

THIS PAPER APPEARED IN LIGHT METALS 1998, PROCEEDINGS OF THE TECHNICAL SESSIONS PRESENTED BY THE TMS ALUMINUM COMMITTEE AT THE 127TH ANNUAL MEETING, SAN ANTONIO, TEXAS, FEBRUARY 15-19, 1998. EDITED BY BARRY J. WELCH. APPEARING ON PAGES 277-285.

Perfluorocarbon (PFC) Generation at Primary Aluminum Smelters

Bernard P. Leber, Jr., Kaiser Aluminum, Alton T. Tabereaux, Reynolds Metal Company, Jerry Marks, Alcoa, Alcoa Technical Center, Brian Lamb, Washington State University, Touche Howard and Ravi Kantamaneni, Indaco Air Quality Services, Inc., Michael Gibbs and Vikram Bakshi, ICF Incorporated, Eric Jay Dolin, U.S. EPA, Atmospheric Pollution Prevention Division

Abstract

The primary aluminum industry is continually working to improve production efficiency and enhance environmental performance. Through a partnership with the U.S. Environmental Protection Agency (EPA) and the U.S. aluminum industry known as the Voluntary Aluminum Industrial Partnership (VAIP) Program, twelve U.S. primary aluminum producers are focusing on reducing perfluorocarbon (PFC) emissions, CF₄ and C₂F₆. PFCs trap heat in the atmosphere, contributing to the greenhouse effect. To better understand PFC emissions and key factors influencing their generation, EPA through the VAIP sponsored a measurement program for PFCs at seven aluminum smelters. The data show a clear trend toward lower PFC emissions with reduced anode effect (AE) frequency and duration. The scatter in the intra-plant and inter-plant data suggests there may be other operational factors affecting emission rates. This paper reviews the data, provides recommendations for improving PFC emissions predictability, and suggests possible means for reducing these emissions.

Introduction

Two perfluorocarbon compounds (PFCs), tetrafluoro-methane (CF₄) and hexafluoroethane (C₂F₆) are formed as intermittent by-products during the occurrence of anode effects in the production of primary aluminum. In addition to generating PFCs, anode effects negatively impact aluminum current efficiency. These PFCs are greenhouse gases, characterized by strong infrared radiation absorption and relative inertness in the atmosphere. The "global warming potential" (GWP) of these compounds, a measure that considers expected atmospheric lifetime and infrared absorbing capacity, is relatively high. One ton of CF₄ and C₂F₆ emissions is equivalent to approximately 6,500 and 9,200 tons respectively of carbon dioxide emissions, when the warming effect is considered over a 100-year period [1]. Annual PFC emissions from U.S. aluminum smelting plants in 1990 were estimated by EPA at 2,700 metric tons, or the equivalent of about 18 million metric tons of carbon dioxide.

To reduce these PFC emissions, the aluminum industry and EPA jointly developed the Voluntary Aluminum Industrial Partnership (VAIP) Program. The VAIP, an element of the U.S. Climate Change Action Plan, set company-specific PFC emission reduction targets and requires periodic reporting of progress achieved toward those emissions reduction goals. To date, 12 of the 13 primary aluminum producers operating in the U.S. have joined the program. The work reported here was sponsored by the VAIP Program and was conducted with the cooperation and assistance of the Program partners. Technical advice on sampling methods, smelter operations, and other issues was provided through the Aluminum Association's PFC Task Force.

Methods

The objective of this work was to measure PFC emissions from primary aluminum smelters while simultaneously collecting data on smelter operating parameters and characteristics. The data were then analyzed to identify whether smelter

characteristics and operating parameters could be used to predict PFC emissions. This work also contributes to the empirical basis for tracking progress toward reducing emissions under the VAIP Program.

