Perfluorocarbon (PFC) Generation during Primary Aluminum Production

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Abstract

The primary aluminum industry is continually working to improve production efficiency, reduce energy consumption, and enhance environmental performance. As part of EPA's Voluntary Aluminum Industrial Partnership (VAIP) Program, eleven U.S. primary producers are focusing on reducing the duration and frequency of anode effects (AEs), which reduce production efficiency and generate two perfluorocarbons (PFCs), CF_4 and C_2F_6. PFCs effectively trap heat in the atmosphere, contributing to the greenhouse effect. To better understand PFC emissions and key factors influencing their generation, VAIP has sponsored two PFC measurement programs. The results of the first round of measurements were reported at the 1998 TMS meeting in San Antonio and appeared in Light Metals 1998, pp 277-285. This paper reports on the second, data-intensive program, which was conducted in 1999 at six primary production facilities. At each facility, PFCs were measured from the potroom exhaust ducts using continuous mass spectrometry. Fugitive emissions were sampled from roof exhausts and measured by FTIR spectrometry. Emissions were related to facility operational parameters such as AE frequency, AE duration, and AE over-voltage. The real-time measurement capability of the mass spectrometer provides the ability to generate highly time- resolved emissions profiles of individual anode effects. This information gives new insights into the factors influencing emissions, in addition to estimating overall facility emissions. Several facilities provided data on the voltage profiles of individual anode effects, which has shown correlation to emissions in both bench-scale laboratory studies at MIT and other measurements. The paper reviews the data, provides recommendations for improving PFC emissions predictability and suggests possible means for reducing these emissions.

Introduction

The production of primary aluminum by the Hall-Heroult process periodically produces small amounts of perfluorinated carbon compounds (PFCs). It has been well established that the compounds produced are tetrafluoromethane, CF_4, and hexafluoroethane, C_2F_6. Past work has established that these compounds are produced during an upset condition known as anode effect, a condition that occurs when the alumina dissolved in the cryolite melt falls to a concentration too low to support the current flow at the nominal voltage for aluminum production. During these periods, which typically occur from 0.03 percent to 0.5 percent of the total electrolysis time, the voltage rises to a level where reactions are initiated that produce the PFCs [1,2,3]. The PFCs are produced at a rate that is dependent on current, voltage, and other factors that are less well understood.

The increased awareness of the potential for enhancing global warming from production of industrial greenhouse gases, and the drafting of the Kyoto Protocol, have increased interest in understanding the production of PFC gases from aluminum production. A fundamental laboratory-based study has produced new understanding of the basic electrochemistry; however, how these results scale to production electrolysis cells remains uncertain [2,4]. For commercial cells there is interest in establishing emission factors for various production technologies, so that current emission levels can be inventoried and compared with emissions as far back as 1990 based on correlation with documented operating data.

This study was undertaken to better understand how emission factors for CF_4 and C_2F_6 vary with reduction technology, what fraction of the overall PFC emissions is emitted as fugitive emissions, and how emission rate is affected by cell voltage during AE. Another objective was to compare the effectiveness of equations based on cell over-voltage [5] with those based on time on anode effect for predicting PFC emissions [6,7,8,11]. The results of measurements at six commercial primary aluminum production facilities are reported here. This work also contributes to the empirical basis for tracking progress toward reducing emissions under the VAIP Program [9].

Experimental

Sampling Locations

At each plant site a group of pots was selected for monitoring based on all the pots exhausting into a common duct where the gases were well mixed and the total volumetric flow could be determined accurately. The monitored pots also had to be representative of all the pots in the plant with respect to design and operation. Because the goal was to measure concentration profiles of as many individually identifiable anode effects as possible, an effort was made to isolate pot groups large enough to produce many non-concurrent anode effects, but not so large as to cause extreme dilution of the PFC's generated in a single anode effect. The pot groups at the various plants that met all of the selection criteria varied in size from 5 pots to 66 pots. The times, durations, and any available voltage data for anode effects on the selected pots were compiled by each plant's operating personnel.

Sulfur hexafluoride, SF_6, was used as a tracer gas, for flow monitoring and for quality assurance procedures. It was infused by mass flow controller into the duct system at some point well upstream from the sampling location.

Fugitive emissions were sampled as time-averaged bag samples from existing EPA Method 14 manifolds where available, or from the outlets of roof wet scrubbers. The sampling locations for fugitives were selected to correspond as closely as possible with the locations of the pots being continuously monitored for primary emissions. Ambient background PFC levels were also sampled as time-averaged bag samples at ground level outside the monitoring location. The bag samples were sent to Alcoa Technical Center for analysis by long-path FTIR, which has a lower limit of detection than the mass spectrometer.

