Protocol for Measurement of Tetrafluoromethane (CF$_4$) and Hexafluoroethane (C$_2$F$_6$) Emissions from Primary Aluminum Production

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EPA 43-R-03-006
May 2003

Acknowledgements

The EPA Voluntary Aluminum Industry Partnership was launched in 1995 to reduce emissions of PFCs emitted as a byproduct of the aluminum smelting process. VAIP members are Alcan Primary Metals Group, Sebree Works; Alcoa, Inc.; Century Aluminum Company; Columbia Falls Aluminum Company; Kaiser Aluminum; Noranda Aluminum Inc.; Golden Northwest Aluminum, Inc.; and the Aluminum Association.

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1.0   Introduction

Although the primary aluminum industry is actively pursuing PFC emission reductions, including completing a number of facility-specific measurements, no single measurement protocol has been developed for consideration and use by the industry. This guidance is intended to advance the industry's emission reduction efforts and serve as a starting point for the global adoption of a common measurement protocol.   The purpose of developing a standardized measurement protocol is to foster consistency across smelter-specific sampling programs and to ensure comparable global data.[1]   Measurements of the two perfluorocarbons (PFCs) – tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) – emitted from the manufacture of primary aluminum are necessary for the calculation of a facility specific emission factor as outlined in the Intergovernmental Panel on Climate Change (IPCC) Good Practice Inventory Guidance Tier 3b method.[2]   The IPCC method is derived from standards and processes developed over the past decade and data from smelter measurement campaigns in a number of countries including Canada, France, Norway, and the United States. This section describes the protocol, why measurements of perfluorocarbons are important, and presents the organization of this document.

1.1   Objective of Measurement Protocol

In response to the link of PFC emissions to the primary aluminum manufacturing process, the aluminum industry is making a global effort to reduce emissions.   The specific objective of the measurement process, as described herein, is to support this effort through high quality measurements of CF_4 and C_2F_6 and the collection of pertinent process data that allow the calculation of a facility specific emission factor as described in the Intergovernmental Panel on Climate Change (IPCC) Tier 3b method[3]. This document provides guidance for individual facilities to develop detailed plans for sampling and analysis based on plant specific technology, anode effect data, and chosen measurement instrumentation. Use of the protocol will improve the consistency and comparability of primary aluminum PFC emission inventories. In addition, integration of the new measurement data into the calculated Tier 2 equation coefficients will lead to improved accuracy of IPCC Tier 2 PFC emissions calculations.

Measurements of perfluorocarbons (PFCs) provide only a snapshot view of emissions for the specific section of cells for which the measurement is carried out. Furthermore, day-to-day variations in anode effect frequency and duration, as well as variations in production levels may well change the PFC emissions for the site. The calculation of long-term average emissions based on the Tier 3b methodology accounts for these temporal variations.

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[1] J. Marks, R. Kantamaneni, D. Pape and S. Rand, "Protocol For Measurement of Tetrafluoromethane and Hexafluoroethane From Primary Aluminum Production," Light Metals (2003), pp 221 – 226.
[2] IPCC, *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*, Section 3.3, PFC Emissions from Aluminium Production, 2000, http://www.ipcc-nggip.iges.or.jp/public/gp/pdf/3_Industry.pdf.
[3] The alternate IPCC Tier 3a method uses continuous monitoring of PFC emissions. Although technically feasible, continuous monitoring is costly and not regarded as necessary for Good Practice by the IPCC.

1.2   Why Measure PFCs?

Central to any study of climate change is the development of an emissions inventory that identifies and quantifies anthropogenic sources and sinks of greenhouse gases. The most accurate estimates of PFC emissions from primary aluminum use facility specific emission factors based on measurements at the individual production site. In general, industry and governments use inventories to support three major initiatives:

- **Benchmarking and Process Improvement.** Benchmarking is an important management tool that helps companies evaluate emissions, set goals and develop strategies for reducing emissions. Estimates derived from measurements of PFC emissions at individual facilities serve as the basis for a well formulated process improvement plan. Accurate inventories of PFC emissions are also important in benchmarking performance against other producers operating with similar technologies.

- **United Nations Framework Convention on Climate Change.** Countries that are signatories of the Framework Convention on Climate Change are responsible for reporting an annual inventory of greenhouse gases. Over one hundred and eighty countries are signatories of the Framework Convention and gather data on industrial processes as part of their national inventory each year. The measurement of PFCs facilitates creation of a more accurate inventory through use of facility specific emission factors rather than default global average values.

- **Market Mechanisms.** One mechanism that has been suggested for achieving reduction of greenhouse gas emissions is a market-based approach in which emission reduction credits are traded. Accurate and verifiable emissions reductions will be required in the event of such trading. Facility specific measurements provide the most accurate documentation of PFC emissions reductions. Accepted and validated measurement procedures will be important to verify reductions and facilitate trading.

The International Aluminum Institute (IAI) currently sponsors global surveys of PFC emissions.[4] In the U.S., primary aluminum producers have committed to PFC emissions reductions through the Voluntary Aluminum Industrial Partnership, a voluntary partnership between individual primary aluminum producers and the U.S. EPA. At least nine other countries are also undertaking industry-government initiatives to reduce PFC emissions from aluminum production.[5] High quality data and improving emissions estimates are a shared goal in each of these initiatives.

1.3   Organization of Remainder of This Document

The remainder of this document is organized into nine sections and four appendices.

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[4] International Aluminium Institute, *Anode Effect Survey 1994 – 1997 and Perfluorocarbon Compounds Emissions Survey 1990 – 1997*, 1999; *PFC Emissions Reduction Program 1990 – 2000*, 2002.
[5] E.J. Dolin, J. Casola and T. Miller, "PFC Emissions in the Aluminum Sector: International Strategies and Reductions," Light Metals (2001).

2.	**Background**.	Description of PFC sources and release mechanisms during primary aluminum production.

3.	**IPCC Three-Tiered Inventory Method**.	Overview of IPCC guidelines for estimating PFC emissions from aluminum production.

4.	**Process Data Requirements.**	Review of process data needed for a developing a PFC measurement strategy, for calculating Tier 3b coefficients and for comparing data with other measurement results.

5.	**Sampling Design.**	Guidelines for sampling.

6.	**PFC Concentration Measurement**.	Guidance on proper instrumentation and techniques for measuring PFCs in ducts and rooftop measurements.

7.	**Calculations and Reporting.**	Calculations and good practices for reporting data.

8.	**QA/QC.**	Steps that should be taken to assure that the measurement process is in control and instruments and sampling systems are performing as needed to achieve an accurate result.

9.	**Safety.**	Recommended steps and procedures to help avoid injury to measurement personnel while taking measurements.

10.	**Measurement Frequency and New Measurements.**	Guidelines on when new measurements should be made to reassess emissions factors.

Appendices.	The appendices provide additional information to aid in the measurement process. Included are spreadsheet templates for data collection, calculations and reporting, a list of suppliers of equipment, and guidance for assessing measurement results.

# 2.0	Background

This section describes what PFCs are and their climate change impact, how they are produced, their possible release mechanisms and factors that affect their emission rate.

## 2.1	What are PFCs?

Perfluorcarbons (PFCs), fluorocarbons, or perfluorocompounds (terms which are often used interchangeably) are derived from hydrocarbons by replacing all the hydrogen atoms with fluorine atoms. Two perfluorinated compounds, tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6), are inadvertently produced during primary aluminum production by the Hall-Héroult process. During normal operating conditions no measurable amounts of perfluorocarbons (PFCs) are generated in the aluminum electrolytic reduction process. PFCs are produced mainly during brief upset conditions known as "anode effects." PFCs can also be produced during the brief period during cell start up when cell voltage in increased for a brief period of time to heat the cell and its contents. The atmospheric concentration of these two compounds is currently about 80 parts per trillion by volume (pptv) CF_4 and 3 pptv C_2F_6 based on projections of past

atmospheric measurements.[6]   Commercial aluminum production has been identified as the largest emitter of these two compounds.   Other smaller industrial sources include the semiconductor industry, uranium processing, and fluorine processing.

2.2   Climate Change Impact of PFCs

While the present contribution of CF_4 and C_2F_6 to climate change is relatively small, the long lifetimes of the two compounds, estimated at 50,000 and 10,000 years respectively, will impact climate change far into the future.   In addition, the impact is magnified because of the high Global Warming Potentials (GWPs) of these two gases.   For example, based on the 100-year GWP, each kilogram of CF_4 emitted is equivalent to 6,500 kg CO_2 emissions and, similarly, each kilogram of C_2F_6 is equivalent to emissions of 9,200 kg CO_2. [7]   In 2000, PFC emissions from U.S. based aluminum production accounted for 7.9 Tg CO_2 equivalents, approximately 3 percent of total CO_2 and non-CO_2 greenhouse emissions from industrial processes.[8]

2.3   Aluminum Production and PFCs

2.3.1   Anode Effects

Anode effects occur intermittently during aluminum production. Anode effects are characterized by a sudden increase in cell operating voltage from normal operating levels of 4.2 to 5.0 volts to levels of 25 volts to 50 volts.   These conditions occur when the aluminium oxide (the raw material for primary aluminium) level drops too low and the electrolytic bath components begin to undergo electrolysis.   Since the aluminium oxide level in the electrolytic bath cannot be directly measured, parameters that vary proportionally to dissolved alumina content such as cell electrical resistance or voltage are frequently used in modern facilities to control additions of alumina to the electrolytic bath. In addition to resulting in adverse environmental impacts, anode effects result in process inefficiencies that increase the cost of aluminum production.

Anode effects can be terminated or "killed" by a combination of mitigation actions depending on the capability of the reduction technology.   These actions include such things as lowering the anodes, stirring the bath by insertion of a green pole[9] under the anode, blowing compressed air under the anode, and feeding additional alumina to the cell.

2.3.2   Reduction Technologies

Primary aluminum production facilities are made up of one or more potlines consisting of electrolysis cells operated in series and located either in an end-to-end or side-by-side

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[6] J. Harnish et. al., "Tropospheric trends for CF_4 and C_2F_6 since 1982 derived from SF_6 dated stratospheric air," Geophysical Letters 23(10), pp 1099-1102, 1996.
[7] Intergovernmental Panel on Climate Change, *Second Assessment Report: Climate Change 1995*, 1995.
[8] U.S. EPA, *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990 - 2000,* EPA 430-R-02-003, April 2002
[9] "Green pole" is the term commonly used by aluminum smelter staff to describe a pole typically 5 to 8 meters in length and about 5 cm at the base cut from a young growing tree with branches trimmed. The moisture content of the pole prevents rapid combustion when inserted under the anode in the hot molten salt bath.

arrangement. Electrical current is provided to the potline through rectifiers that convert AC power to DC power.[10]

Two major types of electrolysis processes are used for the production of aluminum. These processes are characterized by the type of anode in the cell. The two processes are the Søderberg process, and prebake technology. Each of these processes is described below.

