PFC EMISSIONS FROM PRIMARY ALUMINIUM PRODUCTION

ABSTRACT

The primary aluminium production process has been identified as the largest anthropogenic source of emissions of two perfluorocarbons (PFCs): tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6). Primary aluminium is produced using the Hall-Héroult electrolytic process, where the smelting pot itself acts as the electrolysis cell during the reduction process. When the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed "anode effects". Anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, producing CF_4 and C_2F_6. The frequency and duration of anode effects depend primarily on the pot technology and operating procedures. Emissions of CF_4 and C_2F_6, therefore, vary significantly from one aluminium smelter to the next, depending on these parameters.

The *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC Guidelines)* recommend multiplying aluminium production by a CF_4 emission factor (i.e., CF_4 emissions per unit of aluminium production). To estimate the emission factor, different methods have been proposed based on the availability of data. The Tier 1 method uses PFC emission factors that are based on actual emission measurements. This is the most accurate method because PFC emissions vary so significantly from one smelter to the next. Where actual measurements are not feasible due to economic or time constraints, however, a Tier 2 approach can be applied in which operating parameters and an industry model are used to derive emission factors. Where necessary, the *IPCC Guidelines* provide default parameter values by technology type to fit the model. When relevant operating parameters are not available, a simple Tier 3 method can be used, in which aluminium production is multiplied by a default emission factor that is specific to the cell technology. The IPCC provides default emission factors for four technology types, and recommends a default rate for C_2F_6 emission that is 1/10 that of CF_4.

Emission estimates will be highly uncertain unless actual emission measurements have been made at the smelter level because emissions of CF_4 and C_2F_6 vary so significantly from one aluminium smelter to the next, depending on cell type and anode effect parameters. Most aluminium producing countries have a relatively small number of primary aluminium facilities, so it may be possible to develop smelter-specific emission factors. The most common PFC estimation methods available to countries include: the Tabereaux Method (Modified Faraday's Law Method), the Pechiney Over-voltage Method, and the Slope Method. These relationships have been proven to be useful predictors of PFC emission rates for particular smelter technologies and ranges of operating conditions. Default parameters are available for these relationships based on field measurements of PFC emissions. Smelters may adopt one of the above relationships and use the default parameters if it is demonstrated to be representative for their plant characteristics and operating conditions. It is recommended that smelters conduct measurements to estimate the parameters that reflect their particular operating conditions.

When developing measurement programmes, smelters should ensure that the sampling scale provides a comprehensive measurement for the entire facility and is as compatible as possible with the operational data. In addition, if there is high daily variability in emission rates, enough daily samples should be taken to assure that the range of emission rates for the current operating conditions is covered. The analytical system must also be appropriate for the sampling method, stable, and free of (or corrected for) interferences.

Aluminium production data are necessary to estimate PFC emissions from aluminium smelting regardless of the estimation method chosen. Countries should obtain smelter-level data on an annual basis, so that they can use smelter-specific emission factors. At a plant-level, actual production data should be obtained directly from producers. Since aluminium production data may be considered proprietary by producers, it may be necessary to ensure that it is not released to the public, or to publish it in such a way so that individual plants are not identified.

It appears that PFC emissions associated with aluminium production are reported by many emitting countries. The methods, assumptions and data used to develop these estimates are not clear, transparent or well-

documented. Currently, PFC emissions from this source are reported under IPCC category 2C3 (aluminium production emissions, associated with industrial processes). However, the IPCC table does not have specific entries for CF_4 and C_2F_6 emissions. Because CF_4 and C_2F_6 have different global warming potentials (GWPs) and different masses, emissions of different species cannot be on a mass basis.

Ensuring the quality of an inventory also requires countries to implement quality assurance (QA) and quality control(QC) programmes. QA/QC activities need to occur at several steps in the emission estimation process. At the smelter level, key elements should include internal quality control on plant-level measurements, sampling programmes, and aluminium production levels and documentation of data and methods for reviewers. The inventory agency must ensure the accuracy of plant submissions as well as the compiled inventory. It will also be responsible for providing documentation and reporting sufficient information to the United Nations Framework Convention on Climate Change (UNFCCC) Secretariat. One or more types of external reviews and audits may also be appropriate, and each will require complete documentation.

1   INTRODUCTION

## 1.1   Nature, magnitude, and distribution of source

This section provides an overview of the primary aluminium industry and associated worldwide PFC emissions. The PFC generation process and the factors that potentially influence PFC generation are presented.

1.1.1   Overview of primary aluminium production and PFC emissions

The aluminium production process is the largest anthropogenic source of emissions of two PFCs: CF_4 and C_2F_6. In 1996, 44 countries produced aluminium with an annual production of 20.7 million metric tonnes. Production has been on the rise since 1990, with an increasing percentage of production in the developing world. In 1996, however, the majority of production was in industrialised countries and countries transitioning into market economies.

Figure 1 shows aluminium production and the share of global production for the leading producer nations. PFC emissions are expected to increase at a slower rate than aluminium production because PFC emission factors (i.e., PFCs emitted per ton of aluminium produced) are expected to decrease over time. These reductions in PFC emission factors are anticipated because of the diffusion of modernised smelter technologies resulting from capital stock replacement and national level efforts (e.g., voluntary or regulatory programmes) to reduce PFC emissions from aluminium smelting. As shown in Figure 1, most major producer nations have established programmes to reduce PFC emissions from aluminium smelting.

Figure 1   Primary aluminium producers with or without PFC reduction programmes (1996)


(Data in Thousand Metric Tonnes and % of Total)
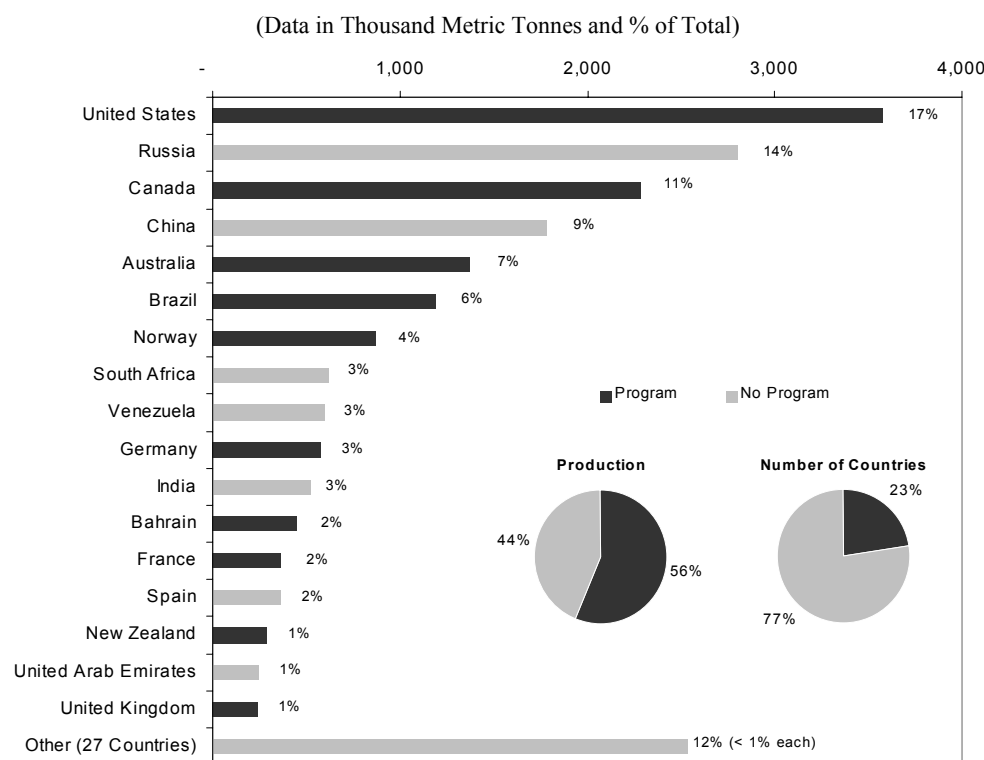
Note: Other Producer Countries are: Netherlands, Indonesia, Taijikstan, Egypt, Argentina, Italy, Romania, Ghana, Greece, Iran, Iceland, Sweden, Ukraine, Cameroon, Slovenia, Turkey, Poland, Slovakia, Serbia and Montenegro, Suriname, Croatia, Switzerland, Hungary, Japan, Mexico, Azerbaijan, Bosnia and Hertzegovina.   Source: USGS Aluminium Industry Annual, 1997 and EPA, 1998.