Smelter Characteristics and Operating Parameters

Measurements were conducted at seven smelters in the U.S. Data were collected to characterize the smelters and their operating parameters during the emissions measurements. Smelter personnel provided data on the following smelter characteristics:

- cell technology type: Vertical Stud Soderberg (VSS); Horizontal Stud Soderberg (HSS); or Center-Worked Prebake (CWPB)
- alumina feed type: Bar Feed (BF) or Point Feed (PF)
- cell operating parameters: operating amperage; current density; and metal pad depth
- computer control system information:
 - anode effect (AE) trigger voltage: voltage that defines the start of an AE
 - AE termination voltage: voltage that defines the end of an AE
 - scan rate: the frequency with which the cell voltage is measured
 - voltage averaging period: the period of time used to calculate the average voltage that is compared to the trigger and termination voltages
- smelter configuration, including potroom locations, number of cells in each potroom, and exhaust duct configuration

While reduction cells and control systems are periodically rebuilt and upgraded, these smelter characteristics do not change often and did not change during the period of this study.

Operating parameters, however, vary on a daily basis. Consequently, the following operating parameters were collected and recorded from smelter personnel for the cells measured during the sampling periods:

- number of cells measured
- aluminum production: the average daily production rate for the 30 days prior to the measurements
- AE data: number of AEs; average AE duration; and total AE duration

In most cases, a record of each individual AE was provided by the smelter personnel, indicating the AE start time, stop time, and cell. These data were used to calculate the necessary AE summary statistics. When a detailed record was not available, summary statistics were provided. AE voltage data for individual cells were not typically recorded and hence were not included in this study.

PFC Measurements

PFC emissions were measured from the exhaust ducts that remove gases from the cells as well as from the potroom roofs. At most smelters, the exhaust ducts from individual cells combine into large exhaust ducts that typically run the length of the potroom. The large ducts are typically several meters in diameter and can be many hundreds of meters long. Large fans draw the exhaust through the ducts and move the exhaust gases to treatment systems that remove various constituents.

In addition to the emissions in the exhaust duct collection system, a potroom also has fugitive emissions as the cell hooding efficiency and operating conditions of the collection system result in less than 100% capture from the cell. The fugitive emissions are transported out the roof by convection or in the case of a potroom equipped with a secondary control system that employs roof scrubbers, a powered ventilation fan. Two of the plants in this study (Northwest and Goldenale) are equipped with roof scrubbers.

Sampling Strategy for Main Ducts. The primary method used to measure PFC emissions from the main exhaust ducts was the tracer ratio method, as follows:

- An inert tracer (sulfur hexafluoride, SF₆) is released into the upstream end of the exhaust duct at a known rate.

- At a downstream exhaust duct location a time integrated sample is taken from the duct.
- PFC and SF₆ concentrations in the sample are measured.
- PFC emissions are calculated using Equation 1:

$$Q_{\text{PFC}} = Q_{\text{tracer}} \times (C_{\text{PFC}} / C_{\text{tracer}}) \quad (1)$$

where: Q_{PFC} is the PFC emissions rate, Q_{tracer} is the known release rate of the tracer, C_{PFC} is the measured PFC concentration, and C_{tracer} is the measured tracer concentration.

This tracer technique works well when the tracer and the PFCs are both well mixed in the exhaust duct. In several cases, the sampling point could not be located adequately downstream from the tracer release point to ensure good mixing. In these cases average exhaust duct flow rate estimates were used to calculate emissions using Equation 2:

$$Q_{\text{PFC}} = F_{\text{Duct}} \times C_{\text{PFC}} \quad (2)$$

where: Q_{PFC} is the PFC emissions rate, F_{Duct} is the estimated flow rate in the duct and C_{PFC} is the measured PFC concentration.

The duct flow rate measurements were provided by smelter personnel. In some cases these flow rates could not be obtained simultaneously with the sampling, adding uncertainty to the method. Emissions measurements were developed using both equations 1 and 2 for all the smelters except for one at which adequate tracer mixing was not achieved.

To implement this duct sampling approach, locations for the tracer release and exhaust duct sampling were selected at each smelter in conjunction with smelter personnel. The criteria for selecting these locations included:

- One or more potrooms or potlines operating under typical conditions were identified.
- The access to downstream sampling ports in the exhaust ducts was reviewed. Because the sampling equipment is relatively small, rooftop locations were considered acceptable. Access to 110 volt power was also required.
- Access to upstream release ports in the exhaust ducts was reviewed.
- Locations were selected that provided for the opportunity to measure entire potrooms or potlines with an expectation of adequate mixing in the exhaust duct prior to the sampling point.

