

PROTOCOL FOR MEASUREMENT OF TETRAFLUOROMETHANE AND HEXAFLUOROETHANE FROM PRIMARY ALUMINUM PRODUCTION

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Abstract

Two perfluorinated compounds (PFCs), tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆), are produced periodically during primary aluminum production by the Hall-Héroult process. The measurement of PFCs is required to assist with developing the most accurate greenhouse gas emissions inventories. These inventories can be used to support company benchmarking and process improvement activities, to facilitate reporting under the United Nations Framework Convention on Climate Change, and to assist with the implementation of Kyoto Protocol mechanisms such as emissions trading and the Clean Development Mechanism (CDM).

This paper describes a measurement protocol to assist with developing accurate PFC inventories based on the Intergovernmental Panel on Climate Change (IPCC) Tier 3b method. The protocol has been produced with an aim to foster consistency in smelter-specific sampling programs. The procedure described here provides a method for making accurate measurements of CF₄ and C₂F₆ emissions and relating those measurements to anode effect process data. A methodology is presented for summarizing the collected data and calculating IPCC Tier 3b emission factors, which provide for the most accurate calculation of long-term PFC emissions from aluminum production. The protocol provides the necessary guidance to allow individual facilities to develop detailed plans for sampling and analysis based on plant specific technology, anode effect data, and chosen measurement instrumentation.

Introduction

Tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆) are extremely stable greenhouse gases, with atmospheric lifetimes estimated at 50,000 and 10,000 years, respectively. While their atmospheric concentrations are not large compared to other greenhouse gases, 80 pptv CF₄ and 3 pptv C₂F₆ (1), their strong infrared absorption properties and extreme atmospheric inertness make them highly potent greenhouse gases. Studies have identified a direct correlation between changes in atmospheric concentrations of CF₄ and C₂F₆ with their anthropogenic sources, particularly aluminum production (2, 3). Perfluorocarbon (PFC) emissions are primarily generated during brief interruptions (“anode effects”) in the aluminum electrolytic reduction process; consequently, the frequency and duration of anode effects define the specific-level of emissions occurring.

In response to the potential risks of climate change, over one hundred and eighty nations have decided to ratify the United Nations Framework Convention on Climate Change. The framework requires that signatories develop and report annual inventories of greenhouse gas emissions. The Intergovernmental Panel on Climate Change (IPCC) has outlined methods to estimate PFC emissions from aluminum production (4). While

default emission factors are provided, the accurate development of emissions inventories requires the use of facility-specific factors, based on the measurement of site-specific PFC emissions. Since there are a number of different methods to measure PFC emissions, this protocol was developed to foster consistency and reduce uncertainty in smelter-specific sampling programs, specifically with respect to the process required to calculate facility-specific emission factors using IPCC Tier 3b methodology.

Background

In the early 1990's, due to growing concerns over the impact of PFCs on the environment, the U.S. Environmental Protection Agency (US EPA) and the U.S. Aluminum Association formed the PFC Task Force to develop strategies to reduce PFC emissions from the aluminum industry. With input from industry members of the PFC Task Force, a voluntary framework was developed to promote PFC abatement strategies that are technically and economically feasible. To seal the framework, a voluntary agreement detailed in a Memorandum of Understanding (MOU), between the US EPA and industry partners, was developed. The MOU defines the roles and responsibilities of each party and reflects each party's expertise and ability to reduce emissions. The Voluntary Aluminum Industrial Partnership (VAIP) was launched in 1995 and currently includes a majority of the U.S. aluminum companies.

Several projects have been undertaken under the VAIP to enhance the understanding of the mechanisms creating PFC emissions and their relationship to operational parameters. Two measurement campaigns were conducted at thirteen U.S. smelters. Study results demonstrated the applicability of various techniques to measure PFC emissions, and confirmed a direct correlation between cell technology type and anode effect minutes to PFC emission rates. Additionally, the VAIP, coordinated by the U.S. Aluminum Association, sponsored an anode effect research study at the Massachusetts Institute of Technology. The study delved into the potential mechanisms controlling PFC generation and the relationship between emissions and process parameters. In particular, results indicated an exponential relationship between PFC emission rates and cell overvoltage (5). Results from these studies have provided VAIP member's operational insights into controlling and reducing PFC emissions at their smelters. PFC emissions within the U.S. aluminum industry have decreased by approximately 55 percent between 1990 and 2000 (6).