The majority of national level PFC emission reduction programmes are voluntary industry-government partnerships. While the framework and requirements of the individual programmes vary, industry and

government stakeholders have typically established a process to monitor and track progress towards reaching agreed upon targets. The methods and strategies used to quantify reductions provide insight into the current state-of-the-art inventory practices and are discussed further in Section 1.2 (The Current State of Inventory Methodologies) of this paper.

1.1.2 PFC generation process

Primary aluminium is produced using the Hall-Héroult electrolytic process. In this process, the smelting pot itself acts as the electrolysis cell during the reduction process. The pot itself forms the cathode, while the anode consists of one or more carbon blocks suspended in it. Molten aluminium is evolved while the anode is consumed in the reaction as follows:
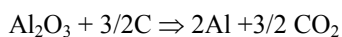
$$Al_2O_3 + 3/2C \Rightarrow 2Al + 3/2\ CO_2$$

When the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed "anode effects". Anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, producing CF_4 and C_2F_6 due to the following reactions:

$$Na_3AlF_6 + 3/4C \Rightarrow Al + 3NaF + 3/4CF_4$$
$$Na_3AlF_6 + C \Rightarrow Al + 3NaF + +1/2C_2F_6$$
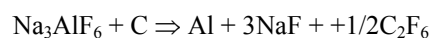
The primary PFC emissions pathway is the exhaust duct collection system, which removes gases from the pots. At most smelters, the exhaust ducts from individual pots combine into larger exhaust ducts, which typically run the length of the potroom and are several meters in diameter and hundreds of meters long. Large fans draw the exhaust through the ducts and move the exhaust gases to treatment systems that remove various constituents. Fugitive PFC emissions result when the pot hooding efficiency and operating conditions of the collection system result in less than 100% capture from the pot. Fugitive emissions can also result from manual intervention to terminate the Anode Effect, when hoods are removed or end doors opened. The fugitive emissions are transported out of the roof by convection or, in the case of a potroom equipped with a secondary control system that employs roof scrubbers, by a powered ventilation fan.

The frequency and duration of anode effects depend primarily on the pot technology and operating procedures. Emissions of CF_4 and C_2F_6, therefore, vary significantly from one aluminium smelter to the next, depending on these parameters. The factors that can potentially influence the PFC generation rate are outlined in Table 1.

1.2 The current state of inventory methodologies

This section outlines the PFC estimation methods outlined in the *IPCC Guidelines*, and discusses the methods used by countries that inventory PFC emissions.

1.2.1 IPCC Guidelines

The *IPCC Guidelines* recommend multiplying aluminium production by a CF_4 emission factor (i.e., CF_4 emissions per unit of aluminium production). To estimate the emission factor, different methods have been proposed based on the availability of data and are outlined below:

Tier 1 The PFC emission factor should be based on actual emission measurements because PFC emissions vary so significantly from one smelter to the next.

Tier 2 Where actual measurements are not feasible due to economic or time constraints, the *IPCC Guidelines* recommend deriving an emission factor using the model proposed by Tabereaux that is based on Faraday's Law (this model and its applicability is further discussed in Section 2.2.1). The *IPCC Guidelines* provide default parameter values by technology type to fit the Tabereaux model, and

Tier 3 When relevant operating parameters are not recorded, the IPCC recommends multiplying aluminium production by a default emission factor, which is specific to the cell technology. The IPCC provides default emission factors for four technology types: modern prebaked; HS Soderberg; "older" prebaked'; and VS Soderberg (2). A default rate for C_2F_6 emission is 1/10 that of CF_4. However, because emissions of CF_4 and C_2F_6 vary so significantly from one aluminium smelter to the next, depending on cell type and anode effect parameters, the estimations will be highly uncertain unless actual emission measurements have been made.

It should be noted that in the *IPCC Guidelines* for this source, the Tier 1 method is the high data method while Tier 3 is the default method. However, in all other Chapters, the Tier 1 method is the default and Tier 3 is the high data method. In this paper, the Tier ratings will be consistent with the *IPCC Guidelines*, i.e., Tier 1 will be the high data method while Tier 3, the default method.

TABLE 1	
FACTORS THAT POTENTIALLY INFLUENCE PFC GENERATION	
Factor	**Specific Examples/Description**
Cell Technology Type	• Vertical Stud Soderberg (VSS), Horizontal Stud Soderberg (HSS), Center-Worked Prebake (CWPB), Side-Worked Prebake (SWPB)
Feed Delivery System	• Automatic break and feed, manual break and feed, bar feed, point feed
Cell Operating Parameters	• Anode effect frequency • Anode effect duration • Anode effect voltage • Operating amperage • Current density • Metal pad depth
Anode Effect Kill Routine	• How the anode effect is terminated (e.g., manual or automatic) • Design of automatic cell control and feed strategies where implemented.
Electrolyte Properties	• Volume of electrolyte relative to cell size and amperage • Chemistry of electrolyte • Operating temperature of electrolyte
Cell Liquid Velocities	• Cell magnetic compensation and geometry • Liquid levels
Alumina Quality	• Physical and chemical properties of alumina that have an effect on the solubility rate in the electrolyte
Anode Coke	• Physical and chemical properties of the anode that can influence the kinetics of reactions taking place on the surface of the anode
Smelter Configuration	• Potroom locations, number of pots in each potroom, exhaust duct configuration, potroom roof configuration

TABLE 2	
IPCC DEFAULT EMISSION FACTORS	
Cell Technology	**kg CF_4 / tonne Al**
Modern Prebaked	0.05
HS Soderberg	1.0
"Older" Prebaked	1.75
VS Soderberg	2.0

1.2.2   National communications to the UNFCCC Secretariat

As of 1998, 42 countries had submitted inventories of greenhouse gas emissions and sinks to the UNFCCC Secretariat. Of these 42 national Greenhouse Gas (GHG) inventories, only twelve included estimates of PFC emissions from aluminium production. These countries were: Australia, Canada, France, Germany, Iceland, Italy, Netherlands, New Zealand, Norway, Sweden, UK, and the US (UNFCCC, 1998). The inventory methods used by these countries are presented in Table 3. Table 3 also includes the methods used by Brazil and Bahrain to quantify PFC emissions from aluminium production for compliance with their national PFC emission reduction programmes.

TABLE 3 PFC EMISSIONS INVENTORY METHODS		
Country	**Inventory Method**	**Data Source(s)**
Australia	Emission factor estimates based on 1) a linear regression model of emissions in US and Norway; 2) International Primary Aluminium Institute (IPAI) international survey; and 3) an estimating method developed for an Australian smelter.	National Communications[1]
Bahrain	Pechiney Over-voltage Model	Ameeri, J.G. (1998)
Brazil	IPCC method	Miguez, J. and V. Lima (1998)
Canada	Smelter Measurements	National Communications
France	Pechiney Over-voltage Model	National Communications
Germany	Smelter Measurements	Salomon, N. (1998)
Iceland	Method not transparent in National Communications	National Communications
Italy	Emission factor estimates based on measurements at French and Norwegian plants with similar technology.	National Communications
Netherlands	Method not transparent in National Communications	National Communications
New Zealand	Method not transparent in National Communications	National Communications
Norway	Smelter Measurements	National Communications
Sweden	Method not transparent in National Communications	National Communications
UK	Method not transparent in National Communications	National Communications
US	US industry-average emission rates are assumed for all smelters for 1990. In subsequent years, PFC emission rates are adjusted based on company-specific operating parameters (e.g., anode effect frequency).	National Communications
[1] The National Communications are submitted by countries to the United Nations Framework Convention on Climate Change (UNFCCC) Secretariat. They are available online at http:\\www.unfccc.de.		