The locations varied at each smelter depending on site-specific conditions. Once the sampling and tracer release locations were identified, the following activities were performed.

Pure SF₆ was released from a gas cylinder through a pressure regulator, a stainless steel capillary restrictor, and a calibrated rotameter into stainless steel or Teflon release tubing which was inserted into a small port in the duct. Tracer release rates were measured using calibrated rotameters approximately three times a day. Ambient temperatures were measured with a calibrated glass thermometer and ambient pressures were obtained from a digital barometer several times during each 24 hour release period. Figure 1 shows a schematic of the tracer release system.

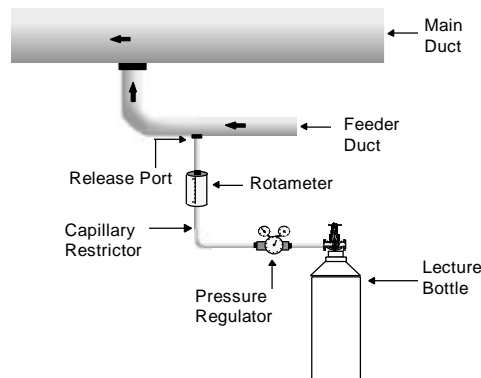


Figure 1: Schematic of Tracer Release System

To collect representative samples of exhaust gas from the duct, a system was developed to collect a “time integrated” sample over approximately a 24 hour period. The time integrated sample represents the average gas composition experienced during the sampling period. A schematic of the sampling system is shown in Figure 2.

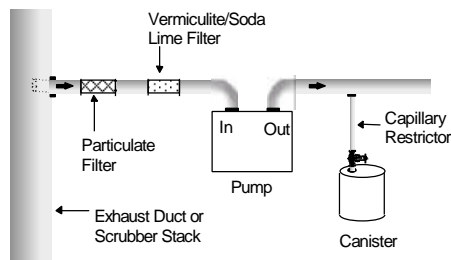


Figure 2: Schematic of Sampling System

As is shown in the figure, a small Teflon/aluminum pump is used to draw air at approximately 1 liter/min from a duct sampling port through a stainless steel sampling line and a filter. Air from the pump exhaust is drawn into an evacuated, stainless steel, SUMMA[®] electropolished sampling canister (6 liter) via a capillary stainless steel restrictor. The restrictor is sized to fill the canister to approximately 0.5 atm. during a 24 hr period. The restrictor behaves as a critical orifice so that the sample intake rate remains constant during the sampling period. A Nupro[®] 7 micron particulate filter and a vermiculite and soda lime filter are placed between the duct and the sampling pump to remove particulates, water, and hydrogen fluoride from the sample stream. Canister pressures are recorded periodically during each sampling period. Following sampling, the canister was pressurized using ultra-pure nitrogen, and the dilution pressure was measured. The canisters were returned to the laboratory for analysis.

As discussed above, the tracer ratio method requires good mixing of the tracer in the duct. To examine the adequacy of mixing, a sampling traverse was conducted across the duct. Using a second pump and sampling line at the sampling location, the sampling line was inserted several set distances into the duct. After several minutes of pumping from the set location in the duct, a syringe was used to draw a sample from the pump exhaust.

To verify the performance of the can sampling, additional syringe samples were taken from the pump exhaust line to which the capillary restrictor and canister were attached. The syringes were returned to the laboratory for analysis.

Sampling Strategy for Potroom Roofs. Because of the need to routinely measure roof emissions from a potroom, the facilities involved in this study have installed either an EPA Method 14 (40 CFR Part 60, Appendix A, Method 14) multi-port manifold collection system in the potroom roof or have adapted this method to their particular physical configuration to acquire a representative roof sample. The sampling strategy for a potroom roof relied on the existing methodologies for determining roof exhaust volumes. The use of a tracer was ruled out due to the inability to release a tracer gas uniformly down the length of a potroom and have adequate mixing within the potroom.

At locations where the existing roof sampling practice utilizes an EPA Method 14 methodology, samples were obtained from the monitoring system's manifold duct. For locations not fitted with an EPA Method 14 sample collection system, the facility's routine compliance sample collection locations were used. The roof samples were taken using the same approach as described above for the duct sampling.