Monitoring System

The monitoring instrument used was a Questor III™ quadrupole process mass spectrometer manufactured by Extrel Corporation (now ABB Extrel) of Pittsburgh, Pennsylvania. The same instrument was described in a 1994 report by Alcoa on PFC monitoring [10]. The 6-component analysis used in this study included CF_4, C_2F_6, SF_6, Ar, O_2 and N_2; it was repeated every 6 seconds. The limit of detection was approximately 50 ppb CF_4.

Calibration gases were purchased from Scott Specialty Gases, and were cross-calibrated with standards certified by the U.S. National Institute of Science and Technology.

Sampling Procedures

A sampling and analytical protocol was developed and field-tested for this program. It specifies sampling configuration, sample validation, and quality assurance procedures.

For real time monitoring, gas was drawn continuously from the duct through a transfer line to the instrument site by an air eductor. Sample was drawn from the transfer line and delivered to the mass spectrometer using a small diaphragm pump.

Design and operating information specific to each site were supplied by location personnel, both as overall operating data that allowed the study data to be scaled to the entire plant, and as anode effect related data during the study period for the cells being monitored.

Facility Characteristics

Characteristics of the various cell technologies were recorded for the six production facilities that were measured. As shown in Table I, these facilities represent four technology types: Center-Worked Prebake (CWPB), Side-Worked Prebake (SWPB), Horizontal Stud Soderberg (HSS), and Vertical Stud Soderberg (VSS). The facility with HSS technology has potlines with two different cell sizes; information for each of the lines is reported. As shown in the table, some of the characteristics that vary among the facilities include operating amperage and production per cell-day. One SWPB, one HSS, one VSS and three CWPB facilities were measured.

One of the CWPB facilities had been recently converted from side-worked, manual feed to center-worked, point feed technology, allowing for analysis of the impact of point feeding on PFC emission rates. Of the other two CWPB facilities, one had 1960's technology with an operating amperage of 68 kA, while the other was a modern, high amperage facility which began production in the early 1990's.

Table I. Summary Production Facility Characteristics

Facility	Technology Type	Operating Amperage (kA)	Total Number of Cells	Production (m tons/cell-day)
A	VSS	105	600	0.78
B	SWPB	140	720	1.06
C	HSS	57, 83[2]	400	0.63
D	CWPB	68	640	0.51
E	CWPB[3]	145	480	1.09
F	CWPB	322	263	2.47

1. Technology definitions: VSS = Vertical Stud Soderberg; HSS = Horizontal Stud Soderberg; SWPB = Side-Worked Prebake; and CWPB = Center-Worked Prebake.

2. Lines 1 and 2 operated at 57 kA; Line 4 operates at 83 kA. Measurements were conducted on Line 4.

3. This facility had been recently converted from side-worked, manual feed to center-worked, point feed technology.

Results and Discussion

Emissions Results

PFC emissions were measured from the exhaust ducts and rooftop sampling system at five of the six facilities. (At the 6th facility roofline optical HF monitors indicated an emissions capture efficiency >95%; therefore the fugitive PFC emissions were deemed to be negligible, and were not sampled.) PFC emission rates were estimated by multiplying PFC concentrations by measured flow rates.

Maximum PFC concentrations measured in the exhaust ducts were 870 ppm and 137 ppm for CF_4 and C_2F_6, respectively. The maximum concentrations correspond with the occurrence of AEs.

Previous studies have indicated that PFC emissions are associated solely with the occurrence of AEs, and emissions do not occur when cells are operating at normal voltage levels [2,10]. At three prebake plants (B, D, and E), CF_4 concentrations of 0.1 to 0.3 ppm CF_4 were observed during periods of normal operation with no AE activity. These excursions above background levels were not an artifact of the sampling system, as tracer pulses injected into the study pots cleared almost immediately when the injection was stopped in all cases. Nor were there observable backgrounds of the PFCs in the mass spectrometer itself. The conclusion is that these non-AE emissions are real, and do contribute slightly to the overall PFC emission rate. At facility E, these PFC excursions were detected during pot start-up conditions. It is unclear exactly what caused the PFC excursions at the other plants. Further investigation is needed to determine their cause(s).