The U.S. EPA and VAIP are continuing their mission to understand and quantify the relationship between PFC emissions and operational variables. To this end, the development of a measurement protocol was identified as an important tool to share the lessons learned from the measurement campaigns, and thus

ensure the consistency and accuracy of estimated PFC emissions from future measurement studies.

Protocol Development

The protocol described here is based largely on experience gained from prior PFC measurement campaigns performed by the authors and additional reports that have appeared in the published literature describing prior measurements. Past measurements have been made for several purposes. First, measurements have been made to provide a snapshot assessment of PFC emission levels for a specific facility. Secondly, other measurements have been orientated at gaining scientific understanding of the nature of PFC emissions from primary aluminum production. Thirdly, another objective has been to develop a correlation of emissions with production process parameters so accurate forward and backward projections of emissions might be made to provide a time series.

One of the earliest quantitative measurements of emissions of PFC gases during anode effects were accomplished by withdrawing sequential samples by gas syringe of anode gas drawn from the base of the carbon anode, or, from the fume exhaust duct of a single cell or small group of cells. The gas syringe samples were analyzed by a portable micro gas chromatography (7). Photo acoustic infrared (PAS) instrumentation has been widely used throughout Europe for PFC measurements (8 - 10). Potential spectral interferences from water and sulfur dioxide are controlled by treating the gas sample prior to measurement. Measurements of both fugitive and duct emissions were reported from Söderberg potlines in a recent series of Norwegian measurements (10).

The US EPA as part of the Voluntary Aluminum Industrial Partnership sponsored two PFC measurement programs at US based smelters. For the first of these two measurement campaigns, smelter exhaust duct samples were collected in stainless steel canisters and PFC concentrations measured by gas chromatography with mass spectrometer detector (11). Fugitive emissions were not measured along with exhaust emissions; however, in a follow on effort fugitive samples were collected in bags and measured by Fourier Transform Infrared (FTIR) spectroscopy. In the second campaign, process mass spectrometry was used to measure exhaust duct measurements (12) at five smelters in the US and one smelter in Canada. Fugitive emissions were collected in sample bags at Söderberg and side work prebake sites and analyzed by FTIR.

The Tunable Diode Laser Absorption Spectrometer (TDLAS) has been used extensively for PFC measurements in Canada (13 - 17). In the more recent measurement campaign duct measurements were made with the TDLAS and fugitive emissions were measured at several locations with open path FTIR spectrometry. Extractive FTIR spectrometry has also been used for measurement of PFCs in aluminum smelter exhaust ducts (18) in addition to the application to fugitive measurements noted above.

The prior reported literature illustrates the variety of approaches that have been used for making PFC measurements from primary aluminum production. The current PFC protocol has drawn extensively from these reports in several respects. These reports have provided the basis for applicable measurement instrumentation and measurement approaches. The previous reports were also evaluated for inconsistencies in reported data as part of the development of the new protocol. The variability in

results for previously reported slope and overvoltage factors resulted from the combination of measurement uncertainty and the underlying variability of the aluminum production process. The protocol is designed to provide a quantitative evaluation of measurement uncertainty so that the process variability might be better understood. The prior reports have also been used to compile a table of ranges of expected results for calculated Tier 3b coefficients as context for calculated results from new measurements. Finally, the experience of many of those involved in the previous measurements was incorporated into the protocol through an extensive review process.

Key Elements of the Protocol

Previous measurement reports have provided details about how the PFC concentrations were measured. However these reports have often not contained the detailed information on other key data necessary for measurement quality control or the process data. This information would allow meaningful comparison of measured results with other results of measurements from similar reduction technologies.