CF₄ and C₂F₆ Analysis. Canister samples were analyzed for the PFCs using gas chromatography/mass spectrometry (HP5890/HP7191A). The gas chromatograph was fitted with a 6 port gas sampling valve with a 0.1 cm³ sampling loop and a stainless steel (1/8" x 12 ft) Alumina 5A 80/100 mesh column. Ultrapure helium was used as the carrier gas. The column temperature was initially held at -50°C for five minutes and then increased by 60°C per minute to a final temperature of 200°C, at which it was held for 20 minutes.

Calibration standards were obtained from the National Institute of Standards (NIST). Because of the late delivery of the NIST standards, interim standards were prepared by static dilution at Indaco. After the NIST standards arrived, the as-

signed concentrations of the interim standards were revised using the NIST standards. The interim standards were used for the analysis of samples from the first three smelters (Kaiser-Mead, Kaiser-Tacoma, and Columbia Falls). The NIST standards were used directly for all other analyses.

A limited number of analyses of roof samples were performed using Fourier Transform Infrared Spectrometry (FTIR). The measurements were made using a BOMEM Model B-104 FTIR unit equipped with a 10 m path length gas cell. Spectra were collected at 1 cm⁻¹ resolution using a liquid nitrogen cooled MCT detector. After collecting 128 scans the data were analyzed against NIST reference standards.

SF₆ Analysis. Both canister and syringe samples were analyzed for SF₆ using electron capture gas chromatography (HP5880). The gas chromatograph (GC) was fitted with a 6 port gas sampling valve with a 1 cm³ sampling loop and a stainless steel (1/8" x 8 ft) Molecular Sieve 5A 80/100 mesh column. Pre-purified nitrogen was used as the carrier gas. The instrument was calibrated using a series of SF₆/air standards (Scott-Marrin, Inc., ± 5% certified accuracy). Typical levels of reproducibility were less than ± 5% and usually within ± 2%.

Results

Site specific information and data were collected for parameters related to the design characteristics of cells, computer control systems, operational data related to anode effects and PFC emissions prevailing during the sampling. The results of this data collection effort are presented below.

Smelter Characteristics

Characteristics of the various cell technologies were recorded for the seven smelters that were measured. As shown in Table I, the smelters represent three technology-types: Center-Worked Prebake, Horizontal Stud Soderberg (HSS), and Vertical Stud Soderberg (VSS). These smelters have of a total of 3,757 cells. Kaiser-Tacoma, a smelter with HSS technology, has potlines with two different cell sizes. The information for each of the lines is reported. As shown in the exhibit, some of the characteristics that vary among the smelters include: operating amperage; scan rate; voltage averaging period; and metal pad depth. In particular, while three smelters have fast scan rates (0.1 seconds) and 6 second voltage averaging periods, four smelters have relatively slow scan rates (1.3 to 30 seconds) and use instantaneous voltage readings to detect AEs. These differences in the computer control systems could affect comparability of the AE frequency and duration data.

Table I. Summary Smelter Characteristics

Smelter	Technology & Feed Strategy ¹	Oper Amp (kA)	# of Cells	Scan Rate (sec)	Volt Ave Period (sec) ⁴	AE Trigger (Volts)	AE End (Volts)	Current Density (amps/cm ²)	Metal Pad Depth (inches)	
									Pre-Tap	Post-Tap
Kaiser-Mead	CWPB – BF	68	1,135	0.1	6	12V	9V	1.13	4	2.5
Kaiser-Tacoma	HSS	57, 83 ²	400	0.1 ³	6	9V	7.5V, 8V	0.95, 0.92	10	8.5
Columbia Falls	VSS	105	600	30	Inst	8V	8V	0.69	19	17.5
Vanalco	CWPB – PF	68	650	1.3	7.8 ⁵	8V	8V	1.00	4	2
Northwest	VSS	108	300	10	Inst	8.5V	8.5V	0.69	15	14
Goldendale	VSS	115	526	4	Inst	9V	6V	0.69	14	12.5
Century	CWPB- BF	92	672	0.1	6	9.5V	8.75V	0.99	4	3
Total			3,757							