The methods, assumptions, and data used to estimate PFC emissions from primary aluminium production in the National Communications are not clear, transparent or well documented. For five countries that addressed PFC emissions in their National Communications, emission estimates are presented without a qualitative discussion of the methods used to obtain these estimates. Brazil, the only country to follow the method outlined in the *IPCC Guidelines*, did not specify if default factors were used or if measurements were taken. All other countries estimated the CF_4 emission factor using smelter measurements or country-specific methods. While these methods may provide accurate emission estimates, the lack of transparency and supporting documentation of methods and data makes review and verification of estimates impossible.

2 METHODOLOGICAL ISSUES

This section discusses the *good practice* methods for determining PFC emissions from primary aluminium smelting for national emissions inventory purposes. The general framework for estimating PFC emissions for each smelter is to multiply activity data (i.e., aluminium production) by a PFC emission factor (e.g., kg CF_4 per ton of aluminium produced). Smelter emissions should then be aggregated to estimate national emissions.

2.1 Selection of an emission estimation method

While the method proposed in the *IPCC Guidelines* may fit measured emission rates to process parameters for some smelters, it does not apply across smelter technologies and operating conditions. Therefore, countries have generally chosen to replace the methodology outlined in the *IPCC Guidelines* with their own country-specific method. While this may result in more accurate estimates, the lack of transparency in reporting makes it impossible to review, compare, or verify emission estimates. Additionally, different methods of estimation used within a single nation's inventory and between national inventories causes further uncertainty in global emission estimates.

Most aluminium producing countries have a relatively small number of primary aluminium facilities, and it is possible to develop a smelter-specific relationship between emissions and potentially relevant operating parameters including anode effect frequency, anode effect duration, and anode effect voltage profile. Given the availability of rigorous calculation techniques, national inventories of PFC emissions from primary aluminium production should be calculated on a smelter basis, using emissions estimation models developed at that site. Alternatively, existing estimation methods may be used by smelters, if deemed representative for their conditions.

2.2 Emissions factors

Given the uncertainties associated with default emission factors, PFC emissions should be estimated at the smelter level. A desirable smelter-specific estimation method would enable emission rates to be calculated based on commonly monitored process parameters. There have been several attempts to develop a robust relationship between PFC emissions and smelter operating parameters (e.g., anode effect frequency, duration, and over voltage). These relationships have been proven to be useful predictors of PFC emission rates for particular smelter technologies and range of operating conditions. However, a relationship that applies to individual smelters across technologies, across countries, and across a range of operating conditions is yet to be developed. This section discusses some existing estimation methods and conditions for their applicability and provides guidance on developing a robust relationship between PFC emissions and operating parameters.

2.2.1 Existing smelter-specific PFC estimation methods

The most common PFC estimation methods available to countries include: the Tabereaux Method (Modified Faraday's Law Method), the Pechiney Over-voltage Method, and the Slope Method. Each of these is described below.

- **Tabereaux Method (Modified Faraday's Law Method):** Recommended in the *IPCC Guidelines* and proposed by Tabereaux (1994), this method assumes that the generation of CF_4 in electrolysis cell follows Faraday's Law. Faraday's Law states that the quantity of gas generated depends on the flow of electrical current in the cell. The emissions factor can be calculated using the following equation:

> **EQUATION 1**
>
> kg CF_4/tonne of Al = 1.698 ● (p/CE) ● AEF ● AED

where p is the average fraction of CF_4 in the cell gas during anode effects; CE is the current efficiency; AEF is the number of anode effects per cell day; and AED is the anode effect duration in minutes. Limiting the usefulness of this approach is how best to estimate p for various operating conditions and cell technologies. In general, producers track the AEF and AED on a daily basis.

- **Pechiney Over-voltage Method:** This method uses the anode effect over-voltage as the relevant process parameter. The anode effect over-voltage integrates the fluctuation in voltage during an anode effect. The correlation formula was derived from numerous test measurements of PFC generation at different smelters using the Pechiney technology.

> **EQUATION 2**
>
> kg CF_4/tonne of Al = 1.9 ● AEO / % CE

where AEO is the anode effect over-voltage in mV.day; and CE is the aluminium production process current efficiency in percent (Bouzat et al., 1996). One of the drawbacks of this method is that many smelter process systems do not have the capability to collect the data required to compute the anode effect over voltage. This limits the application of this method.

- **Slope Method:** This method proposes a linear relationship between anode effect minutes per cell-day and CF_4 emissions, expressed as:

> **EQATION 3**
>
> kg CF_4/tonne of Al = slope ● AE Minutes/cell-day

This relationship was first expressed by workers at Hydro Aluminium and Alcoa based on field measurements at their prebake facilities. Both companies independently arrived at a slope of 0.12 (IPAI, 1996). Recent field measurements in the US also indicate a slope of 0.12 for prebake cells (Leber et al., 1998).

To develop an accurate estimate of the slope, simultaneous measurements of CF_4 emissions and anode effect data are required. These measurements should be repeated over a range of anode effect minutes to ensure that the linear relationship holds for a range of anode effect minutes (alternatively, the equation could be piece-wise linear).

It should be noted that the Slope Method is equivalent to the Tabereaux method quoted in the *IPCC Guidelines*, where Slope = 1.698 ● (p/CE) and AE Minutes/Cell-day = AEF ● AED.

While each of these methods is useful in fitting measured emission rates to process parameters under certain conditions, it is generally acknowledged that all fall short of providing a robust predictor of emissions from process parameters monitored during standard production, across producers, across technologies, and for a range of operating parameters.

Some of the difficulties in developing a robust relationship include (IPAI, 1996):

- lack of adequate measurements across technologies and operating conditions to base a predictive relationship between emissions and operating parameters on;

- different measurement methods used;

- little quality assurance data accompanying reported measurements;

- absence of generally available gas standards for calibration purposes, and

- no common definition of anode effect duration.

In the absence of a universally applicable estimation method, each smelter should develop a relationship between PFC emissions and operating parameters to accurately estimate PFC emissions. Smelters may adopt one of the above relationships if it is demonstrated to be representative for their plant characteristics and operating conditions. Annex 2 provides default coefficients by technology type for the Slope and Pechiney methods.

2.2.2 Developing a smelter-specific relationship to estimate PFC emission rates

The *good practice* method requires developing or choosing a smelter-specific relationship between PFC emissions and relevant operating parameters, for example:

- To develop the relationship between emissions and process parameters, corresponding potroom operational data must be compiled simultaneously with the emissions measurement. Once the relationship is established, the PFC emissions rate can be estimated from the operational data over time. The time series of the PFC emissions factor can be used along with the time series of aluminium production to estimate annual emissions estimate for the smelter. An estimation method that relates emissions to operating parameters will provide an understanding of how the parameters can be altered to reduce emissions.

- If an existing estimation method is used, the smelter must demonstrate that it is applicable to its characteristics and operating conditions. To demonstrate the applicability of an estimation model, smelters must measure emissions at least once to ensure the applicability of the model. Once measurements are completed, the preferred relationship should be statistically validated using standard goodness-of-fit tests against competing methods to ensure it is the best suited model.

The choice of sampling method, sampling scale, and analytical methods is critical in developing a robust relationship and are discussed below and in detail in Annex 1.

- **Several sampling methods may be appropriate:** Both the composite and continuous potroom approach are effective approaches for emissions inventory purposes. While the composite approach is more cost-effective, the continuous potroom sampling and analysis approach provides information on the emissions profile of individual anode effects. The single pot, event sampling approach requires many weeks of sampling to obtain an estimate that is representative for the entire smelter and is therefore not cost-effective for inventory purposes.