Background Information

Measurement personnel are often not entirely familiar with reduction technology and terms. The protocol provides an introduction to elements of the technology important for PFC measurements and background information to understand the key factors that might influence the measurements and what process parameters should be gathered. The different types of reduction technologies are described in sufficient detail to allow measurement staff to know the key differences to be expected in measurement approach for each technology.

Information is also provided on the IPCC three-tiered approach that provides three levels of accuracy for calculating greenhouse gas inventories. The protocol is specifically designed to provide the basis for calculation of the most accurate Tier 3b coefficients for calculating PFC emissions based on anode effect data. The Tier 3b method is based on facility specific measurements of CF₄ and C₂F₆ to establish the quantitative relationship with logged anode effect process parameters, either anode effect minutes per cell day or overvoltage. The less accurate Tier 2 method uses calculation coefficients established from industry average parameters derived from PFC measurements reported prior to 1999. PFC measurements made using the recommended procedures in the protocol should enable future revisions of the IPCC Tier 2 average coefficients that will improve the accuracy of the Tier 2 PFC inventory method.

Process Data Requirements

As noted above, key process data important in comparing measurement reports are often omitted from measurement reports. The protocol provides guidance on describing the reduction cell technology details that should be included in the measurement report. Examples of these details include the information that should be collected on the molten salt bath chemistry and anode effect data. The protocol describes how anode effects should be characterized for correlation with the measured emissions. The average frequency and average duration of anode effects should be recorded. Details about how the anode effect is defined at the facility should also be collected. These details include the trigger voltage that defines when the cell is considered on anode effect and what criteria are used to establish, for the same cell, when the voltage again rises above the trigger level that the cell is on a new anode effect. Also data on the statistical distribution of duration

of individual anode effects should be gathered since previous measurements have shown that for prebake technologies longer anode effects result in lower PFC emission rates as the time on anode effect increases (19). The percent of manual anode effect kills, those for which the computer system is unsuccessful, should be recorded. Overvoltage data must be collected for the cells in the measurement test section for those reduction facilities that operate with Aluminium Pechiney control systems. Some facilities have the capability to collect both overvoltage data and anode effect minutes over trigger voltage per day. In this case, both parameters should be recorded to determine which gives the better correlation with PFC emissions. Any cells undergoing start up with added voltage should be noted as a special condition. PFCs are emitted continuously during this period. Because new cell start ups are normally a minor part of continuous operations, these emissions should not be included in establishing the Tier 3b coefficient.

PFC emissions are normalized to aluminum production and therefore aluminum production data must be recorded for the test cells during the test period. Aluminum production is normally established from tapping records for the previous month. Further details should be collected that describe the computer control system, such as the frequency with which voltage data is collected for each cell, and the time over which the data is averaged for data logging. Also information on how the computer system responds to the detection of the onset of an anode effects with bridge movements and alumina feed can help in understanding the differences in measured PFC emissions among facilities with similar operating technology.

Sampling Design

Sampling design considerations are detailed including both sampling locations as well as time requirements. To establish an accurate Tier 3b coefficient for inventory of PFCs, taking measurements in a manner that reflects normal and ongoing operating conditions is critical. Sampling locations should be established for fume exhaust ducts and, if fugitive emissions are expected to be greater than five percent of total emissions, rooftop locations should also be sampled to measure fugitive emission rates. Fugitive emissions are typically insignificant for point fed Center Work Prebake cells; however, for Söderberg cells and Side Work Prebake cells fugitive emissions may account for more than 10 percent of total emissions and should therefore be measured.

Equations are given in the protocol for making estimates of expected concentrations of CF_4 and C_2F_6 based on historical anode effect data for both continuous sampling and for time average sampling approaches. These estimates allow proper choices to be made of measurement instrumentation and sampling approaches to match instrument capability with the concentrations to be measured.