Table II summarizes the measurements at the six plants. Exhaust duct emissions, normalized by aluminum production vary from 0.007 kg CF_4 and 0.0005 kg C_2F_6 per metric ton aluminum to a high of 1.50 kg CF_4 and 0.40 kg C_2F_6 per metric ton aluminum.

The duct emissions from the SWPB and converted former SWPB plants were 1.18 and 0.44 kg CF_4 per metric ton of aluminum produced, with the lower emissions rate at the facility with the point feed system. The emission rates appear to be correlated with AE minutes per cell-day, which were measured simultaneously at the facilities.

Fugitive emission rates were estimated by multiplying the roof outflow rates by measured concentrations in bag samples. For each facility, the estimated fugitive emissions rate was used along with the duct emissions rate to estimate the apparent duct PFC capture rate. The apparent duct PFC capture rate represents the portion of PFC emissions from the potroom that is captured by the exhaust system; the remaining portion is assumed to be fugitive. The apparent duct PFC capture rate ranges from 91 to 98 percent. The lowest duct capture rates were estimated for the SWPB and HSS plants. The results in Table II show that the fraction of gases lost from the collection duct system as fugitives does vary by technology type. It has been hypothesized that variability in fugitive emission fraction might account for a large part of the difference in emissions among reduction technologies. The current data do not support this notion.

Table II. Summary of Measurement Results

Facility (Tech-Type)	# Cell-Days	AE-Mins/ Cell-Day or mV/Cell-Day	Emissions (kg/mt Al)[1]		Duct Capture Rate[2]
			CF_4	C_2F_6	
A (VSS)	20	12.6	1.50	0.06	95-98%
B (SWPB)	88	4.5	1.18	0.40	91%
C (HSS)	15	2.2	0.17	0.02	92%
D (CWPB)	21	1.4	0.30	0.05	95-98%
E (CWPB)	45	2.7	0.44	0.05	95-98%
F (CWPB)	303	0.69[3]	0.007	0.0005	95-98%

1. Exhaust duct emissions only
2. Duct Capture Rate = 100 [Duct Rate ÷ (Fugitive Rate + Duct Rate)]
3. Overvoltage (mV/cell-day) measured at facility F.

PFC Emissions and AE Duration

Previous studies have indicated that PFC emissions are associated with the occurrence of AEs, and that emissions increase with increased time on anode effect [1,6]. Figure 1 plots CF_4 emissions, normalized by amperage, against AE duration for resolved AEs at each facility except facility F, where overvoltage data was provided rather than duration. Resolved AEs are defined as non-overlapping AEs, which are separated from prior and subsequent AEs by at least 3 minutes. Identifying resolved AEs allows estimation of emission rates for specific AEs.

Figure 1 shows that emissions generally increase with AE duration. The possible exception is facility C, where no clear relationship emerges due to the relatively few data points and significant scatter in estimated emissions. The shorting behavior of Soderberg cells has been suggested as a likely explanation of the higher scatter of those cells [12]. Note that the Soderberg facilities have longer AEs than prebake facilities. The overall trend of increasing emissions with increasing AE duration is seen within smelter types as well as across types. Around this general relationship there is considerable scatter, however. Also of note is that a number of data outliers emerge; further investigation into pot conditions during these AEs is required.

Figure 1 shows only the emissions measured in the exhaust ducts, and does not include fugitive emissions. For plants where fugitive emissions are expected to be a higher portion of total emissions, the apparent trends of the data in the figure may be biased somewhat low. Also adding to the uncertainty in these graphs is the fact that the smelters use slightly different algorithms to determine the beginning and ending of an AE. Consequently, the reported AE data may not be exactly comparable across smelters in all cases.