1. Technology definitions: VSS = Vertical Stud Soderberg; HSS = Horizontal Stud Soderberg; and CWPB = Center-Worked Prebake. Feed strategy definitions: BF = Bar Feed; PF = Point Feed
2. Lines 1 and 2 operated at 57 kA; Lines 4A and 4B operate at 83 kA.
3. During the measurement period, Lines 1 and 2 had a scan frequency of 4 seconds every 1 minute; Line 4 had a scan frequency of 0.1 seconds.
4. Inst = instantaneous voltage reading is used to compare to the AE trigger and AE end voltages.
5. For an AE to be declared, 6 consecutive scans at 1.3 second intervals have to be greater than 8V; the voltage averaging period is therefore estimated as $6 \times 1.3 = 7.8$

PFC Emissions and AE Data

PFC emissions were measured at a total of 20 different locations at the seven smelters. A location is defined as a set of cells (e.g., a potroom or potline) whose emissions were measured as a group from a single duct. Typically, each location was measured for one or two consecutive 24 hour periods, with each 24 hour period being defined as a location-day.

A total of 32 location-day measurements across the seven smelters are reported here, see Table II. These measurements cover 2,617 cells, or about 70 percent of the total cells at the seven smelters.

Table II. Emissions and AE Data by Location-Day¹

Smelter	# Loc Days	AE Mins /Cell-Day	CF ₄	C ₂ F ₆
			Kg/mt Al	Kg/mt Al
Mead (PB)	6	1.42	0.14 - 0.25	0.03 - 0.06
Tacoma (HSS)	4	2.82	0.08 - 0.16	0.01 - 0.02
Columbia Falls (VSS)	5	9.78	0.53 - 0.70	0.02 - 0.03
Vanalco (PB)	6	2.97	0.10 - 0.28	0.02 - 0.04
Northwest (VSS)	2	5.37	0.36 - 0.44	0.03 - 0.03
Goldendale (VSS)	2	2.54	0.28 - 0.38	0.02 - 0.03
Century (PB)	7	1.26	0.10 - 0.24	0.01 - 0.03

1. The emissions data represent the range of observed location-day values for exhaust duct emissions only. The AE data are averages for the location days measured.

For the three prebake smelters, the measured emissions rates from the exhaust ducts range from 0.1 to 0.28 kg CF₄ per metric ton of aluminum produced. The emissions from the three VSS smelters ranged from 0.28 to 0.7 kg CF₄ per metric ton of aluminum produced. The emissions rate for the one HSS smelter was similar to the range for the prebakes, at 0.08 to 0.16 kg CF₄ per metric ton of aluminum produced. As discussed below, these emissions rates appear to be correlated with the number of AE minutes measured simultaneously at the smelters.

In addition to these duct emissions samples, a total of 12 samples were taken from the rooftop sampling system to measure fugitive emissions. CF₄ was detected in only one of the 12 samples, and C₂F₆ was detected in only 4 of the 12 samples. The measured concentrations were extremely low and close to the detection limit of the analytical method. Consequently, fugitive emissions rates could not be estimated reliably from these samples.

Discussion

Following the data collection and sample analyses, a critique of the various methodologies used and the reasonableness of the sampling data collected based upon process knowledge was performed.

Adequacy of Methods

Overall, the methods used to measure the PFC emissions from the ducts proved to be suitable. However, measurements made on samples collected from rooftops over the same period as the duct samples proved unreliable in estimating the amount of PFC emissions not captured in the exhaust duct. The sensitivity of the analytical method was thought to be the major factor generating this unreliability.

The tracer ratio method was found to be workable in most circumstances. Sampling traverses within the ducts demonstrated good SF₆ mixing in nearly all cases. At the Kaiser-Tacoma smelter, the syringe samples indicated inadequate tracer mixing, and consequently only the emissions estimates from equation 2 are reported. At the Goldendale smelter, an SF₆ concentration gradient was found within the duct, indicating incomplete mixing. This gradient was used to develop an average SF₆ concentration for use in equation 1.

The tracer concentration data were used to estimate duct flow rates, which were compared to the pitot tube-measured rates reported by the smelters. As shown in Figure 3, the measured and reported duct flow rates compared reasonably well. Considering that the pitot tube measurements were not conducted simultaneously with the tracer releases, the agreement in the independent estimates is encouraging.