An important sampling issue for which little has been reported in past measurement literature is the need to sample from a exhaust duct location for which the gas flow is homogenous with respect to the exhausts from all the cells in the measured test section. Experience has shown that where sections of exhaust ducting are joined, the gas flows can remain segregated for long distances eliminating these duct sections as potential sampling sites. The only way to be sure that the gas stream is homogenous is to inject a constant flow of a tracer gas into the ductwork upstream of the potential sampling site and then measure the distribution of the tracer in the duct at the potential sampling site. Sampling should

only be considered if there is less than five percent variation in measured tracer concentration across the duct. The data from this homogeneity test should be included in the uncertainty analysis of the overall measurement process.

The protocol provides guidance that sampling should continue until successive calculations of the Tier 3b coefficient over eight to twelve hour periods do not change by more than ten percent. In any case, sampling should be made for a minimum of 72 hours to ensure that long-term average operating conditions are reflected in the measurement. For many of the most modern point fed prebake facilities with anode effect frequency well below 0.1 anode effect per cell day, sampling to get a statistically representative measurement may be difficult. Considerable variation exists in emissions from one anode effect to another and, because of sample flow non-homogeneity, there may be limitations on the number of sampling locations available. For these facilities with very low anode effect frequencies, this statistical variability may be the largest source of uncertainty in the calculated Tier 3b coefficient. Fortunately these facilities contribute little to overall industry PFC emissions and larger uncertainties are inconsequential in the larger scale PFC inventory process for the aluminum industry.

PFC Concentration Measurement

Two different approaches are described for measuring PFC concentration, continuous measurement and time average sampling. Both approaches are effective in giving accurate PFC emissions rates and IPCC Tier 3b coefficients when measurement good practices are followed. The protocol does not recommend any particular instrument for measuring PFC concentration. The selection of a specific instrument for the measurement depends on whether the continuous or time average approach is chosen, and, on the experience of the measurement staff. The characteristics of each instrument should be compared with the measurement requirements before proceeding. If the continuous sampling approach is chosen, the instrument must be capable of measuring rapidly changing concentrations of the PFC components. This requirement is illustrated in Figure 1 where the emission profile for CF_4 and C_2F_6 is illustrated for a typical anode effect from a prebake cell. The profile in Figure 1 is a plot of six second averages of concentrations that have been measured on a frequency of about 25 milliseconds. For the continuous measurement approach to give accurate results, the time response of the instrument must be adequate to accurately integrate the rapid changes in concentration while the anode effect is occurring. The time average sampling method obviates the problem of rapidly changing PFC concentration with time by collecting a continuous sample of all the emissions that occur over the sampling period. The time average method requires an instrument approach with higher sensitivity and better detection limits than for the continuous approach because of the high dilution that results from periods when no anode effects are occurring.

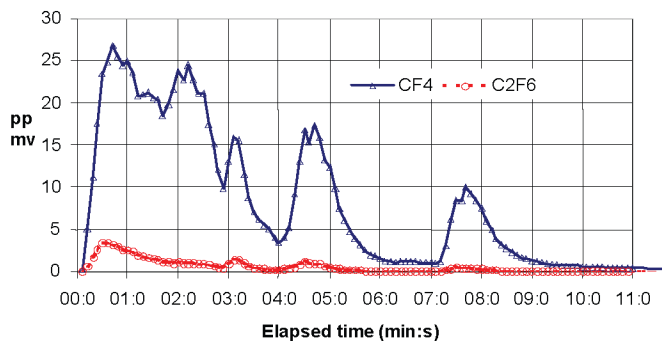


Figure 1 – CF₄ and C₂F₆ Time Emission Profile for a Prebake Cell Anode Effect

Calculations

The protocol provides the equations for calculating emissions of both PFC compounds based on measured concentrations of CF₄ and C₂F₆ in the fume exhaust collection system and from the fugitive measurements from the rooftop samples. All these equations are contained within Excel workbooks provided in the protocol for recording all process data and measurement results. The workbooks help avoid calculation errors and ensure collection of pertinent process data. The ideal gas equation and Avogadro’s principle are used to calculate the mass of PFC emissions over the sampling period. The masses of CF₄ and C₂F₆ emissions per mass of aluminum produced are calculated from known aluminum production of the test section cells. These data are then used in Equations 1 and 2 to calculate slope factors for CF₄ and C₂F₆, if anode effect minutes per cell day is the anode effect process parameter logged by the computer control system. These slope factors are used for calculating long-term PFC emissions from aluminum process data according to IPCC Good Practices.