Figure 1: CF_4 Emissions (kg/kA) versus AE Duration (Exhaust Duct Emissions Only)
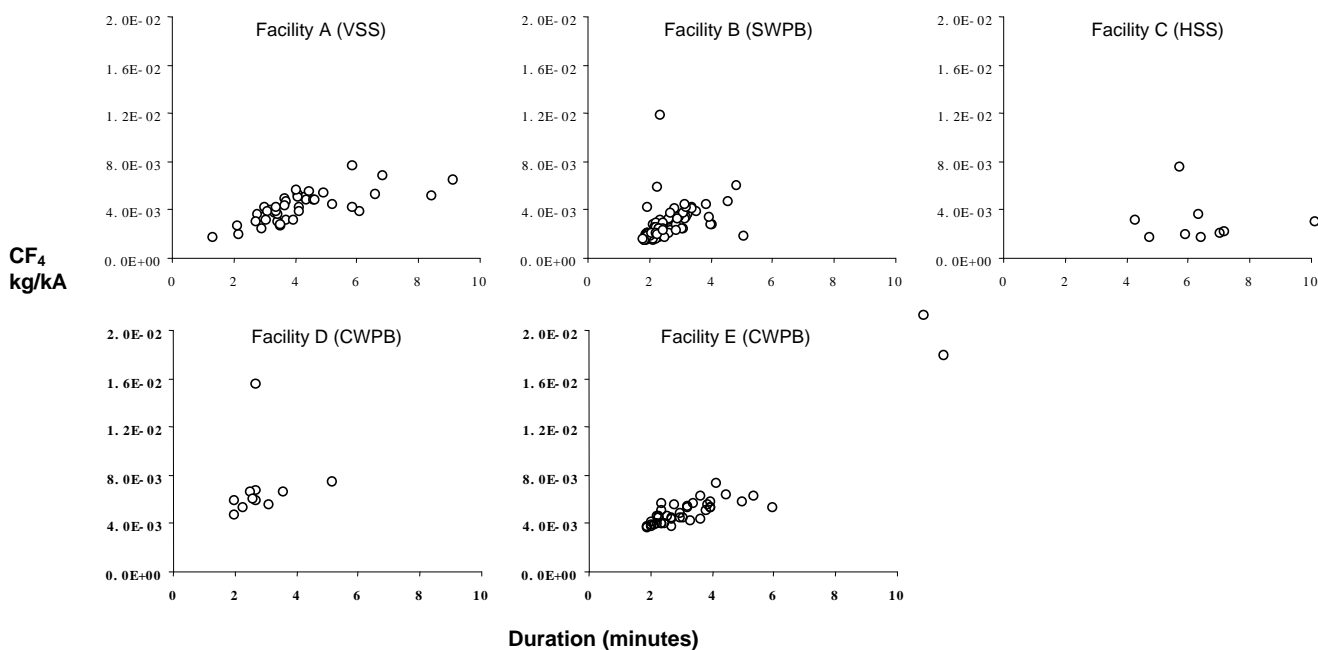
PFC Emissions and Voltage

When aluminum reduction cells are on anode effect the voltage rises rapidly to levels of 20 to 40 volts or higher. Thermodynamics suggests a higher PFC emission rate with increasing voltage and laboratory scale studies have confirmed increased emissions with higher voltage [2]. At facility B, cell voltage readings were available at five second intervals allowing the observation of PFC emissions and voltage fluctuations simultaneously. The effect of voltage variation at anode effect is illustrated in Figure 2. The plot shows a strong correlation of increases and decreases in emission rate of both CF_4 and C_2F_6 with corresponding increases and decreases in voltage.

In this particular anode effect it is noted that the rate of increase in PFC emission for both CF_4 and C_2F_6 with increases in voltage is not as intense as the anode effect duration increases. One explanation that has been offered is that some form of passive layer may be formed on the surface of the anode leading to decreases in PFC generation [13]. Careful additional analysis of emission rate versus voltage for more anode effects appears to offer the opportunity for considerable additional understanding of the dynamics of PFC emissions in industrial cells.

The correlation of overvoltage has been proposed as a method to predict aluminum-specific PFC emission rate [5]. Three prebake plants (B, E, and F) provided data on integrated over-voltage (excess cell voltage attributed to anode effects) which could be used for correlation with estimated emissions rates. The plot of CF_4 in kg versus over-voltage shown in Figure 3 suggests a linear relationship between emissions and over-voltage. Note, the slope for the converted former SWPB facility is lower than the slope for the non-point-fed SWPB.

Figure 2. Effect of Cell Voltage on PFC Emissions
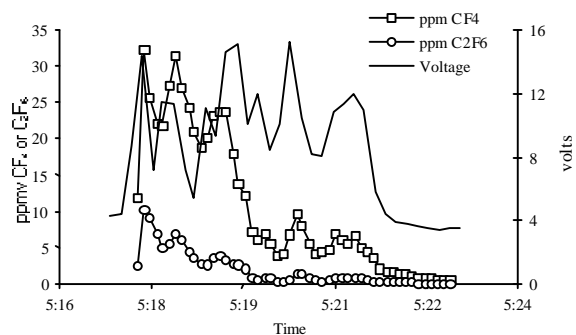
Analysis of emissions versus AE duration and over-voltage for resolved AEs indicates that over-voltage does not appear to be a better predictor of emissions than AE minutes. The standard error for the emissions estimates normalized by over-voltage is similar to standard error of the emissions estimates normalized by AE minutes, indicating that over-voltage does not explain more of the variation in measured emission rates than does time on anode effect.