In the older Søderberg process, a single large anode structure is produced in each electrolysis cell in a continuous process. A mixture of coke and coal tar pitch is added to the top of the anode. This mixture is subjected to successively higher temperatures as the base of the anode is consumed producing a highly baked carbon structure where electrolysis takes place in the molten salt electrolyte. Søderberg cells are subcategorized by the type of electrical connection to the anode. Electrical connections are either through metal rods placed horizontal to the floor surface or, more typically, placed vertically into the anode structure. These cells are referred to as either Horizontal Stud Søderberg (HSS) or Vertical Stud Søderberg (VSS) cells.

The more modern prebake technology involves producing prebaked anodes in furnaces outside the electrolysis cell. The baking process is carried out over a carefully selected temperature-time cycle that results in a finished product of generally higher physical integrity than the Søderberg anode. Also, the fumes from the baking process act as part of the fuel for baking the anode. Any fumes not combusted are captured and treated to remove potentially deleterious environmental products. Each prebake electrolysis cell contains a number of these prebaked anodes that are replaced periodically as they are consumed during the electrolysis reaction.

Prebake technology is also subdivided into several categories depending on the type of alumina feeding mechanism. The most modern of these technologies is the Point Feed Prebake cells (PFPB) where the crust is broken at multiple points along the centerline of the cell by mechanical punches. Alumina is then dropped into the cell through the newly established opening. In some older prebake cells, feeding is accomplished by a metal bar extending along the centerline of the cell that periodically breaks the surface cover and feeds the cells. These cells are referred to as bar broken Center Work Prebake cells (CWPB). In yet another cell design, the cell is fed from the sides rather than the center and these cells are referred to as Side Work Prebake cells (SWPB).

The types of intervention for process control are different for each reduction technology, resulting in differences in anode effect frequency and the pattern of duration. For the older Søderberg technology this intervention can involve steps such as rocking the anode structure, blowing compressed air under the anode or inserting a wooden pole under the anode to initiate turbulence and stirring. Prebake technology allows more sophisticated interventions under computer control such as successive lowering of the anodes to reduce the anode to cathode distance and rapid feeding of alumina. Table 1 illustrates the differences in anode effect frequency and duration for each of the main reduction technology types.

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[10] For more details on aluminum reduction technology see J. Thonstad et al., Aluminium Electrolysis, Fundamentals of the Hall-Héroult Process, 3rd edition, Aluminium-Verlag, 2001.

Table 1. Median Year 2000 Anode Effect Frequency and Duration by Technology Type

Technology	Median Anode Effect Frequency (AE/cell-day)	Median Average Anode Effect Duration[a] (Minutes)
PFPB	0.19	2.2
CWPB	0.80	1.8
SWPB	1.9	3.2
VSS	1.32	3.1
HSS	0.82	4.3

[a]Anode effect duration for Pechiney control systems excluded from median because of differences in definition of duration.

Source: IAI, *PFC Emissions Reduction Program, 1990-2000*, London, UK, March 2002.

2.3.3   Collection Efficiency and Fugitive Emissions

Primary aluminum production releases small amounts of gaseous hydrogen fluoride and some additional particulate emissions composed of fluoride-containing compounds from the molten salt bath, alumina from the feeding and cover, and carbon from the anodes. The electrolysis cells are hooded and large fans produce a negative pressure throughout the hooding system to capture any gaseous or particulate emissions. These emissions are then treated and essentially all the captured material is returned to the cells to increase the efficiency of operation and help control the bath composition. The differences in cell design and work practices for each of the reduction technologies impact fume collection efficiency. During normal operations PFPB and CWPB cells typically have collection efficiencies greater than 97 percent, while SWPB cells have average collection efficiencies of about 90 percent because of the necessity of raising the hoods for feeding alumina. Søderberg cells generally have average collection efficiencies of 80 to 90 percent.   Collection efficiency must therefore be considered in accounting for total PFC emissions and an assessment of fugitive emissions must be made. This protocol recommends making a measurement of fugitives when fugitives are expected to be greater than 5 percent of total PFC emissions. When fugitives make up less than 5 percent of total emissions they should be estimated from historical collection efficiencies previously determined for fluoride capture.

2.3.4   Mechanism of PFC Release

The specific reaction sequences leading to the formation and release of CF_4 and C_2F_6 are still the subject of study and some differences of scientific opinion. Researchers have proposed that a resistive C-F film might be formed on the anode surface and this film is decomposed to produce the PFC compounds.[11] Another proposal suggests that fluorine is formed during the anode effect, and that it reacts with the carbon anode to produce the PFC compounds.[12]   Other proposed mechanisms have intermediate compounds, such as COF_2, that are then thermally decomposed into the PFC compounds.[13]   In any case, previous measurement data have shown that when

[11] H. Zhu and D. Sadoway, "An Electrochemical Study of Electrode Reactions on Carbon Anodes During Electrolytic Production of Aluminum," Light Metals (2000), pp 257 – 263.

[12] T. Utigard, Light Metals 1988, 703-706 (as quoted in J. Thonstad et. Al. Aluminium Electrolysis, Fundamentals of the Hall-Héroult Process, 3rd edition, Aluminium-Verlag, 2001).

[13] M. Dorren, D. Chin, J. Lee, M. Hyland and B. Welch, "Sulfur and Fluorine Containing Anode Gases Produced During Normal Electrolysis and Approaching an Anode Effect," Light Metals (1998), pp 311-316.

anode effects occur, both CF_4 and C_2F_6 are immediately released. The release continues until the anode effect is extinguished. The emission rate is often highly variable during the anode effect. Depending on sampling location, PFC compound concentrations can rise from atmospheric background levels to levels of 5 to 2500 ppmv (parts per million by volume) in a matter of seconds. The emission rate and thus the PFC concentrations can rise and fall by factors of two to five during the anode effect and then rapidly fall again to atmospheric background levels when the anode effect is extinguished. A PFC measurement strategy must be able to accurately account for these variations.

2.3.5 Factors Affecting PFC Emission Rate

As indicated above, PFCs are generally emitted only when reduction cells are on anode effect.[14] Once an anode effect is initiated, the rates at which CF_4 and C_2F_6 are generated depend on several factors. The primary process generating the PFC compounds is electrolytic oxidation of fluoride at the anode; therefore, the rate of the electrolytic reaction is proportional to current flow. The higher the line current, the higher the rate of emission will be during the anode effect. Measurements have shown that overall cell voltage affects the rate of emission.[15] In addition to the voltage increase resulting from formation of a resistive film on the base of the anode, other operating factors play a role in the amount of voltage increase when the cell is on anode effect, such as the bath volume and anode surface area. The emission rate varies with time after anode effect initiation and has been observed to show some decrease as the anode effect duration is extended. The fluoride content of the bath may also play a role in the emission rate.[16] For some Søderberg cells, the emissions of PFC compounds during anode effects is decreased due to intermittent electrical shorting occurring between the carbon anode and the aluminum metal pad.

3.0 IPCC Three-Tiered Approach

The IPCC has developed and documented guidance on good practices for inventory of PFC emissions from aluminum production.[17] IPCC provides three approaches to estimating greenhouse gases from aluminum production. These approaches are referred to as Tiers 1, 2 and 3. The accuracy of these estimates increases from Tier 1 to 3 and the associated degree of uncertainty decreases as summarized below:

- Tier 1 Method – Production-based emission factors. Tier 1 uses default emissions values for specific PFC emissions based on estimates from 1990 anode effect data and technology average slope coefficient data. This method should be used only if no data other than production levels are known.

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[14] Guy Bouchard, J. Kallmeyer, A. Tabereaux, and J. Marks, "PFC Measurements From Canadian Primary Aluminium Production," <u>Light Metals</u> (2001), p 286.

[15] J. Marks, A. Tabereaux, D. Pape, V. Bakshi and E. Dolin, "Factors Affecting PFC Emissions From Commercial Aluminum Reduction Cells," <u>Light Metals</u> (2001), 295 – 302.

[16] R. Haverkamp, S. Rolseth, J. Thonstad and H. Gudbrandsen, "Voltammetry and Electrode Reactions in AlF3 -Rich Electrolyte," <u>Light Metals</u> (2001), pp 481 – 486.

[17] IPCC, *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*, Section 3.3, PFC Emissions from Aluminium Production, 2000, <u>http://www.ipcc-nggip.iges.or.jp/public/gp/pdf/3_Industry.pdf</u>.

- Tier 2 Method – Technology average relationship between emissions and operating parameters based on default technology-based slope or over-voltage coefficients. Tier 2 makes use of the averages of previously reported measurement data to develop technology average coefficients from which emissions can be calculated. Measurement data suggests that the accuracy of Tier 2 results is intermediate between Tier 1 and Tier 3b. The accuracy of Tier 2 calculations varies among reduction technology categories. Results for PFPB cells are generally more reliable than for Søderberg cells. There are no IPCC Tier 2 coefficients noted for the overvoltage method for calculation of hexafluoroethane emissions.

- Tier 3 Methods: Tier 3a Method – Continuous emission monitoring; and Tier 3b Method – Smelter-specific relationship between emissions and operating parameters based on field measurements. Tier 3a uses continuous monitoring to determine emissions directly.[18] Tier 3b methods use measurements of emissions to develop a facility specific correlation between emissions and anode effect data.

The most accurate results are determined by either continuously monitoring emissions, the Tier 3a approach, or, using the Tier 3b approach. The Tier 3b approach is used to develop a smelter specific long-term relationship between measured emissions and operating parameters and to apply the relationship to the appropriate activity data. The activity data are comprised of aluminum production levels and anode effect data. The anode effect data may be expressed as either anode effect frequency and average anode effect duration, or, overvoltage for Pechiney control systems that record potline overvoltage. The procedures described in this document lead to the development of Tier 3b emissions factors to calculate PFC emissions from tracking of aluminum production data and process data. The Tier 3b emission factors can be estimated based on the two following methods, depending on the facility's process control technology:

1) Slope method - anode effect minutes per cell-day, which is the product of anode effect frequency and average anode effect duration, or,

2) Overvoltage method - potline overvoltage, a parameter related to the excess voltage over normal operating conditions that is recorded for potlines operating with Aluminium Pechiney control systems.

Each of these methods is described below.

Slope Method. For this method a linear relationship is established between smelter process data, anode effect minutes per cell-day, and the specific PFC emissions, kg CF_4 or kg C_2F_6 per tonne of aluminum. The slope is the parameter which, when multiplied by the anode effect minutes per cell-day, will give the specific PFC emission factor.

Equation 1:

EF (kg CF_4 or C_2F_6 per tonne Al) = Slope ´ anode effect minutes/cell-day

Rearranging Equation 1 to the form useful for calculating the facility-specific slope, the following result is obtained.

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[18] "Continuous monitoring of emissions is possible and is the most accurate means of determining emissions. Given the likely cost and other resource considerations, however, it is not regarded as necessary for Good Practice." IPCC, *Good Practice*, 2000.