$$S_{CF4} = (\text{kg CF}_4/\text{metric ton Al})/(\text{AEF} \times \text{AED}) \quad (1)$$

$$S_{C2F6} = (\text{kg C}_2\text{F}_6/\text{metric ton Al})/(\text{AEF} \times \text{AED}) \quad (2)$$

Where:

- S_{CF4} = Slope factor for CF₄ (kg CF₄/t Al)/(AE min/cell day)
- S_{C2F6} = Slope factor for C₂F₆ (kg C₂F₆/t Al)/(AE min/cell day)
- AEF = Anode Effect Frequency in anode effects per cell day
- AED = Average Anode Effect Duration (minutes)

Alternatively, if overvoltage (AEO) is the process parameter monitored, then an overvoltage factor is calculated for CF₄ using overvoltage and current efficiency (CE) and a proportion factor is calculated for C₂F₆ as shown in Equations 3 and 4.

$$\text{Overvoltage factor (CF}_4\text{)} = \text{kg CF}_4/\text{metric ton Al} \times \text{CE}/\text{AEO} \quad (3)$$

Where:

- Overvoltage Factor (CF₄) = kg CF₄/metric ton Al/mV/cell day
- CE = Current efficiency (%)
- AEO = Overvoltage (mV/cell day)

$$\text{Proportion factor (C}_2\text{F}_6\text{)} = (\text{kg C}_2\text{F}_6/\text{metric ton Al}) / (\text{kg CF}_4/\text{metric ton Al}) \quad (4)$$

Measurement QA/QC

A number of recommendations are made in the protocol to ensure the quality of the measurement results and the resulting IPCC Tier 3b coefficients that are derived from the measurements. A recovery test is recommended where known quantities of the PFC gases are injected into the duct system and the percent recovery calculated subsequently from the measured results. The use of standard gases certified by or traceable to national standards institutions is recommended for instrument calibration. The protocol also contains an appendix with expected ranges for the calculated slope and overvoltage parameters based on prior measurements that can be used to verify the calculated experimental values. Values obtained that lie outside the expected ranges should be confirmed before reporting as final values. The protocol prescribes that an uncertainty analysis should be conducted and reported to give a measure of the expected measurement uncertainty in the derived Tier 3b coefficient.

Safety Considerations and Recommended Measurement

Frequency

The protocol outlines important procedures to ensure that the measurements are carried out safely. The potroom and surrounding environment where the measurements are made contain a number of potential hazards such as electrical shock, possibility of burns from the high temperature process, falls and hazards from overhead crane operations.

Repeat measurements and recalculation of Tier 3b coefficients are recommended on a triennial basis or whenever there have been sustentative changes in operational practice. Some examples of sustentative changes include changes in the computer control algorithm driving reaction to anode effects, changes in molten salt bath chemistry or when there are changes in the distribution of duration of anode effects from which the average anode effect duration is calculated.

Conclusions

The PFC measurement protocol described here provides guidance in making the measurements of CF₄ and C₂F₆ and for collecting the associated process data needed for calculating the IPCC Tier 3b coefficients used for inventorying PFCs from primary aluminum production. The IPCC Tier 3b method is recommended for the most accurate inventory of PFCs from primary aluminum production. The protocol provides flexibility to use either continuous at line measurement methods or batch measurements on time average samples made at line or in a laboratory facility. Flexibility is also provided in choice of instrument for the measurement. Measurement requirements of time response and sensitivity are defined in the protocol. Use of the PFC measurement protocol and the recommendations for good measurement practices presented here should ensure accurate measurements of PFCs produced during primary aluminum production and a quantitative measure of the measurement uncertainty of the inventories compiled through use of the IPCC Tier 3b methodology. The guidance for collecting and reporting process data should ensure meaningful comparisons among future PFC measurements. The PFC measurement protocol is included as an integral part of the International Aluminium Institute’s Draft Greenhouse Gas Protocol, a consensus standard adopted by the international aluminum industry for inventory of greenhouse gases from primary aluminum production (20).