Relationship of C_2F_6 Emissions to CF_4 Emissions

It has been hypothesized that the relationship between C_2F_6 and CF_4 emissions changes with time on anode effect. Figure 4 plots the mass ratio of C_2F_6 to CF_4 for an individual anode effect (the same anode effect shown in Figure 2). Figure 4 illustrates that the ratio of C_2F_6 generation to CF_4 generation is not constant throughout the duration of the anode effect. The illustration shows that the ratio is highest at the beginning of the anode effect, and decreases as the anode effect time increases.

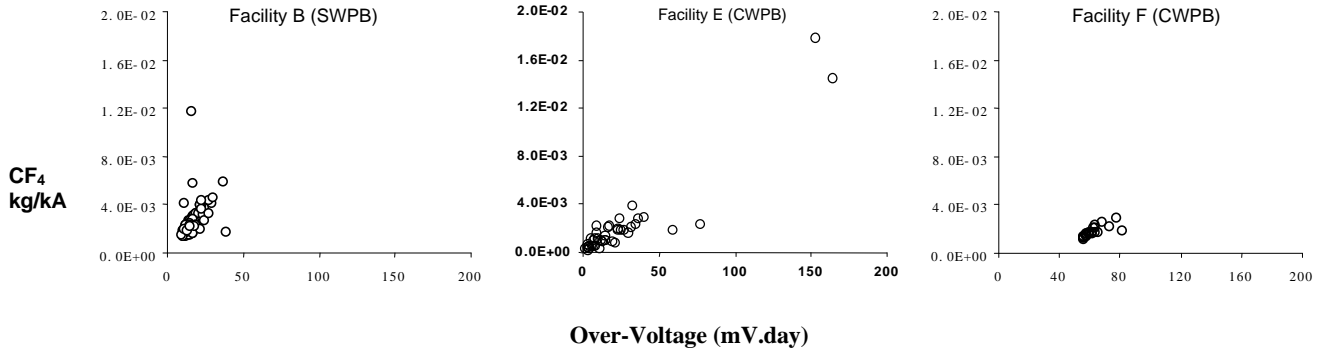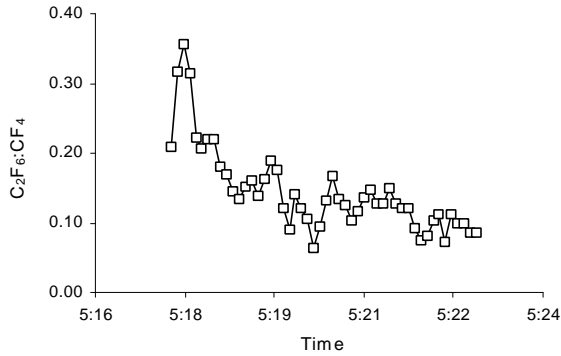Figure 3: CF$_4$ Emissions versus Integrated Over-Voltage (Exhaust Duct Emissions Only)

Over-Voltage (mV.day)

Figure 4: C$_2$F$_6$:CF$_4$ versus AE Duration (Sample AE)

This same trend of C$_2$F$_6$ concentration decreasing more rapidly with time on anode effect than CF$_4$ is illustrated in Figure 5 for all the measurement sites (except facility F where AE duration data were not available). Also shown in the figure is the observation that the C$_2$F$_6$:CF$_4$ ratio is lower for Soderberg cells than for prebake cells. For Soderberg cells, the ratio of C$_2$F$_6$:CF$_4$ ranges from 0.05 to about 0.15, compared to 0.1 to 0.5 for prebake cells.

Figure 5: C$_2$F$_6$:CF$_4$ versus AE Duration
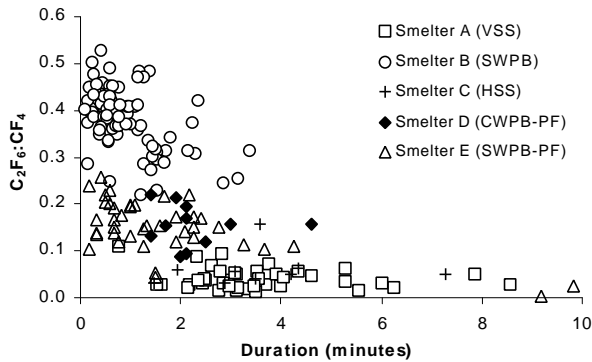
Comparison with IPCC Slope Coefficients

IPCC guidelines for inventorying PFC gases from primary aluminum production recommend multiplying the anode effect minutes per cell day by a slope factor to obtain kg PFC per unit of aluminum production [8]. Alternatively, where over-voltage data is collected, the ratio of over-voltage to current efficiency for aluminum production is multiplied by a slope factor. The current work offered the opportunity to check the effectiveness of the methodology in predicting individual facility emissions. Slope factors from the current work are shown in Table III.