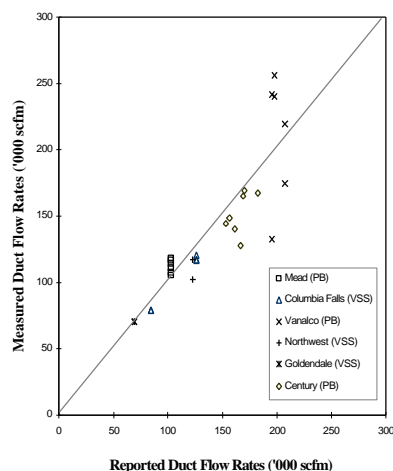


Figure 3: Measured and Reported Duct Flow Rates

The initial laboratory analyses of CF₄ and C₂F₆ were complicated by the late arrival of the NIST standards. Interim standards were used for measurements at Kaiser-Mead, Kaiser-Tacoma, and Columbia Falls.

The CF₄ concentrations in the canisters collected from the exhaust ducts ranged from 30 to 3,200 ppbv. These concentrations were well within the detectable range of the laboratory equipment, and reproducibility of ± 60 ppbv was easily achievable for individual samples. The concentration of C₂F₆ ranged from 4 to 150 ppbv in the canisters, which at the low end approaches the detectable limits of the equipment resulting in more variability in these data. Preliminary attempts at cryogenic concentration did not reduce variability. The reproducibility of the C₂F₆ analysis was on the order of ± 4 ppbv. For both CF₄ and C₂F₆, the measured concentrations at the low end of the observed range are very uncertain because the values are similar to the level of reproducibility of the analytical method itself.

PFCs from the rooftop samples could not be detected due to the concentrations falling below the detectable limit of the analytical method. Additional sampling of fugitive emissions was subsequently conducted at Columbia Falls, Northwest, and Goldendale to test the feasibility of using a more sensitive analytical method, Fourier Transform Infrared Spectrome-

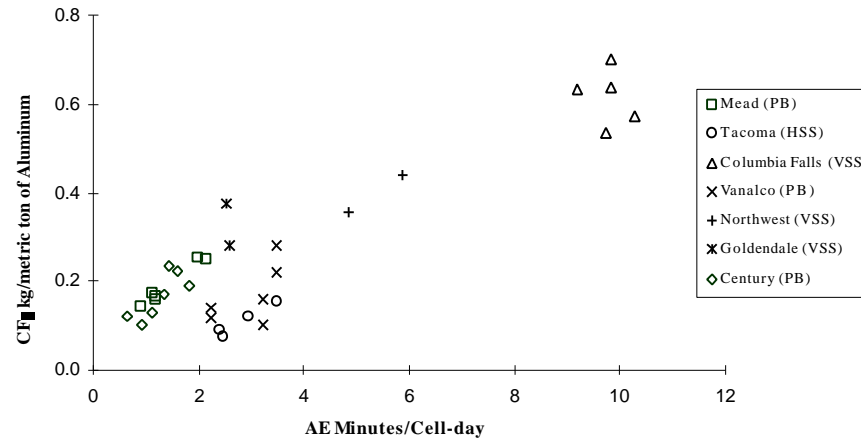


Figure 4: CF₄ Emissions Per Metric Ton Versus Total AE Minutes/Cell-Day (Exhaust Duct Emissions Only)

try. This testing, which included 52 rooftop samples, produced results showing that fugitive emissions from these three VSS smelters are on the order of 10 to 33 percent of emissions from the exhaust ducts. These emissions rates are consistent with expectations for VSS smelters which briefly open cells to atmosphere to terminate a portion of the AEs. Fugitive emission rates for prebake cells are not expected to exceed 2 to 5 percent of the emissions in the exhaust duct because of the relatively high efficiency of the fume collection system.

PFC Emissions and Operating Parameters

Previous studies have indicated that PFC emissions are associated with the occurrence of AEs, and that emissions do not occur when cells are operating at normal voltage levels [2]. Our measurements confirm that emissions roughly track the AE minutes that are observed. Figure 4 shows that CF₄ emissions per ton of aluminum increase with AE minutes per cell-day. Note that the prebake smelters are toward the left side of the graph (fewer AE minutes per cell-day and lower emissions per ton) and the points to the right are two of the three VSS smelters. The overall trend of increasing emissions with increasing AE minutes is seen within smelter types as well as across types. Around this general relationship there is considerable scatter, however.

