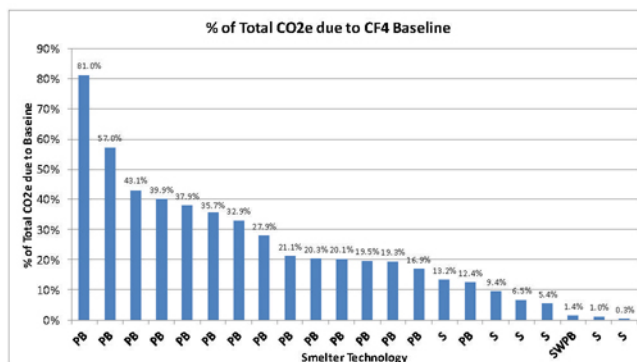


Figure 2. Impact of including NAE-PFC on plant emission inventories.

As noted earlier, any events, either deliberate or unplanned, that reduce pot stability or increase pot noise are likely to induce emission of NAE-PFCs. Figure 3 shows a continuous three day CF₄ emission profile from sampling a duct serving 150 point feed prebake pots. A key observation from the data shown in Figure 3 is that NAE-PFC emissions are not a continuous phenomenon at

this smelter. The existence of significant periods of zero NAE-PFC emission indicates the potential for proactively managing operational control strategies and work practices to reduce NAE-PFC emissions.

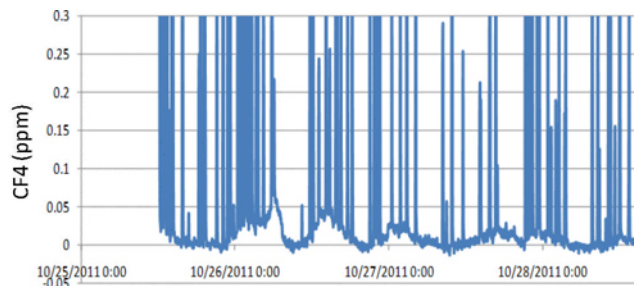


Figure 3. 3-day CF₄ emission profile (150 PB pots).

Currently, many locations, both within and outside Alcoa, are aggressively working to reduce NAE-PFC emissions by improving robustness to, or eliminating, root causes of pot instability and thereby reduce the potential for localized increases in pot voltage.^{9,15,19} Unfortunately, there are no readily available process indicators of the onset, magnitude or duration of NAE-PFC emission. Furthermore, older plants may not have the rapid current/voltage monitoring capabilities required to detect the onset of localized anode voltage transients. In other words, the systematic tracking, management and reduction of NAE-PFC emissions will be a more challenging goal than that required to reduce AE minutes per pot-day.

A significant challenge to including NAE-PFC emissions in smelter reporting inventories is how to modify the existing measurement protocol to assure accurate, representative estimation of NAE-PFCs from limited-duration tests and accurately track forward emission performance. Real-time measurement technologies are the only presently available option for direct measurement of NAE-PFC emissions and thereby facilitating active management of process or work practice changes to minimize NAE-PFC emissions. Time averaging sampling methods such as gas bags, canisters or adsorbent media coupled with off-line analyses can be employed to monitor integrated (AE+NAE) emissions, but cannot differentiate AE from NAE-PFCs unless special efforts are made to capture data during periods when no AE events occur in the test population.¹²⁻²² Given that process events causing AEs also induce NAE PFC emissions, this is may not be a representative solution.

Achieving accurate measurements of NAE-PFC emissions pushes the performance limits of existing real-time measurement technologies regarding sensitivity, long term stability, interference corrections and baseline subtraction practices. These issues will need to be addressed in a more uniform, rigorous manner to assure robust and comparable data between and within locations over future years. Sampling practices will also have to be revised to assure that measured NAE-PFC emissions are truly representative of overall location performance.

Assuming that adequate measurement protocols are developed, the sampling practice also needs to be better specified to assure that NAE-PFC emissions are not over-estimated. PFC measurement practices consistent with the existing protocol are

likely to include re-entrained PFC emissions that can erroneously add to NAE-PFC inventories.¹⁸

Consider the data shown in Figure 4, which is from an FTIR-based PFC monitoring trial at a pre-bake smelter, sampling the common exhaust duct for 30 pots, out of a total of 240 pots in the room.¹⁸ The baseline LOQ assigned for this sampling trial was 10 ppb CF₄. A series of transient CF₄ emissions arising from individual anode effect events from pots within the test population are observed as thin spikes in this figure. It is interesting to note that background CF₄ emissions are clearly evident throughout the entire trial period, regardless of anode effect events. The concentrations of these baseline CF₄ emissions range from 50 to 190 ppb.