- **Sampling scale should be designed to provide a comprehensive measurement for the entire facility and be as compatible as possible with the operational data:** Scale refers to the spatial and temporal extent of the samples. Sampling should be representative of the full range of process variation (including the possible effect of 'sick pots', cell startup or restart etc. which may contribute significantly to total PFC emissions). Continuous potroom sampling and analysis requires balancing competing needs when determining the sampling locations: measuring more pots helps ensure that the measurements are representative of the total smelter but measuring too many pots will prevent the identification of a sufficient number of "resolved" anode effects.

- **If there is high daily variability in emission rates:** Enough daily samples should be taken to assure that the range of emission rates for the current operating conditions is covered. For example, cover the entire distribution of anode effect duration recorded for the entire smelter for the last year. Sampling should be continued until the average emission rate does not change by more than 15% when an additional day is included (Roberts, R. and J. Marks, 1996).

- **Analytical system must be appropriate for the sampling method, stable, and free of (or corrected for) interferences:** The detection limits of the analytical system must be sufficient to detect PFC concentrations in the exhaust duct and potroom roofs. In the pot exhaust gas fully diluted by exhaust air, a detection limit of 0.1 ppmv assures proper detection of all anode effects. Fugitive emissions analysis will require instruments with lower detection limits. The measurement system should be stable enough to maintain accuracy between calibration periods. If interferences occur, corrections must be employed to correct gross measured signals to give a corrected signal for the PFC of interest.

Each smelter-specific relationship should be validated. If resources do not permit additional measurements, the smelter-specific relationship should be compared with other estimation methods, at a minimum. Convergence of emission factors generated by the smelter-specific relationship with those generated by alternative models will increase confidence in the validity of the relationship. Finally, the estimated emission factors can be compared with values seen in the literature for similar smelters.

If the estimates generated by the smelter-specific relationship cannot be validated with alternative approaches, models, or literature values, some explanation of the smelter-specific conditions that may produce such estimates is required. Repeat measurements are recommended if the estimates cannot be validated.

The PFC emissions estimation method should be updated periodically. Measurements should be repeated at a minimum of every 5 years to ensure the validity of the relationship. If process or other smelter conditions that may influence total emissions change significantly in the interim period, the estimation method will need to be re-evaluated with repeat measurements. Significant process or smelter changes that warrant re-evaluation include, for example, variation of process parameters beyond the range of parameter values for which the estimation model was developed.

2.2.3   Default emission factors by technology-type

As a last resort, where the only information available is the annual quantity of aluminium produced, default emission factors by technology type may be used to develop an emissions inventory. This method is the most uncertain and consequently least desirable. Annex 3 provides default emission factors by technology type.

2.3   Activity data

Aluminium production data are necessary to estimate PFC emissions from aluminium smelting regardless of the estimation method chosen. Countries should obtain smelter-level data on an annual basis, so that they can use smelter-specific emission factors. At a plant-level, actual production data should be obtained directly from producers. Since aluminium production data may be considered proprietary by producers, it may be necessary to ensure that it is not released to the public, or to publish it in such a way so that individual plants are not identified.

While smelter level data may not be reported for all smelters, aggregate national production statistics are usually collected by various national and international agencies (e.g., U.S. Department of Commerce, IPAI). Smelter capacity may be used along with aggregate national production statistics to estimate production. Actual production data is preferred as the use of smelter capacity as a proxy for production introduces uncertainty in the total emissions estimate.

2.4   Uncertainty

Parallel to the IPCC sector-specific works on *good practice guidance*, the IPCC is completing a programme of work on emissions inventory uncertainty. This work will result in recommendations to the UNFCCC Secretariat on approaches to assessing and managing uncertainty. During the IPCC Inventory Experts Group Meeting in Paris (October 1998), technical experts in the uncertainty programme came up with a series of questions to be answered in the sectoral expert meetings. Specifically, the sector meetings should provide answers to these questions in the individual source context, so as to facilitate work of the uncertainty programme on establishing a general methodological approach. These questions are listed in Annex 4 and should be discussed during the expert meeting with respect to PFCs from primary aluminium production.

2.5 Completeness

Given that there are a small number of primary aluminium facilities in most producer countries, and it is possible to develop a smelter-specific emissions estimation model, complete reporting of this source should be attainable. Reporting should include qualitative and quantitative information from each primary aluminium smelter including amount of aluminium produced, relevant operating parameters, and associated CF_4 and C_2F_6 emissions.

2.6 Other important issues

Applying an estimation method retroactively: A *good practice* method that requires a smelter-specific emissions estimation method may only be applied to develop current and future inventories. If this method is applied retroactively, then (i) the historical operational data required by the method must be available and (ii) each smelter must demonstrate that the method is applicable to its historical conditions. However, smelters may no longer have a historical record of relevant operating parameters and/or the relationship may not be valid for the conditions in which aluminium was produced in previous years. This creates two problems for developing inventories to assess compliance with international agreements:

(i) **Developing Baseline Emission Estimates:** Baseline emission inventories may be highly uncertain if good practice methods cannot be applied retroactively.

(ii) **Time-Series Integrity:** If good practice methods are not used to estimate a time-series of emissions, emissions reductions estimates will be highly uncertain. These policy issues require further discussion among the various stakeholders.

Defining an anode effect: A common definition of anode effect should be agreed upon for emission estimation methodologies. At a minimum, the definition used by individual smelters should be documented by the smelters in their reporting. This definition should be noted in national inventories where these estimation methods have been applied. This consistency is also important for retrospective estimates to ensure that reductions are not from redefining anode effect parameters.

Developing a database of emissions measurements: A database of emissions measurements covering a range of technology types, anode effect frequency and duration, line current and other smelter characteristics and operating conditions would be desirable. In particular, such a database would be beneficial for developing a universal emissions estimation model, providing an expanded data set for validating PFC estimation models, enabling default emissions factors to be developed for specific technology types and operating conditions and enabling estimation of uncertainty ranges for default emission factors.

Developing and making available gas standards: The absence of generally available gas standard reference materials containing known amounts of CF_4 and C_2F_6 leads to lack of confidence in analytical methods when estimating PFC emissions. This prevents comparison of measurement data across smelters or within smelters across measurement periods. Reliable and accurate measurements available to all standards for CF_4 and C_2F_6 at concentrations over the range encountered in operations are required.

3 REPORTING AND DOCUMENTATION

The *IPCC Guidelines* are used to guide countries in the preparation and submissions of annual greenhouse gas emissions inventories to the UNFCCC Secretariat. The Guidelines establish:

- Standard tables, definitions, units, and time intervals for reporting all types of emissions;

- Necessary documentation to enable comparison of national inventories, including worksheets, major assumptions, methodological descriptions, and enough data to allow a third party to reconstruct the inventory from national activity data and assumptions, and

- An uncertainty assessment.

PFC emissions from primary aluminium production are reported in Table 2, Vol. 2 of the IPCC Guidelines: Sectoral Report for Industrial Processes, which calls for entries for each source emissions totals of carbon dioxide, methane, nitrous oxide, precursor gases (NO_X, CO, NMVOCs, SO_2), HFCs, PFCs, and SF_6. Currently, the table does not have a specific entry for CF_4 and C_2F_6, or any other individual species of HFC or PFC. Because CF_4 and C_2F_6 have different global warming potentials (GWPs) and different masses, emissions of different species cannot be on a mass basis. They can be aggregated on a carbon equivalent basis, but this does not allow for reconstruction of the inventory since a third party will not know the relative share of each gas to the total sum and whether emissions of both gases have been estimated.

PFC emissions from aluminium production are reported under the IPCC category 2C3, which derives from the following classification scheme:

2   : Industrial processes

2C   : Metal Production

2C3 : Aluminium Production

Based upon a review of current reporting guidelines developed by the IPCC and the UNFCCC, as well as the conclusions of the UNFCCC's review of Second National Communications, the following recommendations can be made regarding reporting of PFC emissions from aluminium production.