Equation 2a:

CF₄ Slope = EF (kg CF₄/tonne Al) ÷ (AEF ´ AED)

Equation 2b:

C₂F₆ Slope = EF (kg C₂F₆/tonne Al) ÷ (AEF ´ AED)

Where:
AEF	= Anode effect frequency (number of anode effects/cell-day)
AED	= Average anode effect duration (minutes/anode effect)
AEF × AED	= (anode effect minutes/cell-day)

Overvoltage Method. For this method the anode effect process data for calculating the smelter specific emission factor consists of the time-integrated amount of excess voltage resulting from anode effects.

Equation 3:

EF (kg CF₄ per tonne Al) = Overvoltage Factor ´ AEO/CE

Where:
Overvoltage Factor	= Proportion factor (kg CF₄ per tonne Al x CE per millivolt overvoltage)
AEO	= Anode effect overvoltage (millivolts)
CE	= Current efficiency (%)

Rearranging in the form to calculate the facility specific AEO factor:

Equation 4a:

CF₄ Overvoltage factor = EF$_{CF4}$ (kg CF₄/tonne Al) ´ CE/AEO

The Overvoltage equation is not effective for the estimation of C₂F₆ emissions. An alternative suggestion is to estimate C₂F₆ as a proportion of the CF₄.[19] The proportion is determined from facility specific measurements or from average proportions previously measured for reduction technology categories.

Equation 4b:

C₂F₆ Proportion Fraction = EF (kg C₂F₆/tonne Al)/EF (kg CF₄/tonne Al)

Equations 1 through 4b form the basis for calculation of the Tier 3b coefficients for calculations of CF₄ and C₂F₆ emissions from smelter process data. These equations are embodied in the worksheets included in Appendix A.

4.0 Process Data Requirements

The objective of the measurements is to develop the data necessary to calculate Tier 3b emission coefficients for calculating PFC emissions based on aluminum production data and anode effect data. The collection of accurate process data on anode effects and other facility processes is a key part of the measurement process. This section presents the specific information that should

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[19] G. Bouzat et al., Light Metals (1996), 413 – 417.

be gathered and summarized prior to initiating measurements.[20] Data on reduction technology, anode effects, and cell ventilation flow rate will be used to develop the sampling and analysis plan. These data will allow estimates of concentration of PFCs in the exhaust ducts and in fugitive emissions to prepare operating standards and to establish optimum calibration ranges for instrumentation. In particular, data are needed for characterizing the following facility properties:

4.1	Reduction Technologies;
4.2	Bath Chemistry;
4.3	Anode Effects;
4.4	Overvoltage Data;
4.5	Aluminum Production Data;
4.6	Power Supply Characteristics; and
4.7	Characteristics of Computer Control System.

See Appendix A for a smelter data collection template.

4.1   Reduction Technologies

The reduction cells on which PFC measurements are being made should be characterized as one of the types outlined below. No single naming convention for reduction cells exists. Often prebake cell names begin with the letter "P" for "prebake" followed by a number that describes the line current in kiloamperes for the cell design. For example a 225 kA cell would be referred to as a P-225 cell. Pechiney designed cells have the prefix "AP" for "Aluminium Pechiney" followed by a number that is one-tenth the design line current in kiloamperes. For example, the 180-kiloampere cell would have the name AP-18. Søderberg cells are named in a number of different conventions that incorporate the line current and company that designed the cells.[21]

Some primary aluminum production sites may operate with more than one type of reduction cell at the same site. At such sites, a separate measurement should be made for each type of reduction cell, line current and control system to accurately reflect the emissions of the entire site.

Cells should be classified as one of the following types:

- Prebake cell technologies:

    – Center work: 1) point feeders; or 2) bar break
    – Side work

- Søderberg technologies:

    – Vertical Stud Søderberg: 1) normal side break feeding; or 2) upgraded with point feeders
    – Horizontal Stud Søderberg: 1) normal side break feeding, or 2) upgraded with point feeders

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[20] Prior to or upon arrival at the site, contacts should be made with knowledgeable plant staff to arrange for collection of the anode effect and other data in the section of cells at which the PFC measurements will be made.

[21] For a more detailed discussion on Prebake cell nomenclature see Alton Tabereaux, "Prebake Cell Technology: A Global Review," Journal of Metals, 52(2), 22-28, 2000.

4.2   Bath Chemistry

The bath chemistry should be characterized as part of the process information gathered prior to the measurements. Reduction cells operate with an excess of aluminum fluoride over the inherent stoichiometry for pure cryolite, Na_3AlF_6. Typically aluminum fluoride, AlF_3, is added to the molten cryolite to increase the Lewis acidity with excess AlF_3 ranging from 3 to 12 percent. The percent excess fluoride should be recorded for the cells measured.[22]

At some primary aluminum production facilities lithium fluoride, LiF, is also added to the bath to lower electrolyte temperature. If LiF is added to the bath, the target percent LiF should also be recorded.

4.3   Anode Effects

While anode effects are easily recognized when they occur due to the large increases in voltage, important differences exist in the specific definitions of anode effects that should be recorded for the site.[23]

- **Voltage Criteria.** The specific voltage at which the cells are declared to be on anode effect should be recorded. This voltage is commonly referred to as the "trigger voltage". Prior measurements have shown that PFCs are emitted at cell voltages greater than 5 to 6 volts and that the rate of emissions increases rapidly with increasing voltage. Typical reduction cells operate at 4.2 to 5.0 volts with normal process related variations of several hundred millivolts. Most facilities record the onset of anode effects with computer control systems that scan individual cells at a frequency ranging from fractions of a second to 1 minute or more. Rules are coded into the computer for anode effect detection that include the voltage above which the cell is declared to be on anode effect. Also, some computer systems may require the initial recording of high voltage to be confirmed before the system records an anode effect. Whether the initial time increment is included in the definition of time on anode effect should be recorded.

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[22] The excess acidity is sometimes characterized by bath ratio. This parameter is defined as the weight ratio of sodium fluoride, NaF to AlF_3. For pure cryolite, Na_3AlF_6, the ratio is 1.5. Typically aluminum fluoride, AlF_3, is added to the molten cryolite to increase the Lewis acidity resulting in a ratio between 1.0 to 1.5.

[23] While there is no standard definition of anode effects used by all aluminum production facilities, the most often used approach for non-Pechiney technology plants is as follows:

> A pot enters anode effect status when it exceeds 8.0 volts. The anode effect is considered to be terminated ("killed") when the voltage falls below 6.0 volts. Anode effect minutes per cell-day (AE-min/cell-day) are the total minutes that the pot is at a voltage greater than 8.0 volts. After the anode effect is extinguished, a series of anode raises are made until the pot reaches the lower resistance target range. At this time, a counter is started. If an anode effect occurs within 15 minutes of the pot re-entering this target range, it is considered a repeat anode effect, and is not counted as a new anode effect. After this 15-minute period, any anode effects are counted as new.

Pechiney control systems operate on a quite different control algorithm as described in Section 4.4. Anode effect duration recorded by the older Pechiney control computer systems cannot be compared with those of alternative control systems. The newest Pechiney control systems have the capability of recording anode effect duration in either the time above 8 volts or as the total anode effect treatment time for comparison.

- **Anode Effect Frequency.** The anode effect frequency for the specific group of cells where PFCs are measured should be documented for the specific time interval over which the measurements are made. In addition, the overall anode effect frequency for the potline that contains the group of test cells should also be recorded. How a new anode effect is distinguished from a continuation of a prior anode effect should be determined and recorded. As noted above, the detection of the onset of an anode effect is unambiguous but some differences exist in the way that anode effects are counted by computer control systems. These site-specific rules for how anode effects are counted should be recorded. The specific rule that determines how the situation is treated when voltage dips to a value less than the trigger value but then at a later time again increases above the anode effect trigger voltage value should be recorded. Typically some time interval is defined during which if another voltage increase occurs on the same cell, the increase is recorded as a continuation of the prior anode effect rather than the start of a new anode effect.

- **Anode Effect Duration.** The duration of each anode effect and the average anode effect duration in minutes should be determined for the specific group of cells for which the measurements are being made. The duration of anode effects is typically measured by the computer control system. The computer counts the number of scan cycles when the cell's voltage is above the trigger level for each anode effect. The trigger level should be recorded and reported with anode effect duration data. The number of cycles for which an elevated voltage is detected is then multiplied by the scan cycle time to obtain the duration of the anode effect. If another definition of anode effect duration is used the details of the definition should be reported.

- **Distribution of Duration of Anode Effects.** In addition to the average anode effect duration, the statistical distribution of the duration of individual anode effect events for the most recent month for which data are available should be obtained and documented for the potline(s) for which the calculated emission coefficient is to apply. Changes in the distribution should trigger consideration of making a new measurement (see Section 10, Measurement Frequency and New Measurements).

- **Voltage Profiles of Anode Effects.** If detailed time-voltage information is available for individual anode effects the information should be recorded that illustrate typical anode effect voltage characteristics.

4.4 Overvoltage Data

Overvoltage data should be obtained and recorded for the specific group of cells where CF_4 and C_2F_6 are measured, if this data is available. For those facilities that operate with Aluminium Pechiney process control, the overvoltage data should always be collected.

The overvoltage data are the integral (i.e., sum) of the product of time and voltage above the target operating voltage (corresponding to the target resistance), divided by the time over which the data are collected (hour, shift, day, month).

Equation 5:

$$AEO = \frac{\int_{t1}^{t2} I(R_t - R_{t\,\arg et})\Delta t}{Number\ of\ cells \times (t_2 - t_1)}$$

Where:

AEO	= Overvoltage (Volts)
I	= Line current (amperes)
t_1 and t_2	= Times at the beginning and end of the time period for calculating overvoltage (seconds)
R_t and R_{target}	= Instantaneous resistance and the target resistance of the section of cells considered (ohms)
Δt	= Time interval between successive scan cycles of each cell
Number of cells	= Number of cells in the section being considered

During each anode effect, the cell overvoltage recorded by the control system at each scan cycle is multiplied by the scan cycle time (seconds). The total of these volt-seconds recorded for the group of cells being measured is then divided by the number of cells and the time (seconds) over which the data are collected to calculate the overvoltage data for the group of cells. Since time is included in both numerator (seconds) and denominator (days), the data in the expression can be reduced to units of voltage. These data, expressed in millivolts, are the anode effect overvoltage (AEO) data that are used in equations 4a to calculate the Overvoltage factor for CF_4 emissions. Any deviation from this definition should be reported, such as "algebraic" overvoltage,[24] voltage marking the end of anode effect, or if the target operating voltage is replaced by a fixed conventional voltage to account for overvoltage.