While some fraction of the baseline CF₄ emissions shown in Figure 4 may result from NAE-PFC emissions, a significant fraction also resulted from fugitive PFCs generated by other cells in the potroom that were not part of the 30-pot sampling population.

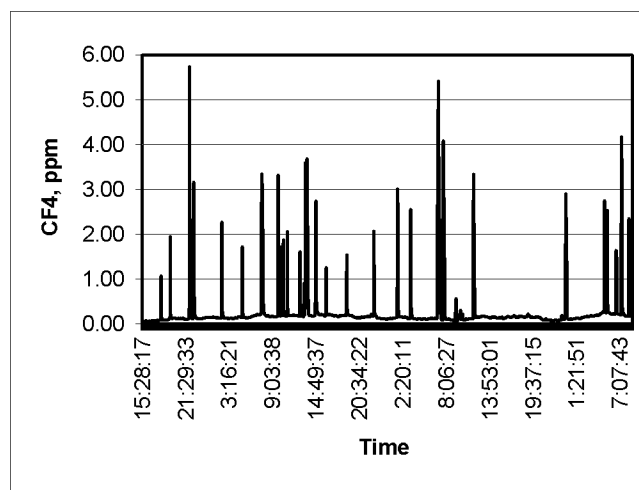


Figure 4. CF₄ Monitoring in a pre-bake smelter using a FTIR CEM.

During this sampling campaign, low intensity, well defined transient peaks were correlated to adjacent cells. CF₄ is over three times denser than air. Upon release from a pot, convective updraft of the gas phase stops quickly upon cooling and the fugitive CF₄ descends to the potroom floor, where it is rapidly swept into the dilution air (i.e. into the hooding) of nearby Hall cells. We have also seen instances where pot starts occurring in an upwind smelter potroom gave rise to elevated “apparent” baseline NAE-PFC emissions in a downwind potroom where active PFC sampling was taking place.

The capture of fugitive potroom emissions from pots outside the test pot population can be readily observed in the temporal CF₄ emission data shown in Figure 5. In this study, the scrubber stack serving half of the pots in a Söderberg potroom (72 of 144) was monitored using an FTIR spectrometer. The NAE baseline rose significantly approximately mid-way through the sampling period shown in Figure 5, owing to pot starts occurring in the ½ room outside the test population, served by a separate scrubber system.

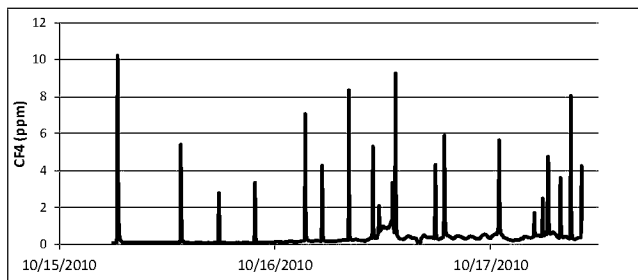


Figure 5. Soderberg smelter CF₄ emission profile showing impact of pot starts outside test population.

In addition to pot hooding inadequacies, deliberate work activities that de-stabilize pots, such as anode change or tap activities will promote fugitive PFC loss to the potroom. Overly aggressive anode kill practices will also contribute to fugitive PFC emissions. For example, manual kills of anode effects severely compromise fume capture efficiencies, since pot covers are commonly removed during the anode kill process.

Conclusion

The inclusion of NAE-PFC emissions will additively impact aluminum smelter emission inventories in a manner that depends on a number of location specific factors such as technology type, operating practices, work practices and AE performance

Several observations regarding NAE-PFCs, measurement and inclusion in plant emission inventories are listed below.

- 1) All commercial aluminum smelters can generate NAE-PFCs, regardless of technology type.
- 2) Temporal NAE-PFC emissions vary considerably depending on plant technology, operating conditions and work practices.
- 3) At present, no readily available process signals have been demonstrated adequate for indirectly estimating NAE-PFC emissions from plant computer data.
- 4) Short term plant measurements are unlikely to adequately represent long term plant NAE-PFC performance.
- 5) Current protocol-consistent PFC sampling practices can include re-entrained PFC emissions that could erroneously inflate NAE-PFC estimations.
- 6) Continuous monitoring may present a viable option for monitoring NAE-PFCs at plants that have a limited number of emission stacks. This same approach may be cost prohibitive for exhaustive application at locations with distributed fume treatment systems (many small emission stacks).
- 7) Inclusion of NAE-PFC emissions may require revision of existing regional emission permit limits.

Acknowledgements

The authors would like to thank Alcoa's Primary Metals and Environmental Management Teams for encouraging publication of environmental research.

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