- **Emissions by Gas:** CF_4 and C_2F_6 should be reported on a mass basis, as well as in CO_2 equivalents. In this way, the GWP used will be transparent. The emissions of each gas and which gases are estimated will be apparent. The GWP used should be consistent with the latest IPCC findings. The *IPCC Guidelines* indicate GWPs of 6500 and 9200 for CF_4 and C_2F_6, respectively.

- **Transparency:** For those countries where PFC emissions were reported in their National Communications, the underlying data, assumptions, and methodologies used were not transparent. Therefore, it is difficult to verify the emission estimates or compare emission estimates across countries. All necessary information to reproduce emission estimates should be provided. A minimum data set should include annual aluminium production data by smelter, smelter-specific CF_4 emission factor relationship and other relevant operating parameters.

- **Documentation:** Documentation necessary to support all data, assumptions and chosen method should be provided. This reporting should include PFC emission estimation method used, definition of relevant operating parameters and validation of method for specific smelters.

3.1   Confidential business information

The issue of confidential business information (CBI) may complicate the desire for clear and transparent national reporting. Since aluminium production data or PFC emission factors may be considered proprietary by producers, it may be necessary to ensure that it is not released to the public, or to publish it in such a way so that individual plants are not identified.
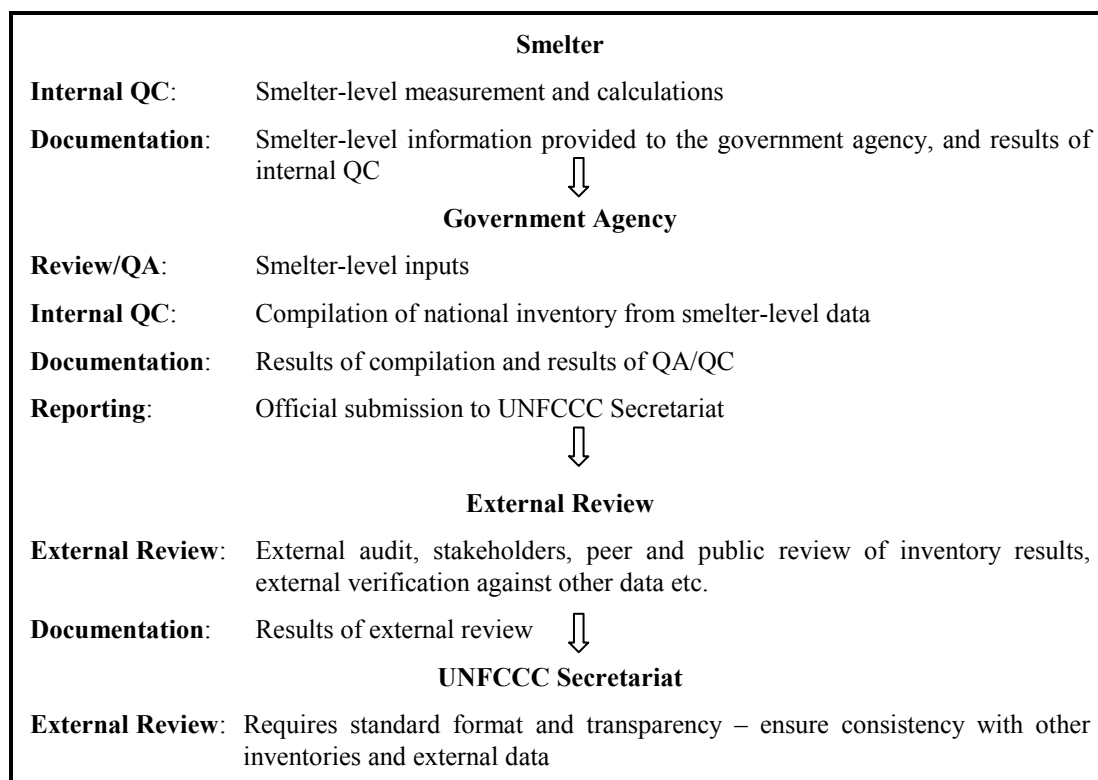
4   INVENTORY QUALITY

Inventory quality assurance and quality control (QA/QC) is a process integral to the development of a credible inventory. A successful quality assurance programme is two-fold, requiring internal smelter level procedures and external review and audit activities. The internal QC activities are designed to ensure accuracy, documentation and transparency. Internal activities should include, for example, the development of a sampling protocol and a well-documented process for data collection and verification. The external review process is designed to minimize errors that occur in the preparation of emissions inventories, and reduce or eliminate potential inherent bias from any given smelter. Figure 2 outlines the flow of information and processes followed at each step.

4.1   Internal inventory QA/QC systems

4.1.1   Smelter-level activities

Measurement and Sampling QC: The inventory QC procedures used at the aluminium smelter level will be determined in large part by plant personnel. There are, however, certain procedures common to monitoring programmes which should be specified:

- sample collection methods (including frequency, container type and preparation),

- written standard operating procedures for sampling and analysis and reporting,

- calibration procedures (number, frequency, standard chosen, acceptance criteria),

- limits for accuracy and precision,

- method to flag suspect data, and

- maintenance of records.

F i g u r e   2   I n v e n t o r y   Q A / Q C   p r o c e s s

<div>

Smelter

Internal QC: Smelter-level measurement and calculations

Documentation: Smelter-level information provided to the government agency, and results of internal QC

⇩

Government Agency

Review/QA: Smelter-level inputs

Internal QC: Compilation of national inventory from smelter-level data

Documentation: Results of compilation and results of QA/QC

Reporting: Official submission to UNFCCC Secretariat

⇩

External Review

External Review: External audit, stakeholders, peer and public review of inventory results, external verification against other data etc.

Documentation: Results of external review   ⇩

UNFCCC Secretariat

External Review: Requires standard format and transparency – ensure consistency with other inventories and external data

</div>

Production Data QC: Annual aluminium production is the activity data required to estimate PFC emissions from aluminium smelters. Accurate production records should be available at the smelter level.

Documentation: The emissions information necessary to allow a thorough analysis by the reviewing/auditing agency will include aluminium production, relevant operating parameters (e.g., anode effect frequency and duration), the relationship between PFC emissions and other relevant operating parameters. Examples include the following:

- description of the methods for sampling and analysis (or a reference to standard methods);

- description of QA/QC procedures for the measurement of volumetric flow rate and concentration (including the results of any determinations of accuracy and precision for the measurements);

- details on the testing procedure (such as the number of samples, period of time sampled, whether sampling is instantaneous or aggregated over time, etc.);

- results of the sampling (volumetric flow rate, concentration) in consistent units of measure;

- a discussion of the process operating conditions at the time of the test and certification that they were representative of normal operation, or explanation of problems encountered that prevented the recommended sampling/analysis, and

- a reporting form is recommended to provide key summary information for the determination of annual emissions, which is to be signed and certified by a responsible plant representative.

4.1.2   Inventory agency level activities

Review (QA) of Smelter-Level Information: Before accepting smelter-level emissions data, the inventory agency should carry out an assessment of data quality and sampling procedures. This type of review requires close cooperation with plant owners to obtain enough information to verify the reported emissions, as discussed above. The assessment should include sample recalculations, an examination of the representativeness of the data and operating conditions, and an identification of potential bias in the methodology, and recommendations for improvement.

QC on Compiling National Emissions: In addition to a thorough quality of assessment of smelter-level data discussed above, the inventory agency should ensure that the process of aggregating smelter data to develop the national inventory undergoes quality control. This should include, among other things:

- cross-referencing aggregated aluminium production statistics with national totals;

- back-calculating national emissions factors from aggregated emissions and production data;

- ensuring all smelters are included, and

- comparison with industry trends to identify anomalies and patterns.