4.5   Aluminum Production Data

The time rate average aluminum production should be obtained and recorded for purposes of normalizing the time rate of emissions of CF_4 and C_2F_6 to obtain emission factors for kg CF_4/tonne Al and kg C_2F_6/tonne Al. The actual aluminum production, as measured using tap weights, should be compared to the calculated value, as calculated using line current and current efficiency:

- **Tap Weights.** The time rate of aluminum production should be obtained and recorded from the average of tonnes Al per cell-day over the past one month period from production tap weight data.

- **Line Current and Current Efficiency.** The average line current in kiloamperes and current efficiency should be obtained from location staff and recorded for the potline to which the measurements apply. The expected average production rate for primary aluminium should be calculated and recorded as a comparison with the value obtained from tap weight data, according to the following equation:

Equation 6:

Aluminum Production (tonne Al/cell-day) = 0.008058 (tonne Al/(kA-cell-day)) ´ I ´ CE

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[24] "Albegric" refers to a method of overvoltage accounting where voltages under target operating voltage result in a discount on overvoltage.

Where:

I   = Line current (kiloamperes)

CE   = Current efficiency (as a decimal fraction)

From Faradays Law, 0.008058 tonnes of Al are produced per kA-cell-day at 100% current efficiency.

If the result from this calculation differs by more than 5 percent from the previous months tap weight data as collected in the smelter data sheet, Appendix A, both pieces of information should be confirmed.

4.6   *Power Supply Characteristics*

While the type of power supply has no explicit impact on determining the Tier 3b coefficients, the added information may be useful in helping location staff estimate the cost impact of anode effects to the site. Two major types of power supplies are used for potlines: 1) constant power level; and 2) constant current power sources. For a constant power level system, a small reduction in line current and an associated reduction in aluminum production occurs due to the increased resistance across the bath-anode interface during an anode effect. A different type of impact is experienced at those facilities utilizing constant current power sources. In this case, the added resistance caused by the anode effect results in a higher power requirement to maintain the constant current with a subsequent increase in unit production power cost.

4.7   *Characteristics of Computer Control System*

Information should be recorded about the process computer control system. Section 4.3 defines some of the characteristics of the computer control system. The additional key information needed to characterize the system is the scan rate and what steps are taken to automatically kill an anode effect once the anode effect is initiated.

The scan rate is the frequency at which the potline is interrogated and cell voltage data collected. The scan rate represents the upper limit of temporal resolution of anode effect data. When the scan rate is very fast, many cycles per second, a large amount of data are generated and some amount of time averaging is done on the data before storing in the computer data recording system. This averaging does not affect the accuracy of time average data such as anode effect overvoltage or the responsiveness of the system to the onset of anode effects. However, high-resolution voltage information may not be available to correlate with PFC emission rate because of this averaging.

Also, the nature of mitigation steps that are initiated when the cell is on anode effect by the computer control system should be described and recorded. For prebake cells these actions are typically movements of the bridge structure to which the anodes are attached. These movements lower the anodes in response to the detection of an anode effect. The lowering of the anodes reduces the cell resistance and momentarily shorts the electrodes to kill the anode effect. The cycle of times and corresponding movements of the bridge structure from which the anodes are suspended should be diagramed. In particular, the distance the bridge is lowered, the wait-time before additional action and the subsequent raises that the computer control system initiates should be diagramed. The average efficiency of the computer system in killing anode effects should be recorded. This parameter is typically quoted as "percent manual kills." The percent of manual kills impacts overall PFC emissions in that the duration of these anode effects is typically

relatively long and manual intervention by inserting a wood pole into the cell is necessary to kill the anode effect. Fewer mitigation options are available for Søderberg cells, however, in some Søderberg cells, compressed air is injected under the anode on computer detection of an anode effect. If anode effect kill mitigation is employed at a Søderberg facility then it should be noted.

5.0 Sampling Design

Care should be exercised to ensure that PFC sampling fairly represents the long-term operations of the potline. Also, attention should be given to proper measurement and treatment of gas flow temperatures and pressures in which PFC concentrations are being measured. This information is important so that the measured PFC concentrations can be properly converted into emission rates. This section presents the seven key factors for defining the sampling design:

     5.1   Reflection of "Normal" Conditions;
     5.2   Sampling Configuration;
     5.3   Sampling Locations;
     5.4   Flow Homogeneity Requirements;
     5.5   Sampling Time;
     5.6   Duct Flow Measurement; and
     5.7   Potroom Rooftop Flow.

5.1 Reflection of "Normal" Conditions

Before considering measurement of PFCs for the purpose of establishing IPCC Tier 3b equation coefficients, the potline should be operating in a control condition with respect to those process variables that would affect the Tier 3b coefficients. Key process parameters that should be stable include bath chemistry, distribution of anode effect durations, anode effect termination algorithm, percent manual terminations, and cell control and feed strategy. The start up of a new cell, while a normal event in the long-term operation of a potline, should be avoided if possible during the sampling for determination of emissions factors. Prior work has shown that the impact of new cell start-ups on overall emissions is negligible unless there is a major restart campaign.[25] Other events that would result in atypical operation of the line should be avoided during the measurement campaign. All the cells for which the measurements are made should be controlled with control algorithms for which the Tier 3b emission coefficients are to be applied. A change in the control algorithm should trigger new measurements and recalculation of Tier 3b coefficients (see Section 10.0, Measurement Frequency and New Measurements).

A histogram of anode effect duration should be prepared and compared with the histogram of the previous month's data to assure that the test period is representative of longer term performance. Similarly, a comparison should be made on the percent of manual kills of anode effects. In particular, some PFPB facilities have low anode effect frequencies where slope or overvoltage coefficients may have to be based on a limited number of anode effects. For these facilities, exhaust emissions measurement data from any anode effect when the cell hood must be opened

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[25] Guy Bouchard, Jens Kallmeyer, Alton Tabereaux and Jerry Marks, "PFC Emissions Measurements from Canadian Primary Aluminum Production," Light Metals (2001), 283 – 288.

during termination of the anode effect should be excluded from the data set used for calculating Tier 3b coefficients.[26]

5.2 Sampling Configuration

Several sampling designs have been tested and found effective in measuring PFCs in exhaust ducts and for sampling fugitive PFC emissions. These designs serve as examples for assembling a sampling system. The specific system of pumps, sample lines, filters, scrubbers and other gas transfer equipment depends on the needs of the site and the sampling requirements. Summarized below are two approaches that have proven effective for measuring PFCs.

- **For sampling PFCs in smelter exhaust ducts.** The exhaust gas intake is first filtered through a sintered stainless steel filter on the end of a length of stainless steel tubing inserted through a sample port in the duct. The sample is drawn continuously out of the exhaust duct by use of sampling pumps or a gas eductor through the stainless steel tubing, through a Teflon or polyethylene sample transfer line, through a dust filter, and any needed sample stream conditioning treatment. The flow is directed to the at-line analyzer, or, alternatively, to the sample container if a time average sample is being collected.

- **For sampling PFCs in the potroom roof and background emissions.** The intake consists of a polypropylene particulate filter on a Teflon or polyethylene sample transfer line connected to a low flow rate sampling pump, which draws the gas into a gas sample bag.

5.3 Sampling Locations

PFC sampling locations in the fume collection ducts should be chosen to ensure that the gas sampled is homogenous and fully representative of the cells for which anode effect data are being collected. Safe access should be a key criterion for all sampling operations. Below, the key considerations are described for the three sampling locations necessary for measurements:

5.3.1 Duct locations;
5.3.2 Fugitive sampling locations; and
5.3.3 Background sampling locations.

5.3.1 Duct locations

Duct locations should be chosen to include the maximum number of cells and still maintain concentrations of CF_4 and C_2F_6 that are accurately measurable with the chosen instrumentation. The ventilation gases from all the other cells in the section being measured act to dilute emissions resulting from an anode effect in one cell. By combining knowledge of the dynamic response range of the measurement instrumentation and estimates of the concentration of PFC gases to be expected as described below, sampling locations can be properly selected. Another

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[26] C. Martin and E. Couzinie, "PFC Emissions Measurement from Aluminium Pechiney Smelters," Light Metals (2003), pp 233 – 240.

important factor in the choice of sampling location is accessibility since periodic access is required to check duct flow rate and to do routine checks of the sample probe.

Prior to beginning sampling and measurements, CF_4 concentrations should be estimated to establish the instrument measurement and calibration range and to determine the optimum number of cells to be included in the test section. C_2F_6 concentrations can be estimated by multiplying CF_4 estimates by typical ratios of C_2F_6 to CF_4 for each reduction technology as follows: 0.1 for PFPB, CWPB and HSS, 0.05 for VSS and 0.3 for SWPB.[27] In general two measurement techniques are available for estimating CF_4 concentrations:

- **At-line measurements.** Estimates of duct concentrations of CF_4 in near real time measurements can be made for an anode effect of duration, D, by applying an empirical calculation. The equation is based on IPCC recommended average values for the slope method for CF_4.

  Equation 7:

  CF_4 Concentration (ppmv) = S ´ K ´ I /(f ´ N)

  Where:
  S = IPCC recommended Tier 2 slope values for each reduction technology type (kg CF_4/tonne Al)/(anode effect minutes/cell-day)
  K = Constant (µl CF_4-tonne Al)/(kg CF_4-kA-cell-day) = 2.2×10^6
  I = Line current (kA)
  f = Ventilation flow rate per cell at 0ºC and 760 mm Hg (liters/minute-cell)
  N = Number of cells in test section of cells to be measured (cells)

- **Time average sampling into bags.** For time average samples for duct samples approximate concentration of CF_4 should be estimated according to the following equation below.

  Equation 8:

  CF_4 Concentration (ppmv) = S ´ K ´ I ´ D/(f ´ N ´ t)

  Where:
  S, K, I, f and N = As defined for Equation 7.
  t = sampling period duration (minutes)
  D = Duration of anode effects expected in sampling period (minutes)

5.3.2 Fugitive Sampling

Fugitive samples should be collected if fugitive emissions are likely to be greater than 5 percent of the total PFC emissions. When fugitive emissions are judged to be equal to or less than 5 percent of total emissions, the measurement made in the duct should be adjusted by an amount based on the measured hydrogen fluoride collection efficiency. If fugitives are judged to be less than 5 percent of the total and hydrogen fluoride collection efficiency data are not available, the

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[27] Ratios of C_2F_6 to CF_4 are based on coefficients provided in the IPCC Good Practice Guidance. However, the SWPB coefficient in the IPCC Guidance has been shown to be low based on measurements; the 0.3 factor reflects this measurement data.

duct value should be increased by 2.5 percent. This increment would be equivalent to an estimated duct PFC collection efficiency of 97.5 percent.