Figure 4 shows only the emissions measured in the exhaust ducts, and does not include fugitive emissions. Because fugitive emissions are expected to be a higher portion of total emissions at VSS smelters, the apparent slope of the curve in the exhibit may be biased downward because the VSS data points (toward the right side of the graph) should be higher. Also adding to the uncertainty in this graph is that the smelters use slightly different algorithms to determine the beginning and ending of an AE (see Table I). Consequently, the reported AE data may not be comparable across smelters in all cases.

PFC Emissions and Smelter Characteristics

The measured emissions rates were compared to the smelter characteristics listed in Table I to identify potential driving factors that may influence emissions rates. As shown in the table, the VSS smelters have lower current densities and deeper metal pads as compared with prebakes. The HSS smelter falls between these two groups. All the smelters have similar AE trigger voltages and termination voltages, although there are significant differences in the scan rates and voltage averaging periods, which again tend to fall along the lines of prebakes versus VSS smelters.

Due to the similar groupings of characteristics by smelter technology (prebake versus VSS), the potential impact of each of the characteristics on emissions rates cannot be evaluated. For example, the potential importance of pad depth in determining emissions rates cannot be assessed because all the prebake smelters have about the same pad depth and only the VSS smelters have significantly larger values. Whether pad depth is an important factor, or whether other characteristics similarly grouped by technology are important, cannot be determined.

Table III. Comparison with Previous Measurements (Exhaust Duct Emissions Only)

Smelter	AE/Cell Day	Avg Dur. (min)	AEmin/Cell-day	Kg CF ₄ /mt Al	Kg C ₂ F ₆ /mt Al	CF ₄ /C ₂ F ₆ Ratio	Kg CF ₄ /mt Al) AEmin/Cell-day
<i>Prebake Cells</i>							
Kaiser-Mead	0.73	1.95	1.42	0.19	0.045	4.3	0.134
Vanalco	1.14	2.61	2.97	0.17	0.028	6.0	0.057
Century	0.74	1.70	1.26	0.17	0.019	8.7	0.132
Hydro1 ¹	0.13	3.77	0.49	0.06	NA	-	0.122
Alcan1 ²	1.48	2.64	3.90	0.54	0.053	10.2	0.138
Alcan2 ²	0.42	1.17	0.49	0.08	0.009	8.9	0.163
Alcoa ³	1.44	1.18	1.70	0.20	0.020	10.0	0.118
Average:	0.87	2.01	1.75	0.20	0.029	8.0	0.124
<i>Soderberg Cells</i>							
Kaiser-Tacoma	0.77	3.68	2.82	0.11	0.01	8.0	0.040
Columbia Falls	3.43	2.86	9.78	0.62	0.03	21.2	0.063
Northwest	1.92	2.80	5.37	0.40	0.03	12.9	0.074
Goldendale	1.24	2.05	2.54	0.33	0.02	14.8	0.129
Hydro2 ¹	2.40	4.00	9.60	0.80	NA	-	0.083
Average:	1.95	3.08	6.02	0.45	0.02	14.22	0.078

1. Berge, et.al. [3]
2. Kimmerle, et.al. [4]
3. Roberts, et.al. [5]
4. NA = Not available

Comparison With Previous Measurements

Table III lists the emissions measurements from this study along with recently-published emissions data from other prebake and Soderberg smelters. As shown in the table, the data from this study and the previously published data fall in the same range for AE frequency and duration as well as PFC emissions. Additionally, the emissions per ton of aluminum produced appear to generally increase along with AE minutes per cell day. As shown in Figure 5, the emissions rate generally increases with total AE duration, although there is considerable scatter. As shown in Table III, the ratio of CF₄ to C₂F₆ emissions is lower for prebake smelters as compared with Soderberg smelters.