Documentation on Compiling National Emissions: For the PFC emission inventories, a QA/QC management plan should address the specific items needed to perform audits and reviews. When the estimates are provided by each smelter, the details should be documented at the smelter level to account for differences in the procedures among plants. Examples of the types of information needed for documentation and external audit include:

- a detailed description of the inventory methodology;

- identification of the input parameters that are needed and how the input parameters are obtained (measured or estimated);

- frequency of the measurements and results of determinations of accuracy and precision for the measurements; and

- an estimate or discussion of uncertainty and variability for input parameters that are estimated instead of measured.

When smelters use a PFC emission factor relationship derived from measurements at another smelter, local measurements must be taken to verify that the relationship is valid due to differences in smelter operating conditions. Countries should provide information on the origin and basis of the factor, compare it to other published emission factors and explain any significant differences, and attempt to place bounds on the uncertainty.

4.2 External inventory QA/QC systems

External QA activities include a planned system of review and audit procedures conducted by personnel not actively involved in the inventory development process. The key concept is independent, objective review to assess the effectiveness of the internal QC programme, the quality of the inventory and to reduce or eliminate any inherent bias in the inventory processes. Several types of external reviews, or audits, may be appropriate for PFC emission inventories.

- **Third party audit by an accredited organisation, expert, independent third party:** An audit of the documentation and calculations ensures that each number is traceable to its origin. Given that much of the information used in developing PFC emission estimates may be proprietary, a third party audit that protects confidentiality may be a necessary type of review.

- **Expert (peer) review:** A detailed peer review would be appropriate when a procedure for determining PFC emissions is first adopted or revised; it would not be needed on an annual basis. Such a review is designed to ensure that the methodology accurately represents the plant's particular situation, is as rigorous as possible, and that the data and assumptions used reflect the best available information.

- **Stakeholder review:** Review by aluminium producing companies, industrial organizations, and government can provide a forum for review of the methods used. This type of review would be of most value early in the inventory process when smelter-specific details are shared, which can lead to ways for some companies to improve their methods to the levels achieved by the plants with the best methodology.

- **Public review:** Some countries make their entire inventory available for public review and comment. This process may result in a range of comments and issues broader than those from other review processes.

4.3 QA/QC good practice guidance

QA/QC good practice guidelines include the following:

- **Prepare a QA/QC plan that would outline the steps and information needed**

  An effective QA programme will include planning, numerous QC checks during inventory development, and QA audits at strategic points in the process. QA/QC should not be left until the end of the inventory process or the appropriate data and documentation will not be available;

- **Develop a standard reporting format for smelters to complete and submit to national inventory managers**

  The key to third party verification of emission estimates is the transparency and documentation of all assumptions, data and methods. The information and records which must be included in a data report

package should be itemised. Documentation can include raw data, field logs, instrument printouts, and results of calibration and QC checks. Sampling and analytical methods should be specified and documented. The smelters should also state the criteria used to review and validate data and methods;

- **External peer review audits**

  These should be conducted when smelters first develop or change their emission estimation methodologies. Because each smelter will have to develop an estimation model specific to their technology and operating conditions, these equations should be verified by an external review process. In this way, emission estimation methodologies can be compared across different smelters, and can contribute to ongoing research to develop a robust predictor of PFC emissions with wide applicability;

- **Internal review should be conducted when emissions change significantly**

  A significant change in PFC emissions from a smelter translates into a significant change in anode effects. Changes in anode effect parameters may fall outside the range of the estimation methods applicability. The smelter should conduct measurements to ensure that the estimation method is still valid. If not, the estimation method should be updated and undergo external review.

- **Ensure that aluminium production data and emission factors will be published in such a way that individual smelters are not identified**.

  Aluminium production data or PFC emission factors may be considered proprietary by producers. However, these data are needed for the QA/QC process. This practice should allow for an adequate level of detail for the review and at the same time address the sensitivity of some aluminium companies to issues of confidentiality.

5   CONCLUSIONS

The *IPCC Guidelines* present three methods for estimating emissions. Tier 1 is based on smelter-specific measurements and Tiers 2 and 3 are based on default values. Protocols for measurement techniques (e.g., sampling method, sampling scale, analytical methods) need to be developed and well-documented. Protocols should address the variability among smelters with regard to the definition of an anode effect, cell technology, potroom design, and smelter operating procedures. To make measurements comparable, reliable gas standards should be made available. The construction of a measurements database will aid in validating emissions models and default emission factors and will contribute to quantifying uncertainty in emissions estimates. Lastly, data must be reported in a transparent and complete manner while protecting smelters' proprietary information, and an appropriate system for internal and external review should be established.

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ANNEX 1 DEVELOPING A SMELTER-SPECIFIC RELATIONSHIP BETWEEN PFC EMISSIONS AND OPERATING PARAMETERS

Developing a smelter-specific relationship between PFC emissions and operating parameters requires measuring of PFC emissions during representative operating conditions. The general approach for measuring PFC emissions involves measuring the PFC concentration and gas flow rate from the exhaust ducts and potroom roofs. Using these data, the total mass of PFC emissions per unit time can be calculated. The emissions rate per unit of aluminium production (i.e., the emissions factor) can be calculated using the PFC emissions rate per unit time and the rate of aluminium production per unit time. Simultaneously with the sampling measurements, facility process data and characteristics are gathered so that the relationship between the emissions rate and the process can be established.

Once the relationship between the emissions rate and the process parameters is established, the PFC emissions rate can be estimated from the operational data over time. The PFC emissions factor can be used along with the time series of aluminium production to estimate annual emissions for the smelter. To confirm that the relationship between emissions and process parameters are valid over time, measurements should be repeated periodically (e.g., every 5 years) or in the event of significant process changes that would affect the rate of PFC generation.

This section provides guidance on techniques and approaches used to measure PFC emissions from an individual smelter.

Sampling and Analysis Methods

Field and laboratory measurements confirm that PFCs are generated only during anode effects. Anode effects occur as isolated, random events during production operations. The random nature of the anode effects and their relatively short duration requires rapid response, continuous measurement methods to develop an emissions profile for individual anode effects and also identification of potential control strategies. Sampling and analysis methods for such data lean towards reducing the number of pots to be sampled. At the same time, developing an emissions inventory for the entire smelter requires measurements over a large number of pots to gather a representative sample. The three commonly used sampling and analysis methods for measuring PFC emissions are summarized in Table 4

As indicated in Table 4, while the time-integrated potroom approach may be the most cost-effective means of measuring PFC emissions, the continuous potroom sampling and analysis approach can provide information on the emissions profile of individual anode effects. The single pot approach, while useful for investigating the time profile of emissions and evaluating the implications of modifications in pot operations, requires many weeks of sampling to obtain an estimate that is representative for the entire smelter and is therefore not cost-effective for inventory purposes. The composite and continuous pot-room sampling and analysis approach are both effective approaches for estimating emissions based on operating parameters. The continuous pot-room sampling approach has the additional advantage of developing an emissions profile for individual anode effects. This information is useful in understanding the events that contribute most to emissions and develop emission control strategies accordingly.

Sampling Scale

Choice of the appropriate sampling scale is an essential prerequisite for extrapolation to the smelter level. Scale refers to the spatial and temporal extent of the individual samples. The sampling scale should be designed to provide a comprehensive measurement for the entire facility and be as compatible as possible with the operational data.

Sampling should be representative of the full range of process variation. For the potroom level, potroom emissions measured in the ducts must be consistent in terms of scale with the fugitive samples taken from the potroom roofs. The decision of the sampling locations will be driven by the logistics of sampling (e.g., access to ductwork at appropriate locations), time and resources. The spatial extent of the samples must coincide with the spatial extent of the process data collected. Continuous potroom sampling and analysis requires balancing competing needs when determining the sampling locations: measuring more pots helps ensure that the measurements are representative of the total smelter but measuring too many pots will prevent the identification of a sufficient number of "resolved" anode effects (i.e., where there is no overlap between anode effects). For the single pot sampling and analysis, the scale is straightforward, requiring the selection of a pot that is representative of the smelter.