Collection efficiencies for PFPB facilities are typically 95 percent or greater while for SWPB, VSS, and HSS facilities collection efficiencies may range from 85 to 95 percent. The fugitive emission rate may be quite different when the surface cover is disturbed during the manual killing of anode effects than values typically recorded for hydrogen fluoride collection efficiencies. For this reason, a measurement of fugitive PFC emissions should be made for SWPB, VSS, and HSS facilities rather than correcting duct PFC measurement results based on hydrogen fluoride collection efficiency. Also, as noted previously, data from anode effects where the hoods are opened during termination of the anode effects should not be included in the data set from which slope and overvoltage coefficients are calculated.[28]

Rooftop sampling locations, similar to duct locations, should be chosen for good accessibility, safety and availability of any needed services. Samples of fugitive emissions from potroom roofs should be taken from EPA Method 14 or similar available sampling systems if that system is available.[29] Method 14 provides for sampling a representative section of the rooftop flow through a series of funnel shaped intakes. These sample intakes are joined in a manifold and then are brought to ground level through a duct operated at a slightly negative pressure.

If no such sampling system is in place, sampling locations that represent the average flow from the rooftop should be selected based on discussions with the smelter contact person. Fugitive samples are collected by pumping a constant small flow into special multi-layer sample bags to develop a time average composite sample. A minimum of three point locations should be chosen to reflect the overall average flow out of the potroom. The concentrations of CF_4 and C_2F_6 in rooftop gas samples are very low because the PFC emissions have been diluted with large quantities of potroom air. Consequently, measurement methods for these samples may require detection limits of 0.001 ppmv for accurate measurements for facilities with good fume collection efficiency and low anode effect frequencies.

5.3.3 Background Sampling Locations

A background sample should be taken from an area adjacent to the potroom where measurements are being made in a similar manner to the rooftop fugitive sample. The purpose of the sample is to test for any interference that might contribute to the analyte signal. Background CF_4 and C_2F_6 levels should be insignificant compared to average concentrations in the fume ducts or to fugitive emissions for those facilities where measurement of fugitive emissions is recommended. While some potential exists for back ingestion of PFC emissions from the fume treatment facility, dilution of these emissions should make these concentrations insignificant compared with primary emissions from potrooms.

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[28] C. Martin and E. Couzinie, "PFC Emissions Measurement from Aluminium Pechiney Smelters," Light Metals (2003), pp 233 – 240.

[29] U.S. EPA, *Environmental Protection Agency Method, 40 CFR, Ch. 1, Pt. 60, App.A, Method 14*, 1993, http://www.epa.gov/ttn/emc/promgate.html. This method describes a rooftop sampling system that draws an air sample from the roof monitor to ground level.

5.4 Flow Homogeneity Requirements

For accurate calculation of Tier 3b emission coefficients, direct correlation of anode effect data and the resulting emissions measured in the fume collection duct is essential. The measured concentrations of CF_4 and C_2F_6 in the duct must be representative of the entire flow in the duct location where sampling takes place. Mixing must be complete in the duct at the sampling location. To evaluate the extent of mixing, the homogeneity of PFC concentrations should be evaluated.

5.4.1 Evaluating Homogeneity of Duct Flows

Before measurements are begun, full mixing of all gas components at the sampling point must be demonstrated. Design of potroom fume collection systems typically involve collection of fumes from each cell into a duct that is merged into a header that collects fumes from a group of cells. These headers are then merged with other ducts that may in turn be further merged to collect fumes for gas fume treatment. Experience has shown that gas flows may remain segregated for some distance after merging. The impact of this effect is that the concentration of PFC components may be quite different across the cross section of the duct. When these concentrations are applied to the full flow in the duct, erroneous emission fluxes will be recorded. To avoid such errors a new sampling location should be chosen whenever non-homogeneity of greater than 10 percent is measured across the duct cross section.

5.4.2 Testing for Homogeneity

The homogeneity of PFC concentration across the duct cross section should be tested to confirm the viability of the sampling point. The homogeneity test is accomplished by injecting a small constant flow of a tracer gas[30] into the exhaust duct of one of the reduction cells and then monitoring the concentration of the tracer at the candidate sampling point in the main duct. A stainless steel probe is inserted into the duct and the concentration of the tracer is measured at five equally spaced points across the duct cross section. The concentrations should not vary by more than 10 percent at any of the sampling points. If the variation is greater than 10 percent another sampling location should be tested.

5.5 Sampling Time

The sampling strategy should allow for a good statistical sampling of long term anode effect frequency and anode effect duration distribution. Because anode effects of similar duration have high variability in emissions of CF_4 and C_2F_6, the sampling strategy needs to give a robust average value of emission coefficient by reflecting all aspects of the aluminum production process. Consequently, the duration of sampling during all the cycles of smelter operation needs to be addressed in the sampling strategy. Each of these factors is described below.

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[30] The specific tracer gas compound and injected tracer concentration should be chosen with consideration of the measurement instrument in mind. Sulfur hexafluoride (SF_6) has been used in a number of applications because it has good sensitivity for infrared measurements, is not normally present in the gas stream, and is relatively stable at the temperature encountered in the fume duct system. However, SF_6 is also a strong greenhouse gas with a long atmospheric lifetime and should be avoided if another tracer such as HCFC-123 can be successfully used.

- **Sampling Time.** A running average for each emission factor, CF_4 and C_2F_6, should be calculated after each sampling period as new measurement data is being collected. Sampling should continue until the running average factor does not change by more than 10 percent from the previous average value. In any case, sampling and measurement should be made for a minimum of 72 hours. For the most modern smelters operating with anode effect frequencies at or below 0.1 anode effects per cell-day, the 10 percent variability standard may be difficult to achieve. For these locations a criterion of sampling for a minimum number of anode effects may be a more realistic goal. The minimum number should include anode effects that have a range of duration and anode move cycles that are representative of long term operation. Adequate sampling time should be assessed by convergence of the calculated Tier 3b coefficients to a constant value with an acceptable uncertainty by calculating a running average of the values as the sampling continues.

- **Reflection of Smelter Production Cycles.** Sampling should include all the normal cycles of smelter operation (i.e., tapping, tracking, feeding, anode changing). Preferably the sampling should be done in integrals of the time for a complete cycle of operation. Normal smelter operations involve repeating several different operational steps during which time cells are tapped of aluminum and fed under predetermined schedules. In addition, anodes are changed on a specific schedule. Finally, there is a time period when cells are allowed to electrolyze the available alumina in the bath without new additions to confirm whether the resistance is decreasing or increasing over time ("tracking"). Incorporating all the production cycles into the sampling period is consistent with the sampling time requirements described above.

5.6 Duct Flow Measurement

The gas flow velocity in the duct where PFCs are sampled should be measured at time intervals sufficient to accurately convert CF_4 and C_2F_6 concentration values into mass emission rates. The flow rate should be measured by either one of the methods described below. Temperature and pressure in the duct should also be measured so that the mass flow rate can be calculated.

- **Pitot Tube Method.** The volumetric flow rate can be determined using the methodology described in EPA Method 1 – Sample and Velocity Traverses for Stationary Sources.[31]

- **Tracer Gas Injection Method.** Alternatively, the volumetric flow rate can be assessed by injecting a constant known amount of a tracer gas into the duct upstream of the sampling point. The concentration of the tracer is then measured at the sampling point. From the dilution factor the volumetric flow rate can be calculated as follows:

Equation 9:

Duct flow rate (l/min at 0 °C and 1 atm) = I ´ 10^3/C

Where:
I   = Tracer injection rate (ml/min @ 0 C and 1 atm)

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[31] U.S. EPA, *Environmental Protection Agency Method 1, Pt. 60, App. A, Method 1, Sample and Velocity Traverses For Stationary Sources*, 1993, http://www.epa.gov/ttn/emc/promgate.html

C = Measured tracer concentration at sampling point (ppmv or µl tracer per liter exhaust flow)

10^3 = µl/ml

The tracer method has an advantage of being capable of assessing short-term variation in duct flow rate. The method is particularly advantageous when instruments capable of simultaneously measuring the tracer gas and the PFC components are in use.

5.7 Potroom Rooftop Flow

Roof sampling should be conducted concurrent with duct sampling. While no specific requirement exists to isolate the rooftop emissions of the particular cells for which measurements in the fume duct are made, fugitive emissions should be measured in the specific potroom where duct measurements are made.[32]

Roof ventilation rates (volume flows out the roof) should be calculated using whatever flow measurement system is in place and routinely used by the smelter personnel. Substantial variability in rooftop flow rate with the diurnal cycle or changes in wind patterns around the potroom can occur, consequently, potroom rooftop flow should reflect the conditions during the actual measurement period. These measured flows should then be applied to the specific samples taken in the rooftop location to calculate PFC fugitive emissions for the sampling period.

Time-averaged samples should be drawn from the chosen sampling location using constant flow pumps. The samples should be collected into multi-layer laminated gas bags[33] or other bags equivalent in performance over periods of time corresponding to work shifts, or logical divisions in the operating cycle of the potroom. The exhaust gas should be pumped at a constant rate of about 30 to 40 cc/min to collect about 20 ± 2 liters of sample over an 8 to 12 hour period. These samples should be taken concurrently with the continuous monitoring of the duct gas, and labeled as to date and time of collection.

Temperature and atmospheric pressure should be recorded so that rooftop flows can be reduced to standard conditions for calculation of PFC flux rates.

6.0 PFC Concentration Measurement

Two different approaches can be used to measure PFC concentrations. First measurement can be made to determine CF_4 and C_2F_6 concentrations in sample bags that are collected at the measurement site over some extended sampling period. The measurement of the PFC concentration in the bag samples can be measured either at the test site or transported to a laboratory for measurement. Alternatively CF_4 and C_2F_6 concentrations can be measured at the site using at-line instruments measuring PFC concentrations in near real time as anode effects

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[32] In some measurement applications, duct emissions result from cells in two different potrooms. If operational procedures are similar in both potrooms, fugitive measurements in one of the potrooms is adequate. The approach here is to measure duct and fugitive specific emissions separately and then add the two specific emissions to arrive at the total specific emissions. The main requirement for the efficacy of this approach is that the factors affecting capture efficiency in the cells where duct PFCs are measured are similar to those in the potroom where fugitives are measured.

[33] http://www.calibrated.com/home.htm

occur. Either approach, when implemented according to the good measurement practices described here, results in an accurate Tier 3b measurement coefficient.

Typically the measurement of time average bag or canister samples in the laboratory or by portable equipment transported to the test site is a less costly approach. If smelter staff are available who are trained in sampling and gas volume measurement, the samples can be taken and forwarded to a laboratory for measurement. The immediate feedback of measurements conducted at the production line in near real time provides the opportunity to adjust measurement and sampling strategy if unexpected problems are encountered. The near real time continuous measurement also allows the collection of data on emissions from individual anode effects if such data is of interest to test the conformity of accepted algorithms for calculating PFC emissions from anode effect process data. The final choice of method should depend on what measurement equipment is available, the experience level of facility staff, and whether data on emissions of individual anode effects is of interest to the facility.

