

## A Review of Equipment for Accurate PFC Measurements

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### Abstract

To obtain reliable perfluorocarbon (PFC) measurement results requires expertise and competence in the measurement methodology and knowledge of the smelting technology. We enumerate different measurement methods that have been used to measure PFC emissions. The Fourier Transform Infrared method is the most versatile of all the methods and gives the most information about the smelting process. It has the best temporal resolution making 10 interferometer scans each second and can measure low voltage emissions at the same time as anode effect emissions. Both authors have extensive experience measuring PFC emissions (CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>) at aluminum smelters worldwide. We will present available measurement technology with a checklist to ensure accurate and reliable measurements.

**Keywords:** Perfluorocarbon (PFC), Tetrafluoro methane CF<sub>4</sub>, Hexafluoro ethane C<sub>2</sub>F<sub>6</sub>, Anode effect, High and low voltage PFC emissions.

### 1. Introduction

The perfluorocarbon gases (PFCs) tetrafluoromethane (CF<sub>4</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) are known greenhouse gases (GHG) with long atmospheric lifetimes, estimated at 50 000 and 10 000 years, respectively. These trace gases are linked to global warming due to their ability to efficiently absorb infrared radiation. The global warming potentials (GWP) of these gases are reported as CO<sub>2</sub> equivalents (GWP of CO<sub>2</sub> = 1). Every kilogram of CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub> emitted is equivalent to 7 380 kg CO<sub>2</sub> and 12 400 kg CO<sub>2</sub>, respectively [15].

PFC emissions occur during a condition known as an anode effect (AE), an event that occurs when the ore (Al<sub>2</sub>O<sub>3</sub>) concentration in the electrolytic bath drops below ~ 1 %, the pot voltage rises, and the bath and carbon anode(s) begin to react. The 2019 Refinement to the 2006 IPCC Guidelines includes CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emissions coming from high voltage (HV), low voltage (LV) and pot start-up PFC emissions. The refinement includes updated values for Tier 1, Tier 2 and Tier 3 methods that can be used to calculate PFC emission depending on the pot technology and if facility specific data per technology are available [1]. The International Aluminum Institute (IAI) published a PFC measurement guideline with a review of all methodologies to accurately account for high-voltage PFC emissions, produced when the pot voltage is above 8 V, and low-voltage PFC emissions, produced when the pot voltage is below 8 V [2]. Any PFC reporting protocol will require reporting total PFC emissions, including LV PFC emissions. LV PFC emissions occurred during pot room operation activities such as anode changes, tapping, pot starts, underfeed periods, and high pot noise periods [3–5]. Any localized increase in pot voltage can induce PFC emissions from the pot. During anode changes, LV PFC emissions occur when anode current distribution is unbalanced, and the critical current density is reached on one or more of the anodes that have been subjected to alumina depletion.

The International Aluminum Institute (IAI) gas initiative has launched a long-term gas emission reduction target by December 2024 and to identify an interim greenhouse gas emission reduction

milestone, ideally by 2030, to ensure early progress can be tracked for all its members. This initiative was launched at the United Nations's Climate Change Conference (COP 28) in Dubai [6]. To accomplish this goal, it is recommended that the aluminum industry report total PFC emissions on an annual basis. We recommend direct measurement by real time extractive sampling for Tier 3 reporting offers the most efficient and accurate technique giving all PFC emissions.

## **2. How to Decide Which Equipment to Use to Measure Total PFC Emissions**

The best approach to measure PFC emissions depends on the main objective of the PFC measurement campaign. The decision to use monitoring equipment relies on if the objective is for GHG inventory, e.g., total PFC emissions reporting or for process improvement like LV PFC emissions reduction or benchmarking. To define root cause mechanisms and eliminate or reduce LV PFC emissions, a proper understanding and quantification of how pot operations impact these non-desired emissions are required for accurate PFC accounting to enable appropriate countermeasures. LV PFC emissions can contribute from 5 to 80 % of overall PFC emissions from smelting locations, depending on anode effect performance, pot operation and size, and work practices. Process data cannot predict and estimate LV PFC emissions. Solutions for comprehensive PFC reporting require the use of continuous monitoring or time-integrated sampling in canisters during a period. This measurement period should be ideally selected to be representative of each potline in all smelters. Thus, when emissions are being measured for compliance or determination of site emissions, one would choose as large a section of pots as possible. For process improvement a small section of pots or even a single pot might be sampled. The PFC concentrations will vary from parts per billion for a large section of pots to tens, or even hundreds of parts per million for a small section of pots when conducting process improvement research.

The ideal monitoring technique should provide the most information to measure and manage to reduce PFC emissions. There are four main techniques to use to measure PFC emissions.

## **3. Analytical Techniques**

### **3.1 Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR has been one of the preferred techniques to measure and report GHG inventories as well as measure and manage PFC emissions to gain process improvements. The main advantage of FTIR spectroscopy is the simultaneous measurement of most gases coming from a smelter pot exhaust, which gives additional emission information. Furthermore, spectral data can be reprocessed to verify  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  emissions at different ranges e.g., single part-per-billion to hundreds of parts-per-million concentrations, which can occur from single-pot or a section of several pot exhausts. FTIR requires extractive sampling with filters to avoid instrument intensity degradation, corrosion of internal optics, and might need maintenance during measurement campaigns. FTIR is a reliable technique, but it can drift over time and needs to be accurately calibrated in the low ppb range [7]. Another advantage of doing a FTIR continuous measurement for a limited time is to develop coefficients to calculate HV and LV emissions simultaneously without waiting from an analytical lab to get results if canisters samplers are used.

For smelters measurements a small table is needed to place the instrument and laptop as shown in Figure 1.

The Fourier Transform Infrared method is the most versatile of all the methods and gives the most information about the smelting process. It has the best temporal resolution making 10 interferometer scans each second and can measure low voltage emissions at the same time as anode effect emissions. Additionally, FTIR can measure other gaseous carbon compounds simultaneously with the PFCs and duct flow rates can be calculated from the potline net carbon consumption figure. The results are available immediately and there is no need to ship samples and wait for results.

The capital investment of FTIR and sampling equipment may be paid off by process improvements that can be obtained by reducing PFC emissions. Therefore, more metal can be produced by avoiding the generation of LV PFC emissions during anode changes, feeding improvements, or avoiding any pot instability that will lead to better pot performance.

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