Sampling should also be representative of the temporal variation in emission rates. If there is high daily variability in emission rates, enough daily samples should be taken to assure that the range of emission rates for the current operating conditions is covered. Sampling should be continued until the average emission rate does

not change by more than 15% when an additional day is included (Roberts, R. and J. Marks, 1996). Measurements should be repeated every 5 years to ensure the validity of the relationship. If process or other smelter conditions that may influence change significantly in the interim period, the estimation method need to be re-evaluated with repeat measurements. Significant process or smelter changes that warrant re-evaluation include variation of process parameters beyond the range of parameter values for which the estimation model was developed, installation of a pot line with higher amperage, different pot type, increasing the line current, or cell technology for an existing potline, changing the alumina feed strategy etc.

TABLE 4

PFC SAMPLING AND ANALYSIS METHODS

Method	Description	Advantages	Disadvantages
Composite Pot Room Sampling and Analysis	This approach involves taking time-integrated samples from an exhaust duct that is connected to a group of pots in one or more potrooms. The time integration may be on the order of hours (e.g., 8 to 24 hours) and the number of pots may vary depending on the facility and its configuration.	The advantage of this approach is that the sampling equipment can be integrated with other sampling apparatus that is typically used for compliance measurement activities at smelters such that expensive special equipment is not required. This method provides good estimates of the emissions rate per unit of aluminium production.	The disadvantage of this approach is that it cannot produce information on how emissions rates from individual anode effects differs for anode effects of different duration. However, the estimated emissions rate per unit of aluminium production is expected to be reliable, making it the most cost-effective method for developing an emissions estimate for a given point in time.
Continuous Pot Room Sampling and Analysis	This approach involves taking continuous samples from an exhaust duct that is connected to a group of pots in one or more pot rooms. The samples are analyzed continuously using a rapid response instrument such as a mass spectrometer or Fourier Transform Infrared Spectroscopy (FTIR) instrument. The frequency of analysis would be on the order of seconds or faster.	This method provides good estimates of the emissions rate per unit of aluminium production. In addition, a detailed time profile of emissions can be constructed for individual anode effects. A large number of individual anode effects can be analyzed in a relatively short period of time. This information will be helpful in understanding which event types contribute most to emissions. Furthermore, these data are particularly needed if one or more emissions estimation models are to be developed and verified.	The principal disadvantage of this approach is that it requires more costly equipment than the composite sampling approach discussed above. The real-time analytical instruments are relatively costly and require specially trained operating personnel.
Single Pot, Event-Driven Sampling and Analysis	This approach involves taking a sample from the exhaust of an individual pot when an anode effect occurs. The sample may be time integrated or a series of discrete samples can be taken using an automated sampling system which would allow a very detailed time profile of the emissions rate to be developed for the individual anode effect.	By isolating a single pot, this method provides a means of evaluating alternative emissions control strategies (it may not be prudent to modify the operation of an entire potline when evaluating alternative control strategies). By avoiding the use of real-time analytical equipment, the cost of this method is less than the continuous sampling approach. However, the sampling equipment is more complex than the sampling equipment in the composite sampling approach, making it more costly.	For inventory purposes, this approach is the least suitable of the three. Many weeks of sampling may be required to generate an adequate database for estimating the average emissions rate per unit of aluminium production.

Analytical Methods

Several analytical methods have been used to measure PFC emissions. PFC measurements have been reported using mass spectrometry (MS), infrared spectrometry (IR), tunable diode laser absorption spectroscopy (TDLAS), Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC), gas chromatography/mass

spectrometry (GC/MS), and photoacoustic spectrometry. Table 5 compares some of the common analytical methods used for PFC measurements.

TABLE 5 COMPARISON OF ANALYTICAL METHODS USED FOR PFC MEASUREMENTS			
Method/Criteria	**Resolution/Sensitivity**	**Availability/Price**	**Other**
Mass Spectrometry (MS)	Unambiguous measurement of CF_4 and C_2F_6 Adequate sensitivity	Available at $100 to $250K	Limited portability; Capable of measuring other gas components
Infrared (IR)	Confounded measure of CF_4 and C_2F_6 Adequate sensitivity	Inexpensive	Subject to interferences that require separations or correction
Tunable Diode Laser (TDLAS)	Unambiguous measurement of CF_4 and C_2F_6 Excellent sensitivity	Not commercially available	Limited portability
Fourier Transform Infrared Spectroscopy (FTIR)	Unambiguous measurement of CF_4 and C_2F_6 Very good sensitivity	Field instrument available for $50K	Capable of measuring other gas components
Gas Chromatography (GC)	Sensitivity inadequate for fluorocarbons except in raw anode gas or ducts of single cells on anode effect	Inexpensive	Portable Capable of measuring other gas components
Gas Chromatography / Mass Spectrometry (GC/MS)	Unambiguous measurement CF_4 and C_2F_6 Good sensitivity	Commercially available	Portable Response time not suitable for on-line measurements
Source: Roberts, R. and J. Marks, 1994			

The choice of the analytical method depends in part on the sampling strategy. Continuous sampling and analysis requires the use of a portable system, which will not be affected by the magnetic fields at the smelter. Fugitive emissions analysis with composite sampling requires instruments with low detection limits (e.g., on the order of 1 ppbv). Recent measurements in the US indicate that the FTIR method was better than the GC/MS method when analyzing fugitive samples (Leber et al., 1998).

Because a number of different methods may be satisfactory for measuring PFCs, a single standard measurement method is not necessary or desirable. However, there are certain characteristics required of the analytical system in order to accurately measure the PFC concentrations:

- **Detection limits:** Detection limits for dynamic measurements systems should be adequate to assure detection of anode effects of the shortest duration measured. In the pot exhaust gas fully diluted by exhaust air a detection limit of 0.1 ppmv assures proper detection of all anode effects (Roberts, R. and J. Marks, 1994). For fugitive samples from the potroom roof, analytical sensitivity on the order of 1 ppbv is required to detect PFC concentrations accurately.

- **Stability:** The measurement system should be stable enough to maintain accuracy between calibration periods. Stability is normally described in terms of instrument drift. Drift should be no more than ± 2% between calibrations (Roberts, R. and J. Marks, 1994).

- **Interferences:** If interferences occur corrections must be employed to correct gross measured signals to give a corrected signal for the fluorocarbon of interest. If an adequate correction cannot be achieved the interfering component must be separated from the sample stream before the measurement is made. In addition to the exhaust air used to remove contaminants from the smelting pots, there are the products from the smelting process itself - CO, CO_2, SO_2, HF, CF_4, and H_2O. A successful measurement system must filter condensed phase material from the gas stream to prevent clogging of the sampling cell (Roberts, R. and J. Marks, 1994).

Validating the Smelter-Specific Relationship

Once the smelter-specific relationship is developed or chosen, it is necessary to validate it. Validation of the estimated relationship can be accomplished by comparing the smelter-specific relationship with other estimation methods. The measurements will generate a data set which, in addition to forming the basis for the smelter-specific relationship, can be used to generate emissions factors for alternative, commonly used estimation methods (such as those discussed earlier). Convergence of emission factors generated by the smelter-specific relationship with those generated by alternative methods will increase confidence in the validity of the relationship. Finally, the estimated emission factors can be compared with values seen in the literature for similar smelters.

If the estimates generated by the smelter-specific relationship cannot be validated with alternative approaches, models, or literature values, some explanation of the smelter-specific conditions that may produce such estimates is required. Repeat measurements are recommended if the estimates cannot be validated.