6.1 Standards

Standards containing CF_4 and C_2F_6 covering the expected range of concentrations should be prepared that cover the full range of concentration expected to be encountered in the measurements. Working standards can be purchased from commercial gas suppliers and should be traceable to or certified by the U.S. National Institute of Standards and Technology (NIST), or a comparable national standard setting organization.

6.2 Instruments for Laboratory Based Measurement Methods

If a laboratory based measurement approach is chosen, either gas chromatography with mass spectrometry detection (GC/MS) or Fourier Transform Infrared Spectrometry (FTIR) should be used for measurement of CF_4 and C_2F_6 from fume duct samples. Each of these approaches is described below.

6.2.1 GC/MS

GC/MS analysis results are free of interference from other gas species that accompany the PFCs. Separation of CF_4 and C_2F_6 is accomplished using liquid nitrogen to cool the GC column to –40 ℃. The chromatography takes place on a stainless steel (3.2 mm x 3.7 m) Alumina 5 Å 80/100 mesh column or the performance equivalent. The temperature is then ramped from –40℃ to +40℃ to elute reduction cell exhaust gas components. Carbon dioxide and traces of water are eluted after running a series of samples by ramping to high temperature. The mass spectrometer detector is operated in the single ion monitoring mode at m/z 69 which is characteristic of both PFC components. Working standards should be prepared by diluting more concentrated CF_4 and C_2F_6 standards in nitrogen. Gas should be measured with gas-tight syringes. Using fifty microliter injections of both samples and standards, detection limits of 0.05 ppmv and 0.04 ppmv CF_4 and C_2F_6, respectively, can be achieved.

6.2.2 FTIR

CF_4 and C_2F_6 contents should be measured in a 10-meter path length gas cell. The spectrometer should be calibrated with gas standards certified by or directly traceable to the U.S. National

Institute for Standards Technology (NIST), or a comparable national standard setting organization. The smelter fume duct gas sample is allowed to fill an evacuated FTIR gas cell to atmospheric pressure. If desired, the sample can be treated to remove components which might result in spectral interference or damage to the gas cell. The sample absorption spectrum is recorded at a suitable resolution[34] using a HgCdTe (MCT) detector cooled with liquid nitrogen or a thermo-electrical cooler. The absorptions at the characteristic wavelengths for CF_4 and C_2F_6 are compared to that of standards measured in a similar manner. Detection limits of 0.7 ppbv CF_4 and 1.1 ppbv C_2F_6 have been measured. When appropriate precautions are taken with regard to spectral background correction for traces of water in the samples, detection limits of less than 0.1 ppbv can be achieved in long path gas cells.

6.3 Instruments for Field Measurement Methods

The mass spectrometer, tunable diode laser absorption spectrometer, photoacoustic spectrometer, and the FTIR spectrometer are all commercially available instruments suitable for measuring PFCs in fume duct samples at-line at primary aluminum production sites. Each of these methods is summarized below:

- **Mass spectrometer.** The process mass spectrometer provides a near real time measurement of both PFC gas components, as well as several other sample components if desired. The detection of the PFC gases is without any serious interference and the sensitivity of the instrument is adequate for the range of concentrations expected for duct measurements. The instrument must be calibrated in place, prior to the start of PFC monitoring. The detection limit for PFC compounds is typically about 0.1 ppm so there is not adequate sensitivity for direct measurement of fugitive PFC emissions and an alternative strategy must be used when measurements of fugitives are required. While the mass spectrometer has demonstrated good performance in the relatively strong magnetic fields common around smelter facilities, it is desirable to position the instrument in a location where magnetic fields are relatively invariant, since strong, fluctuating magnetic fields can affect the instrument's response. This equipment is relatively heavy and requires a mobile truck to transport to the measurement location in the facility.

- **Tunable Diode Laser Absorption Spectrometer (TDLAS).** TDLAS is an infrared absorption technique that uses a diode laser to achieve a very narrow emission source bandwidth. As a result, the specificity of the technique is very good. The sensitivity is also excellent and the instrument is capable of direct measurement of both PFC gas components in electrolytic cell exhaust ducts. It has not been applied to fugitive gas measurements, consequently, if fugitives are to be measured, a laboratory based approach, or open path methodology using FTIR techniques would provide a viable strategy. The TDLAS unit as used for previous PFC measurements is relatively large. A mobile laboratory or trailer is needed to transport the instrument and ancillary sampling equipment from site to site. The equipment as used for past PFC measurements, is not broadly commercially available, is relatively expensive and specialized and requires

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[34] Spectral interferences are best avoided by use of operating resolutions of 1 cm[1] or better; however, the measurement can be made using a lower resolution when adequate corrections are made for spectral interferences arising from other components of the exhaust gas stream.

experienced specialists to operate it. A newer, lower cost TDLAS instrument has been developed for the measurement of CF$_4$, however, the instrument has not been yet field-tested.[35]

- **Photoacoustic Spectrometer (PAS).** The PAS is a filter type infrared spectrometer that uses a sensitive microphone as a detector to measure changes in absorption of infrared energy. The instrument is quite sensitive for the PFC gas components; however, interference can occur from any water, sulfur dioxide or methane accompanying the PFC gases. The sample must be conditioned to minimize or remove these potential interferences prior to measurement. Scrubbers with sodium carbonate or Ascarite can remove hydrogen fluoride and sulfur dioxide. Water vapor is removed by passing the sample stream through a copper tube at dry ice temperature. The instrument calculation software also allows for compensation for limited quantities of interferences by measuring interfering compounds at alternate wavelengths. The PAS does not sample the gas stream continuously as do the other instrument methods described here. Instead the instrument operates in a sequential cyclic analysis mode with a new sample introduced to the analyzer detector on a frequency of once each three to five minutes. The sampling cycle is typically about 15 seconds of this total three to five minute cycle. Accommodation must be made for the substantial dead time of the basic instrument sampling system to prevent bias in results. Collection of time average samples in canisters or sample bags and subsequently analyzing with the PAS is an effective approach to overcome the dead time limitation. The instrument is the most portable of the instruments described here weighing approximately 10 kg and is easily operated by staff with a basic knowledge of measurement science.

- **FTIR.** The FTIR spectrometer has been used in an open path mode for fugitive emission PFC measurements at aluminum smelters[36] and has been used in the extractive mode for PFCs[37] and other field analysis applications.[38] There are a number of potential advantages from use of FTIR including the ability to measure other components of interest in the gas stream and the ability to post process the spectral data. As with some of the other methods, potential interferences from overlap of interfering spectral bands must be overcome through calibration procedures or spectral stripping algorithms.

7.0   Calculation of Emission Coefficients

This section presents the approach for using the measurement data for estimating emission coefficients. In particular, equations are provided for calculating specific PFC emission factors as kg CF$_4$ and kg C$_2$F$_6$ per tonne aluminum produced. In addition, slopes are computed for each

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[35] H.A. Gamble, D.R. Karecki, G.I. Macka and H.I. Schiff, "A Streamlined, Portable Mid-IR TDL Based System for On-site Monitoring Of PFCs From Potroom Exhaust Ducts," Light Metals (2003), pp 215 – 220, 2003.

[36] H.A. Gamble, G.I. Mackay, D.R. Karecki, J.T. Pisano and H.I. Schiff, "Development of a TDLAS Based Method for Monitoring Perfluorocarbon Production During the Aluminum Smelting Process," Light Metals (2001), 275 – 281, 2001.

[37] N.R. Dando, "In-Plant PFC Monitoring: Technology Options and Performance Concerns," Light Metals (2003), pp 205 – 210, 2003.

[38] U.S. EPA, *Environmental Protection Agency Test Method 320, 40 CFR Part 63, Appendix A, Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Infrared (FTIR) Spectroscopy*, http://www.epa.gov/ttnemc01/promgate/m-320.wpd.

PFC compound as well as the overvoltage factors for facilities where overvoltage is recorded. The spreadsheets included in Appendix A, Data Collection, Calculations, and Reporting Template, have the calculations embedded in them.

7.1 Option A: Calculating Emission Factors Based on Sampling into Bags for Measurement

This section presents the equations for calculating specific emissions for CF_4 and C_2F_6 when measurements are made on time average samples using sample bags or canisters. Equations are also presented for calculating slope and overvoltage coefficients from the specific emissions. The slope and overvoltage factors are the coefficients in the IPCC Tier 3b method for inventory of PFCs based on anode effect data. Each of the recommended 10 steps is described below.

Step 1: Calculate total gas flows for the sampling period for each duct sampling location and for potroom rooftop flows when fugitive measurements are made.

- Step 1a: Calculate the fume collection duct flow rate after measuring average gas velocity, duct cross section area, duct temperature, and duct pressure:

$$f = V \times S \times 273/(T+273) \times P/760 \times 3600$$

Where:

f	= Flow rate (m^3/h at 0ºC and 1atm)
V	= Average gas velocity (m/s)
S	= Duct cross section area (m^2)
T	= Duct temperature (ºC)
P	= Duct pressure (mm Hg)
273	= Addition factor converting ^oC to ^oK
3600	= Factor converting hours to seconds (3600 s/hr)
760	= Atmospheric pressure (mm Hg)

Calculate total flow, F, for the sampling period in m^3 at 0ºC and 1 atm:

$$F = f \times t$$

Where:

F	= Total flow (m^3 at 0ºC and 1 atm)
f	= Flow rate (m^3/h at 0ºC and 1atm)
t	= Sampling time (h)

- Step 1b. Similarly, calculate the total flow through the potroom rooftop:

$$f = V \times S \times 273/(T+273) \times P/760 \times 3600$$

Where:

f	= Rooftop flow rate (m^3/h at 0ºC and 1atm)
V	= Roof monitor average gas velocity (m/s)

S	= Roof monitor cross section area (m^2)
T	= Average rooftop temperature (ºC)
P	= Rooftop pressure (mm Hg)
273	= Addition factor converting *ºC to ºK*
3600	= Factor converting hours to seconds (3600 s/hr)
760	= Atmospheric pressure (mm Hg)

Step 2: Calculate total kg CF_4 for sampling period captured by the exhaust duct and the kg CF_4 per anode effect minute for the sampling period.

- Step 2a. Calculate total kg CF_4 for sampling period captured by the exhaust duct.

  Total kg CF_4 captured by duct for the sampling period (kg $CF_{4\ duct}$)=
  C (ml CF_4/l air) ´ (1 l CF_4 /10^6 ml CF_4) ´ (1mole CF_4 /22.4l CF_4) ´ 0.088 (kg CF_4/mole CF_4) ´ 1000 (l air/m^3 air (0ºC, 1atm)) ´ F (m^3 air @ 0ºC, 1atm)

  Where:
  C   = CF_4 concentration (µ l CF_4/l air) = ppmv CF_4

- Step 2b. Calculate the total kg CF_4 captured by the duct for the sampling period per anode effect minute by dividing the total kg CF_4 from above by the total anode effect minutes recorded for the test section during the sampling period.

  kg $CF_{4\ duct}$/AE minute =   kg $CF_{4\ duct}$/à (duration of all anode effects in sample period)(min)

Step 3: Calculate total kg C_2F_6 for the sampling period captured by duct.