REFERENCES

1. IPCC, Climate Change 2001: The Scientific Basis, Intergovernmental Panel on Climate Change, Third Assessment Report, 2001.
2. J. Harnisch, R. Borchers, P. Fabian, Estimation of Tropospheric Trends (1980-1995) for CF₄ and C₂F₆ from Stratospheric Data, SPIE, Vol. 2506, p. 384, 1995.
3. J. Harnisch, R. Borchers, P. Fabian, M. Maiss, CF₄ and the Age of Mesospheric and Polar Vortex Air, Geophysical Research Letters, Vol. 26, p. 295-298, 1999.
4. IPCC, Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, Section 3.3, PFC Emissions from Aluminium Production, http://www.ipcc-nggip.iges.or.jp/public/gp/pdf/3_Industry.pdf.
5. D. Sadoway and H. Zhu, "The Electrode Kinetics of Perfluorocarbon (PFC) Generation," *Light Metals 1999*, 214-246.
6. US EPA, Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2000, U.S. Environmental Protection Agency, 2002.
7. A. Tabereaux, N. Richards, C. Satchel, "Composition of Reduction Cell Anode Gas during Normal Conditions and Anode Effects," *Light Metals 1995*, 325 – 333.
8. I. Berge, R. Huglen, M. Bugge, J. Lindstrom and T. Røe, "Measurement and Characterisation of Fluorocarbon Emissions from Alumina Reduction Cells," *Light Metals 1994*, 389 – 392.
9. G. Bouzat, JC. Carraz and M. Meyer, "Measurements of CF₄ and C₂F₆ Emissions from Prebaked Pots," *Light Metals 1996*, 413 – 417.
10. H. Kvande, H. Nes and L. Vik, "Measurements of Perfluorocarbon Emissions From Norwegian Aluminium Smelters," *Light Metals 2001*, 289 – 294.
11. B. Leber, A. Tabereaux, J. Marks, B. Lamb, T. Howard, R. Kantamaneni, M. Gibbs, V. Bakshi and E. Dolin, "Fluorocarbon (PFC) Generation at Primary Aluminium Smelters," *Light Metals 1998*, 277 – 287.
12. J. Marks, R. Roberts, V. Bakshi and Eric Dolin, "Perfluorocarbon (PFC) Generation during Primary Aluminium Production," *Light Metals 2000*, 365 – 371.
13. Unisearch Associates, Report on the Measurements of CF₄ and C₂F₆ in the Emissions from Canadian Aluminium Smelters by Tunable Diode Laser Absorption Spectrometry, April 5, 1994.
14. Unisearch Associates Inc Integrated Report Version 1.3c, "The Measurement of Fluorocarbon Emissions From Canadian Aluminum Reduction Plants," April 30, 2001.
15. F. Kimmerle, G. Potvin and J. Pisano, "Measured Versus Calculated Reduction of the PFC Emissions from Prebaked Hall Hérault Cells," *Light Metals 1997*, 165 – 171.
16. G. Bouchard, J. Kallmeyer, A. Tabereaux, and J. Marks, PFC Emissions Measurements from Canadian Primary Aluminum Production," *Light Metals 2001*, 283 – 294.
17. H. Gamble, G. Mackay, D. Karecki, J. Pisano and H. Schiff, "Development of a TDLAS Based Methodology for Monitoring Perfluorocarbon Production During the Aluminum Smelting Process," *Light Metals 2001*, 275 – 281.
18. N. Dando and M. Atkinson, Private Communications, June, 2002.
19. J. Marks, A. Tabereaux, D. Pape, V. Bakshi and Eric Dolin, "Factors Affecting PFC Emissions From Commercial Aluminum Reduction Cells," *Light Metals 2001*, 295 – 302.
20. International Aluminium Institute, "The Aluminium Industry Greenhouse Gas Protocol (Addendum to the WBCSD/WRI Greenhouse Gas Protocol), available at www.world-aluminium.org.

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