ANNEX 2 DEFAULT COEFFICIENTS FOR THE SLOPE METHOD AND PECHINEY OVER-VOLTAGE METHOD

	TABLE 6					
	DEFAULT COEFFICIENTS					
Technology[1]	Slope[2,4]				Over-voltage coefficient[2]	
	CF_4	Uncertainty	C_2F_6	Uncertainty	CF_4	C_2F_6
CWPH	0.14	0.009	0.018	0.004	1.9	[6]I.H.P.
SWPB	0.29	0.02	[3]0.029	0.01	1.9	T.B.P
VSS	[3]0.068	0.02	[8]0.003	0.001	See note [6]	-
HSS	[7]0.18		0.018			

Centre Worked Prebaked (CWPB), Side Worked Prebaked (SWPB), Vertical Stud Soderberg (VSS), Horizontal Stud Soderberg (HSS).

[1] Source IPAI, EPA field measurements, and other company measurement data.

[2] There is inadequate data for establishing a slope coefficient for C_2F_6 emissions from SWPB cells based on measurement data: therefore a default of one tenth at the CF_4 coefficient is recommended, consistent with the IPCC Guidelines.

[3] Embedded in each Slope coefficient is an assumed emissions collection efficiency as follows: CWPB 95%; SWPB 90%; VSS 85%; HSS 90%. These collection efficiencies have been assumed based on expert opinion. While collection efficiency for HSS cells may vary, the company measurement data used for calculation of these coefficiencies are consistent with a collection efficiency of at least 90%.

[4] T.B.P. means to be published. Measurement programs that may provide sufficient data to provide these coefficiencies are underway but are not expected to be completed unitl early 2000.

[5] Overvoltage coefficients are not relevant to VSS and HSS technologies.

[6] The HSS Slope coefficients are based on 1991 IPAI survey data.

[7] It is good practice to pursue further work on emission measurement and uncertainty analysis for VSS.

Note: see the Final Draft Report on Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories Document for more detail.

ANNEX 3 DEFAULT EMISSION FACTORS BY TECHNOLOGY-TYPE

<table>
<tr><td colspan="5" align="center">TABLE 7

DEFAULT EMISSION FACTORS</td></tr>
<tr>
<td rowspan="2" align="center">Technology</td>
<td colspan="2" align="center">CF$_4$</td>
<td colspan="2" align="center">C$_2$F$_6$</td>
</tr>
<tr>
<td align="center">Kg/tonne Al[3]</td>
<td align="center">Uncertainty Range [2]</td>
<td align="center">Kg/tonne Al[1]</td>
<td align="center">Uncertainty Range [2]</td>
</tr>
<tr>
<td align="center">CWPH</td>
<td align="center">0.31</td>
<td align="center">0.0003 – 1.3</td>
<td align="center">0.04</td>
<td align="center">0.00004 – 0.2</td>
</tr>
<tr>
<td align="center">SWPB</td>
<td align="center">1.7</td>
<td align="center">0.8 – 3.8</td>
<td align="center">[3]0.17</td>
<td align="center">0.08 – 0.4</td>
</tr>
<tr>
<td align="center">VSS</td>
<td align="center">[4]0.61</td>
<td align="center">0.4 – 1.1</td>
<td align="center">[4]0.061</td>
<td align="center">0.04 – 0.1</td>
</tr>
<tr>
<td align="center">HSS</td>
<td align="center">[5]0.5</td>
<td align="center">0.0006 – 1.4</td>
<td align="center">[5]0.05</td>
<td align="center">0.00006 – 0.13</td>
</tr>
</table>

[1] Source IPAI, EPA field measurements, and other 1990 company measurement data, except for HSS, which is based on 1991 data.

[2] Uncertainty is estimated to a 95% confidence interval on the basis of the variance of anodes effect minute data from IPAI Survey Data for 1990 <or 1991 for HSS> for each technology type.

[3] There is inadequate data for establishing an emission factor for C$_2$F$_6$ emissions from SWPB cells based on measurement data; therefore a default of one-tenth of the CF4 is recommended, consistent with the IPCC Guidelines.

[4] The VSS default emission factors are based on IPAI, EPA linked measurements and other 1990 company measurement data.

[5] The HSS default emission factors are based on 1991 IPAI survey data.

ANNEX 4 UNCERTAINTY ASSESSMENTS

(1) Can default quantitative uncertainties be identified for the default emissions factors recommended?

The use of default quantitative uncertainties and the use of a default numerical method to combine the resulting uncertainty (such as the current IPCC method) are highly problematic for PFC emissions. While the uncertainty in the activity data – aluminium production – is relatively low (for all 1 to 2%), the uncertainty in the emission factor can range from 10% to 100%. The use of a default numerical method to combine uncertainties, such as the IPCC method, requires making assumptions that likely do not hold for PFC emissions (e.g., normally distributed emissions factors).

(2) What is the appropriate level of uncertainty analysis for PFC emissions?

Quantitative techniques are directly applicable for smelter-specific estimation models based on measurements. This requires a determination of statistical parameters (e.g., mean, probability distribution) for the emission estimation model and activity data as well as a method for combining uncertainties to determine total uncertainty at the smelter and national level. Testing of alternative estimation models with the measurement data or alternative parameters to models can be done through standard statistical techniques (e.g., sum of squares or maximum likelihood). The uncertainty range of the smelter-level emissions estimate should be developed using Monte-Carlo stochastic simulation techniques. This technique accounts for the variability in annual aluminium production estimates and the different operational parameters that are used in the estimation model (e.g., distribution of anode effect minutes). The Monte-Carlo technique should be extended to the emission estimates at the national inventory level. This is the most robust method of aggregating uncertainty at the smelter level to the national level.

If quantified uncertainty estimates are unavailable, it may be possible to make a qualitative judgment on uncertainty based on knowledge of process variability from other plants with such data, evaluation of the accuracy and precision of the measurement methods. Consequently, estimating the uncertainty of the emissions estimates will be a somewhat subjective process, relying on technical and expert judgment regarding levels of uncertainty. These assumptions will have a critical impact on the estimated uncertainty at the smelter and national level. Qualitative uncertainty estimates will require discussions of why the uncertainty estimates assigned are considered appropriate.

(3) What caveats are necessary on quantitative uncertainty estimates?

Quantitative uncertainties based on Monte-Carlo simulation requires the following caveats:

- Discussion of how the distributions for model variables and parameters for the distributions were developed is required. If distributions were assigned qualitatively, the basis for such judgement must be indicated. For example, the distribution of anode effects based on US smelter records is exponential or log-normal, with mostly short duration events and few longer duration events, and

- Correlation between variables must be accounted for as it could have a significant impact on the simulated emissions estimate at the smelter and national level.

(4) Can areas of potential covariance between emissions estimates for different sources or sub-sources be identified?

Aluminium production and semi-conductor manufacture are the two known anthropogenic sources of PFC emissions. PFC emissions from these two sources are independent.

(5) Are there specific weak spots or areas of inconsistency with respect to estimating PFC emissions from primary aluminium production that should be addressed in uncertainty analysis (i.e. missing sources, systematic errors, trend errors)?

The uncertainty analysis should address both random uncertainty and systemic (non-random) uncertainty. Random uncertainty could arise from naturally occurring variations, such as the real variation in emissions from anode effects of different duration or natural variations in human reaction times in taking measurements. This type of uncertainty can be detected through repeated experiments and, therefore, can be estimated through statistical analysis. Systemic uncertainty or bias is more problematic. It arises from a failure to identify all of the relevant source activities (e.g., exclusion of fugitive emissions in the emissions estimate), use of faulty instruments or equipment to measure emissions (e.g., poor gas standards), use of non-representative sample, or use of incorrect or incomplete estimation procedure (e.g., using an emission estimation equation that does not accurately characterize the emission generation process) to estimate emissions.

(6) What documentation will be necessary for the default and specific uncertainty estimates?

The documentation should include: (1) a discussion of the algorithms and equations in the inventory method, (2) identification of the main sources of statistical (random) uncertainty (3) discussion of whether systematic uncertainty (bias) may also be present (4) identification of strategies for reducing uncertainty, e.g., for improving the accuracy or precision of estimated emissions factors or activity levels (5) description of data trends, i.e., what types of changes or improvements are occurring or could occur that would improve the inventory estimates and how rapidly changes are occurring.