  Total kg C_2F_6 captured by duct for the sampling period (kg $C_{2}F_{6\ duct}$)=
  C (ml C_2F_6/l air) ´ (1l C_2F_6/10^6 ml C_2F_6) ´ (1 mole C_2F_6/22.4 l C_2F_6) ´ 0.138 (kg C_2F_6/mole C_2F_6) ´ 1000 (l air/m^3 air (0ºC, 1atm)) ´ F (m^3 air @ 0ºC, 1atm)

Step 4: Calculate the weight ratio of C_2F_6 to CF_4:

  $$Ratio_{C_2F_6/CF_4} = kg\ C_2F_{6\ duct}/\ kg\ CF_{4\ duct}$$

Step 5: Calculate p, total aluminum production for the duct sampling period:

  p (tonne Al) = P (tonne Al/cell-day) ´ N (cells) ´ t(h)/24(h/day)

  Where:
  P   = Aluminum production rate (tonne Al/cell-day)
  N   = Number of operating cells in sampled section
  t   = Sampling duration (hrs)

Step 6: Calculate PFCs emitted as fugitive emissions.

- Step 6a. When fugitive PFC emissions are expected to be less than 5% of total PFC emissions, estimate fugitive CF_4 and C_2F_6 as 2.5% of total PFC emissions as follows:

$$kg_{CF_4\text{-}fugitive} = kg_{CF4\text{-}duct} \times 0.025/0.975$$

$$kg_{C_2F_6\text{-}fugitive} = kg_{C_2F_6\text{-}duct} \times 0.025/0.975$$

- Step 6b. When fugitive PFC emissions are expected to be greater than 5% of total PFC emissions, fugitive emission rates are based on measurements. Measurement can be made by direct open path FTIR spectrometry or by the time average bag method. The equations below are based on the time average bag method; however, they also apply to FTIR measurements by use of the average CF_4 concentration measured by the FTIR process rather than the average concentration calculated in Step 6b.1

  - Step 6b.1. First calculate the average CF_4 concentration from the rooftop bag samples for each sampling period

$$C_{CF_4\text{-}avg} = (C_{bag1} + C_{bag2} + C_{bag3} \dots + C_{bag\,n.})/(Total\ number\ of\ bag\ samples\ n)$$

  - Step 6b.2. Next, similar to the method in Step 2 above, convert the average bag CF_4 concentration into kg CF_4 emitted from the potroom rooftop for the sampling period by multiplying by the total potroom ventilation flow through the rooftop from Step 1b. for the sampling period.

Total kg CF_4 emitted as fugitive emissions for the sampling period =
$kg_{CF_4\text{-}fugitive} = C_{CF4\text{-}avg}\ (\textbf{m}l\ CF_4/l\ air) \times (1l\ CF_4/10^6\ \textbf{m}l\ CF_4) \times (1mole\ CF_4/22.4\ l\ CF_4) \times 0.088\ (kg\ CF_4/mole\ CF_4) \times 1000\ (l\ air/m^3\ air\ (0^oC,\ 1atm)) \times F\ (m^3\ air\ @\ 0^oC,\ 1atm)$

Where:
 F   = total flow through potroom rooftop for sampling period (m^3 air at 0ºC and 1atm)

  - Step 6b.3. Next, calculate the fugitive kg CF_4 per anode effect minute by dividing the total kg CF_4 emitted as fugitive emissions from Step 6b.2 by the total anode effect minutes for the entire potroom for the sampling period.

(kg CF_4/AE minute)$_{fugitive}$ = Total kg CF_4 emitted as fugitive emissions for the sampling period calculated from Step 6a. or Step 6b.2 divided by the total anode effect minutes for the potroom for the fugitive sampling period.

  - Step 6b.4. Calculate the fraction of total PFC emissions emitted as fugitives, Fraction$_{fugitive}$, by dividing the (kg CF_4/AE minute)$_{fugitive}$ from Step 6b.3 by the sum of (kg CF_4/AE minute)$_{duct}$ from Step 2b and the (kg CF_4/AE minute)$_{fugitive}$ as follows.

Fraction$_{fugitive}$ = *(kg CF$_4$/AE minute)$_{fugitive}$/[(kg CF$_4$/AE minute)$_{fugitive}$ + (kg CF$_4$/AE minute)$_{duct}$]*

Step 7: Calculate specific emission rates in kg CF$_4$/tonne Al and kg C$_2$F$_6$/tonne Al for the combined duct measurement and fugitive emissions. The total kg CF$_4$ emissions are equal to the sum of the fugitive CF$_4$ emissions and the CF$_4$ emissions measured in the duct. The total kg CF$_4$ emissions are then calculated from the fugitive fraction, Fraction$_{fugitive}$, as follows. The Fraction$_{fugitive}$ is the value from <u>Step 6b.4</u> if fugitives are measured, otherwise the fraction is estimated to be 0.025 if fugitives are expected to be less than 5% of the total PFC emissions.

- <u>Step 7a</u>. Calculate total CF$_4$ emissions adjusted to include fugitive emissions,

Total kg CF$_4$ = kg CF$_{4duct}$/(1-Fraction$_{fugitive}$)

Where:
kg CF$_{4duct}$ = kg CF$_4$ obtained in <u>Step 2a</u>.
Fraction$_{fugitive}$ = measured fraction from <u>Step 6b.4.</u>, if fugitives are measured. If fugitives are not measured use a value of 0.025.

- <u>Step 7b</u>. Then, calculate the aluminum specific rate for CF$_4$ emissions.

R$_{CF4}$ = (Total kg CF$_4$ for the sampling period)/ p (tonne Al)

Where:
R$_{CF4}$ = Aluminum specific CF$_4$ emission rate (kg CF$_4$/tonne Al)
Total kg CF$_4$ for the sampling period = CF$_4$ emissions, including both duct and fugitive emissions (from <u>Step 7a.</u>)
p = Tonnes primary aluminum production (from <u>Step 5</u>) (tonne Al)

- <u>Step 7c</u>. Calculate the aluminum specific emission rate for C$_2$F$_6$ as follows.

R$_{C2F6}$ = R$_{CF4}$ ´ Ratio $_{C_2F_6/CF_4}$

Where:
R$_{C2F6}$ = Aluminum specific C$_2$F$_6$ emission rate (kg C$_2$F$_6$/tonne Al)
R$_{CF4}$ = Aluminum specific CF$_4$ emission rate from Step 7b. (kg CF$_4$/tonne Al)
Ratio $_{C_2F_6/CF_4}$ = Weight ratio of emissions of C$_2$F$_6$ to CF$_4$ from <u>Step 4</u> (decimal fraction)

Step 8: Calculate CF$_4$ slope, S$_{CF4}$.

S$_{CF4}$ (Total kg CF$_4$/tonne Al)/(AE min/cell-day)= (R$_{CF_4}$)/(AE min/cell-day)

Where:

R_{CF4} = Aluminum specific CF_4 emission rate from <u>Step 7b</u> (kg CF_4/tonne Al)

AE min/cell-day = Total anode effect minutes recorded for the cells in the test section for the period over which kg CF_4 is measured in the duct divided by the cell days for the same period.

<u>Step 9</u>: Calculate C_2F_6 slope, S_{C2F6}, by multiplying the slope determined for CF_4 by the weight ratio of C_2F_6 to CF_4 as calculated in <u>Step 4</u>.

S_{C2F6} *(Total kg C_2F_6/tonne Al)/(AE min/cell-day)= S_{CF_4} ´ Ratio $_{C2F6/CF4}$*

<u>Step 10</u>: If applicable, calculate overvoltage coefficient and C_2F_6 proportion factor. The overvoltage factor is expressed as kg CF_4-%CE / tonne Al / millivolts.

Overvoltage factor $_{CF4}$ {(kg CF4 - %CE)/(tonne Al - mV)} = kg CF_4/tonne Al ´ CE/AEO = R_{CF4} ´ CE/AEO

Proportion factor $_{C2F6}$ {decimal fraction} = (kg C_2F_6/tonne Al) / (kg CF_4/tonne Al)

Where:

CE = Current efficiency for aluminum production (percent)

AEO = Overvoltage for the specific cells in the test section during the sampling period (millivolts)

Proportion factor = Measured weight ratio of C_2F_6 to CF_4 from <u>Step 4</u>. (decimal fraction)

7.2 Option B: Calculating Emission Factors Based on at Line Instruments Measuring Duct PFC Concentrations Continuously

This section presents the calculations for specific emissions of CF_4 and C_2F_6 as well as for the facility specific slope and overvoltage parameters when direct at line measurements of PFCs are made. The workbook included in Appendix A, Part B, provides a template for these calculations.

<u>Step 1</u>: For each time increment for which the instrument reports PFC concentrations calculate the kg CF_4 and C_2F_6.

Total kg CF_4 for the instrument measurement increment =
*C (**m**l CF_4/l air) ´ (1 l CF_4/10^6 **m**l CF_4) ´ (1mole CF_4/22.4l CF_4) ´ 0.088 (kg CF_4/mole CF_4) ´ 1000 (l air/m^3 air (0ºC, 1atm)) ´ F (m^3 air @ 0ºC, 1atm)*

Total kg C_2F_6 for the instrument measurement increment =
*C (**m** l C_2F_6/l air) ´ (1l C_2F_6/10^6 **m** l C_2F_6) ´ (1 mole C_2F_6/22.4l C_2F_6) ´ 0.138 (kg C_2F_6/mole C_2F_6) ´ 1000 (l air/m^3 air (0ºC, 1atm)) ´ F (m^3 air @ 0ºC, 1atm)*

Where:

F = Air flow for each time increment (m^3 at 0°C and 1 atm)
C = CF_4 or C_2F_6 Concentration, ppmv

Step 2: Sum the total kg CF_4 and C_2F_6 for the total sampling period.

Total kg CF_4 = sum from time = t_1 to time = t_2 of all the kg CF_4 for each instrument reporting period

$$Total \quad kg\ CF_4 \quad = \quad \sum_{t_1}^{t_2} kg\ CF_4$$

Where:
t_1 = Start of continuous sampling period
t_2 = End of continuous sampling period

Total kg C_2F_6 = sum from time = t_1 to time = t_2 of all the kg C_2F_6 for each instrument reporting period

$$Total \quad kg\ C_2F_6 = \quad \sum_{t_1}^{t_2} kg\ C_2F_6$$

Where,
t_1 = Start of continuous sampling period
t_2 = End of continuous sampling period

Step 3: Calculate the aluminum production for the sampling period as in Section 7.1, Step 5.

Step 4: Calculate specific emission rates and slopes as in Section 7.1, Steps 6 through 9.

8.0   QA/QC

QA/QC should be conducted in four key areas: 1) measurement system; 2) data; 3) standards; and 4) uncertainty. This section presents general guidelines for each of these areas.