Using the data presented in Table III, a simple linear relationship between CF₄ emissions per metric ton of aluminum and AE minutes per cell-day can be examined as follows:

$$\left(\frac{\text{Kg CF}_4}{\text{metric ton Al}} \right) = S * \left(\frac{\text{anode effect (min)}}{\text{cell day}} \right) \quad (3)$$

where S is the estimated slope of the relationship. As shown in the table, there is good agreement in the estimated slope for the majority of the prebake smelters. The reasons for the deviations at the Vanalco and Alcan2 smelters have not been determined. The smelters with Soderberg cells also show general agreement.

Conclusions and Recommendations

This study demonstrated the ability to measure PFC emissions from aluminum smelter exhaust ducts using a time-integrated sampling technique. The methodology proved suitable for measuring emissions from large groups of cells operating under normal conditions. The GC/Mass Spec analysis method used here was not adequate for measuring fugitive emissions from smelter rooftops due to inadequate analytical sensitivity. Initial analyses indicate that PFC concentrations in fugitive emissions samples can be measured using FTIR techniques.

The measurement results both across smelters and within smelters support the hypothesis that reducing AE minutes will reduce PFC emissions. This conclusion is also supported by the combined data set that encompasses previously published emissions data. The large variability in emissions across smelters may indicate that consideration of additional process parameters may be needed to better predict emissions from operating parameters and smelter characteristics. However, the smelter characteristics examined in this study (other than cell technology and AE minutes) did not help explain the variation in the observed emissions rates. This result is due in part to the fact that as a group the prebake smelters have similar characteristics, as do the Soderberg smelters. Consequently, the impact of the individual characteristics, such as metal pad depth or current density, on emissions rates cannot be determined from the available data. Cell technology (prebake versus Soderberg) and AE minutes per cell-day are the two characteristics found in this study to correlate with emissions rates per ton of aluminum produced.

It is recommended that repeat measurements be taken at smelters following the implementation of steps to reduce AE minutes to confirm the emissions reductions achieved and to improve the ability to predict emissions reductions from changes in operating practices.

Acknowledgments

The authors wish to express their appreciation to Lisa Williams of the Aluminum Association who assisted in the coordination of many of the activities undertaken as part of this work, and in particular the PFC Task Force activities. Additionally, the authors would like to thank the members of the PFC Task Force and the smelter representatives for their valuable assistance and advice. Although the research described in this paper was funded in part by the Environmental Protection Agency contract 68-D4-0088 to ICF Incorporated, it has not been subject to the Agency's review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

References

1. U.S. Department of State, "Climate Action Report: Submission of the United States to the Framework Convention on

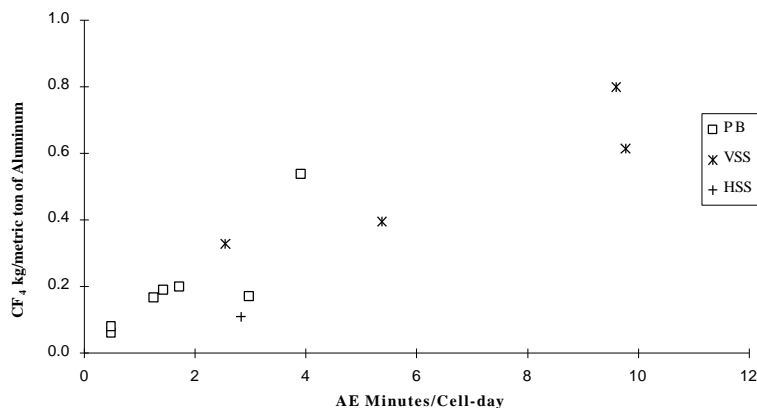


Figure 5. CF₄ Emissions Versus AE Minutes per Cell-Day (Data from Table III)

Climate Change." Washington D.C.: U.S. Government Printing Office, July 1997.

2. A. Tabareaux, "Anode Effects, PFCs, Global Warming, and the Aluminum Industry." Journal of Metals, November 1994

3. L. Berge et al., "Measurement and Characterization of Fluorocarbon Emissions from Alumina Reduction Cells." Light Metals 1994, 389-392

4. F. Kimmerle and G. Potvin, "Measured Versus Calculated Reduction of the PFC Emissions from Prebaked Heroult Hall Cells." Light Metals 1997, 165-171

5. R. A. Roberts and P.J. Ramsey, "Evaluation of Fluorocarbon Emissions from the Aluminum Smelting Process." Light Metals 1994, 381-388