As shown in Table III, the emission factors for CWPB and for SWPB agree fairly well with suggested IPCC values for CF$_4$ emissions, with the exception of smelter D. There were substantial differences found for calculated emission factors for both CF$_4$ and C$_2$F$_6$ for VSS and HSS technologies. This data suggests that additional careful measurements are needed to better define emission factors for Soderberg facilities.

Table III. Slope Factors Calculated from Current Measurements[1]

Facility Technology-Type	CF$_4$		C$_2$F$_6$	
	IPCC Values[2]	This work	IPCC Values	This work
A (VSS)	0.07	0.12	0.003	0.005
B (SWPB)	0.29	0.29	0.029	0.098
C (HSS)	0.18	0.09	0.018	0.011
D (CWPB)	0.14	0.22	0.018	0.036
E (CWPB)	0.14	0.16	0.018	0.017
F (CWPB)	1.9	0.98	NA[3]	0.069

1. For all facilities except F, the slope factor is reported for AE minutes/cell-day; for facility F, the slope factor is reported for overvoltage.

2. *Source*: [12]

3. To be published by the IPCC.

Conclusions

PFC emissions were measured in near real-time at six primary aluminum production facilities. The facilities included a VSS, a HSS, a SWPB and three CWPB facilities. The objective of this

work was to measure PFC emissions from primary aluminum production facilities 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.

Measured aluminum-specific emission rates varied by about a factor of two hundred from the newest CWPB technology to the older VSS technology. The contribution of fugitive emissions at the sites measured, while significant at two locations was not enough to account for major differences in emission rates among different technologies.

It appears that, contrary to previous evidence, low-level PFC emissions may be produced without a defined anode effect occurring. The cause of these emissions has not been identified.

The measurement results, both across smelters and within smelters, support the hypothesis that reducing AE minutes will reduce PFC emissions. The variability in emissions across smelters may indicate that consideration of additional process parameters may be needed to better predict emissions from operating parameters and facility characteristics. AE minutes per cell-day and over-voltage are the two process parameters found in this study to correlate with emission rates.

A linear relationship of PFC emissions with anode effect minutes per cell day or anode effect over-voltage reported in previous work was confirmed in this study. Analysis of the data indicate that over-voltage does not appear to be any more robust a predictor of emissions than AE minutes.

Reduction in either anode effect frequency or average anode effect duration will reduce PFC emissions. Examination of profiles of individual anode effects shows that reducing the frequency of anode effects should be more effective than reducing the duration, since the emission rate for both CF_4 and C_2F_6 is highest at the start of the anode effect.

The effect of variations in anode effect voltage on rate of PFC emissions first suggested in laboratory scale studies was confirmed in commercial electrolysis cells. Two effects of AE duration were seen. First, the broad trend of decreasing emission rate with increasing time on anode effect for extended duration anode effects was shown. Secondly, the more rapid decrease in C_2F_6 emissions with time on anode effects relative to CF_4 emissions was noted for individual anode effects.

Measurements at one SWPB facility and one converted formerly SWPB facility showed that the conversion to point feed achieved a double benefit with respect to PFC emission reduction. First, the anode effect frequency and duration were decreased. Second, the change to point feeders lowered the slope factor relating PFC emissions per unit of aluminum produced to AE-min/cell-day by about a factor of two.

Emission factors for CWPB and for SWPB agreed fairly well with suggested IPCC values for CF_4 emissions. There were substantial differences found for calculated emission factors for both CF_4 and C_2F_6 for VSS and HSS technologies. This data suggests that additional careful measurements are needed to better define emission factors for Soderberg facilities.

This study demonstrated the ability to measure PFC emissions from exhaust ducts using a continuous real-time sampling technique and from the roof using time-integrated bag samples. The real-time sampling and analysis provided detailed time profiles of emissions for individual AEs.

A measurement protocol and a spreadsheet-based data analysis tool were developed for this work to minimize sources of potential measurement and data reduction variability. These tools are available to share with those making PFC measurements at aluminum reduction facilities.

Acknowledgments

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