Measurement System Checks.   Three types of measurement system checks should be conducted: leak checks, recovery tests, and instrument calibration.

1) **Leak checks.** Sampling systems for all locations should be leak checked. Leaks in transfer systems at pressures under ambient pressure can be detected by closing the system and checking to see if there is a noticeable change in system pressure.

2) **Recovery tests.** Recovery tests check the integrity of the sampling system and instrument function by injecting a known amount of analyte and testing for the complete recovery of the injected amounts of PFC or tracer compound.

   - **Sampling system:** Recovery of sample through the sampling transfer line should be checked by rapidly exhausting a gas bag filled with a known amount of PFCs into the sample line through the T-connection at the duct end. The resulting peak

should be integrated to give the total amount of PFCs recovered. Recovery should be within 5 percent of the amount released.

- **Overall system recovery**: The accuracy of the overall analytical system should be tested by releasing approximately 200 g of CF_4 and 20 g C_2F_6 at a point far enough upstream of the sampling point to give complete mixing. Preferably this point should be into the exhaust of one of the cells in the test section. Recovery should be within 5 percent of the amount released.

3) **Instrument calibration.** At-line instruments should be calibrated in the laboratory prior to field deployment using vendor calibration procedures. The instruments should be calibrated on CF_4 and C_2F_6 gas standards traceable to or certified by the National Institute of Standards Technology (NIST). In the field, the instrument response should be tested at the measurement site on appropriate standards covering the range of expected PFC concentrations calibrated before and after each 24-hour monitoring period.

Data checks. Results should be checked against expected ranges in Appendix C. If outside the range is indicated, a check of appropriate calculations and procedures should be carried out before reporting results.

Standards. Gas standards obtained from commercial sources should be certified by NIST, or a comparable national standard setting organization.

Uncertainty. Statistical quantitative approaches should be applied to estimate uncertainty ranges for Tier 3b coefficients. Based on IPCC Good Practice Guidance[39], the overall uncertainty in the Tier 3b coefficients can be calculated as the square root of the sum of the variances (U^2):

$$U^2_{Total} = U^2_1 + U^2_2 + \ldots + U^2_n$$

Where,
U_{Total} = percentage uncertainty in the product of the quantities;
U_i = percentage uncertainties associated with each of the quantities (aluminum production, instrument measurement, duct flow rate, etc.).

9.0 Safety

Safety of location staff and measurement staff should be the highest priority. Individuals participating in measurements are responsible for acquainting themselves with the hazards that exist in the potroom environment and taking all steps to avoid injury. Before any work is initiated on site, contact should be made with the responsible location safety staff for a briefing on all local safety requirements.

9.1 Personal Protective Equipment (PPE) Requirements

Minimum personal protective requirements for measurement staff in potroom areas include:

- Head Protection (Hard Hat) ANSI Z89.1;[40]

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[39] IPCC, *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*, Intergovernmental Panel on Climate Change, National Greenhouse Gas Inventories Programme, Chapter 6, 2000.

- Foot Protection (Potroom Boots) ANSI Z4.1;
- Eye Protection (Safety Glasses with nonconductive side, shields, and frames) ANSI Z87.1;
- Flame Retardant Clothing;
- Conductive apparel including rings, metal rimmed glasses, metal watch bands and metal dangling jewelry prohibited: OSHA 29 CFR 1910.333 (c) (8) Conductive Apparel; and
- Hearing protection in designated areas.

9.2 Hazards

The potroom environment has a number of key potential hazards including:

- Electrical shock hazard;
- Thermal burns;
- Moving equipment including overhead cranes as well as vehicles;
- Some processes within the smelter may release hazardous gases or fumes that would require appropriate respiratory protection; and
- Falls.

These hazards and prevention measures should be reviewed with appropriate facility personnel.

10.0 Measurement Frequency and New Measurements

Measurements of CF_4 and C_2F_6 should be repeated on a frequency consistent with the objectives determined from Section 1.1, Objective of Measurement Protocol.

The measurements of CF_4 and C_2F_6 and recalculation of Tier 3b emissions coefficients should be repeated due to one or more of the following events:

- Thirty-six months have passed since last measurements (i.e., triennial measurements are recommended);
- A change occurs in the control algorithm that affects of anode effect data or the nature of the kill routine;
- Changes occur in the distribution of duration of anode effects (e.g., when the percent manual kills change, or, if, over time the number of anode effects decreases and results in a fewer number of longer anode effects), or, for Pechiney control technology when the algorithm for bridge movements and anode effect overvoltage accounting changes;
- Substantial changes occur to the bath chemistry such as changing the target bath ratio; or
- Need arises to answer a specific question regarding the mechanism of PFC emissions.

The results of measurements should be carefully docume nted. Results should only be used to calculate Tier 3b emission factors if the measurements were carried out using the good practices described above.

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[40] American National Standards Information (ANSI) Z89 standard for industrial head protection.

Appendix A: Data Collection, Calculations, and Reporting Template

A.1   Reporting of Results

Following the completion of the measurements, a full report should be prepared containing the pertinent details describing the facility, the sampling strategy, the measurement instrumentation and the results. Data tables should contain sufficient information to allow independent checking of all reported results. Any deviations from the procedures contained in this protocol should also be reported along with the numerical results. The following parameters should be reported for each sampling period and the running time weighted average of the parameter:

1) CF_4 slope or Overvoltage factor;
2) C_2F_6 slope or Proportion factor; and
3) Total kg CF_4 and C_2F_6 per tonne Al
    – kg CF_4 and C_2F_6 per anode effect minute collected in fume collection ducts
    – kg CF_4 anode effect minute emitted as fugitives.

The following data collection templates are for the 1) time average bag sampling, and 2) near real time measurement approaches:

A.   Time Average Bag Sampling

A data collection form is included in the Excel workbook at the location below for time average bag sampling that includes forms for both duct sampling and for potroom rooftop monitor sampling.

"PFC Bag Sampling
Data Workbook_reva

B.   Near Real Time Measurements

A data collection form is included in the Excel workbook at the location below for near real time measurements.

PFC Real Time Data
Workbook

Appendix B: Suppliers

The following list of suppliers is not intended to be a comprehensive list of all suppliers of the equipment. Rather, this list was compiled from readily available information supplied by the authors and reviewers.

1. Process mass spectrometers, ABB, http://www.abb.com/, Process Instruments
2. Multi-layer sample bags, http://www.calibrated.com/home.htm
3. Photoacoustic infrared filter photometer, http://www.innova.dk/
4. FTIR spectrometers:
    a) Midac, http://www.midac.com/
    b) Gasmet, http://www.gasmet.fi/
    c) MKS, http://www.mksinst.com/
    d) IMACC, http://www.imacc-instruments.com/
    e) Temet Instruments Oy, http://www.gasmet.fi/
5. Sample pumps:
    a. Gast Manufacturing, http://www.gastmfg.com/
    b. KNF Neuberger, http://www.knf.com/usa.htm
6. Low volume sample pumps:
    a) A.P. Buck, Inc., http://www.apbuck.com/
    b) SKC Inc., http://www.skcinc.com/skc.html
7. PFA Teflon sample tubing:
    a) Omega Engineering, http://www.omega.com/tubing/flexibletubing/teflonpfa.html
    b) Swagelok, http://www.swagelok.com/
8. Gas standards:
    a) Matheson Tri-Gas, http://www.matheson-trigas.com/
    b) Scott Specialty Gases, http://www.scottgas.com/

Appendix C: Expected Range of Results by Technology

The following range of slope values and overvoltage coefficients are taken from analysis of reported prior measurement data and are calculated to include approximately 95 percent of the expected distribution of values.

Table C: Range of Slope Values

	CF_4 slope (kg CF_4/t Al)/(AE min/cell-day)	C_2F_6 slope (kg C_2F_6/t Al)/(AE min/cell-day)
CWPB or PFPB	0.11 – 0.23	0.015 – 0.035
SWPB	0.20 - 0.32	0.056 – 0.078
VSS	0.051 - 0.14	0.0039 – 0.0066
HSS	0.041 – 0.15	0.0053 – 0.013

	CF_4 overvoltage coefficient (kg CF_4 t Al/ millivolts/cell-day)	C_2F_6 overvoltage coefficient (kg C_2F_6 t Al/ millivolts/cell-day)
PFPB or SWPB	1.05 – 2.44	0.12 - 0.19

Source: J. Marks, selected measurement results from data reported in the literature and private communications.

Appendix D: Checklist

Check Item	∨	Bookmark
Contact Smelter Staff		
• Obtain site overview		
• Obtain safety orientation		
• Assess safety requirements		Safety
− Personal protective equipment requirements		
− Site hazards		
• Obtain historical data to establish expected ranges of PFCs in measurements		
Obtain Process Data		Process data needs
• Type of reduction technologies		
• Bath Chemistry		
• Definition of anode effects		
• Overvoltage data		
• Production data		
− Tap weights		
− Line currency and current efficiency		
• Type of power supply		
• Computer control system scan rate and anode effect kill routine		
Select Sampling Sites		Sampling_locations Cell_technology
• Establish separate sampling site for each operating cell type		
• Check if more than one type of anode effect control algorithm is used for controlling anode effect termination		Control_algorithm
• Assess whether fugitive emissions are expected to be greater than five percent of total emissions. Rooftop sampling sites required for fugitive sampling if greater than 5% fugitives expected.		Fugitives
• Select representative site for background sample collection		Background_sampling
• Conduct duct flow homogeneity tests .		homogeneity
• Select duct locations		

Check Item(continued)	v	Bookmark
• Make choice on continuous measurement or average sampling and measurement method based on conditions listed below: − Is there interest in individual anode effect emissions or short term variability in emissions? − Are the calculated expected average CF_4 and C_2F_6 concentrations below the detection limit of the instrument chosen for the measurement? − If the answer to either of the two above questions is "yes" choose an at line measurement approach with a field instrument. Otherwise, choose the average sampling and measurement approach or a combination of both methods.		Average Concentration Field_instruments Lab_based_instruments
Select instruments for laboratory based measurement methods		
• GC/MS		
• FTIR		
Select instruments for field measurement methods		
• Mass spectrometer		
• TDLAS		
• PAS		
• FTIR		
Commission equipment at site		
Conduct QA/QC tests at site		QA_QC_checks_1_to_3
• Measurement system checks		
− Leak tests		
− Recovery tests		
• Instrument calibration		
• Data checks		
• Standards		
Calculate and report results		
• Complete Excel workbook with sampling and measurement data depending on whether at line measurements were made, or, alternatively, average samples are taken.		Average_sampling_work book Real_time_workbook
• Check that calculated Tier 3 coefficients from measurements are acceptable		Sampling_time Data_checks
• Document results along with an estimate of uncertainty and notation of any deviations from the protocol's recommended practices.		Reporting Uncertainty

Appendix E: References and Information Sources

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