EVALUATION OF FLUOROCARBON EMISSIONS FROM
THE ALUMINUM SMELTING PROCESS

Ruth A. Roberts and Phillip J. Ramsey

Alcoa Technical Center
100 Technical Drive
Alcoa Center, Pennsylvania 15069-0001

Abstract

Evolution and emission of carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6) were characterized by continuous on-line monitoring of the common exhaust from 40 pots of a commercial potline, using a process mass spectrometer. The average emission rates from the potline section over 510 pot-days determined by statistical analysis of the data were 0.2 kg CF_4/tonne Al and 0.02 kg C_2F_6/tonne Al. Undiluted anode gas was monitored in a pilot-scale Hall cell, where it was demonstrated that fluorocarbons are not produced during steady-state operation, but only during anode effects. The fate of fluorocarbons in dry scrubbing was investigated in both bench-scale and full-scale dry scrubbers; no change in emission rate due to dry scrubbing was observed.

Introduction

Fluorocarbons, specifically carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6), have been identified as greenhouse gases; that is, as having the chemical capability of blocking some of the earth's radiant cooling, and thus contributing to global warming. These gases are broken down very slowly, if at all, by chemical reactions in the atmosphere; their lifetimes are estimated to be thousands of years (1). Consequently, the total atmospheric burden of fluorocarbons essentially never decreases; it has been estimated to be increasing by 2% per year (2).

The impact on global climate of atmospheric fluorocarbon concentrations, which are currently estimated to be at parts per trillion levels (2), is small compared to more abundant greenhouse gases such as carbon dioxide; and it will remain so for hundreds of years at present rates of accrual. Nevertheless, it is generally agreed that the incremental annual increase in fluorocarbon levels is due in large part to emissions from aluminum smelting. This raises the question of whether the continuous increase in fluorocarbon concentration is avoidable, and places much of the responsibility for avoidance on the aluminum industry.

Fluorocarbons are evolved primarily during anode effects, and then only in such small quantities that they are very difficult to detect once the anode gas has been diluted by the hooding air. As a result, very little quantitative information has been available on the actual evolution rates of CF_4 and C_2F_6 from industrial cells.

In 1991 renewed worldwide concern about greenhouse gases focused attention on fluorocarbon emissions from aluminum smelting, and a detailed evaluation of the evolution and fate of these compounds was undertaken. The study had three objectives:

1. Determine if there is an unavoidable background production of fluorocarbons during normal operation, or if it is possible to operate without evolving these compounds except during anode effects; i.e., determine if fluorocarbon production could be eliminated by eliminating anode effects.

2. Determine if there is any capture or conversion of fluorocarbons in fluidized alumina dry scrubbers.

3. Measure the overall average emission rates of CF_4 and C_2F_6 from a typical point fed, pre-bake potline.

A three-phase program was carried out to address these objectives:

1. Continuous composition measurements were made both in the anode gas under a working anode in a 24 ka pilot Hall cell to monitor the evolution of gaseous species during normal operation and during anode effects.

2. Bench-scale experiments contacting a mixture of 50 ppm CF_4 and 50 ppm C_2F_6 with a fluidized bed of metal grade alumina simulating a dry scrubber were carried out. Temperatures of 100 and 300°C, and gas stream moisture contents of 0 and 5% were employed, covering the full range of conditions that might be encountered in dry scrubbing operations.

3. A sampling program involving 40 pots in a pre-bake potline was carried out. Both the combined exhaust from the 40 pots and the outlet of one of the dry scrubbers that treat the exhaust gas were monitored for portions of 18 days in November and December of 1991, representing a total of 720 pot-days of operation. The hours of data actually collected summed to 12.75 days or 510 pot-days.

Experimental

Monitoring Instrument

The instrument employed in all phases of the present investigation was a process mass spectrometer, the Questor model made by Extrel Corporation of Pittsburgh, Pennsylvania. This instrument is designed to be a continuous process monitor. It has two detectors which are switched automatically to provide the appropriate sensitivity. With the Faraday detector it can detect concentrations from 100 ppm to 100%, while with the electron multiplier detector it is capable of detecting concentrations from parts per billion to over 100 parts per million. The mass range scanned by the analyzer is 2 to 200 atomic mass units. In the single ion monitoring mode, the analyzer software continuously corrects the intensity of each analyte for interferences due to fragments of other components. The 11-component analysis used in this investigation could be repeated as frequently as every 8 seconds.

Calibration Gases

Calibration gases were purchased from Scott Specialty Gases or Alphagaz, with the exception of SO_2, which was generated from a Metronics permeation tube and oven.

Pilot Cell Studies

A 24,000 amp pilot-scale Hall cell with four full-sized anodes operated at the Alcoa Technical Center provided the opportunity to monitor pure anode gas, without dilution by hooding air.

Test anodes were prepared by drilling holes through them from top to bottom, then sealing a pipe nipple into the top of each hole. The pipe nipple was connected through a series of reducers to a length of stainless steel tubing, which was in turn connected to a heated Teflon sample line for transport to the mass spectrometer. An air eductor was used to draw the gas through the sample line.

Monitoring the anode gas, with a detection limit of 0.1 ppm, provided a very sensitive test for background CF_4 evolution; that is, CF_4 evolution occurring during normal or non-anode effect operation. The electron multiplier detector was used during normal operation because of its greater sensitivity; however, it had to be switched off as soon as an anode effect started to avoid destroying the detector.

Figure 1 shows the CF_4 and C_2F_6 evolution in the anode gas from the 24 ka pilot cell during 3.5 hours of tracking to an anode effect. There is a slight baseline offset of the CF_4 calibration, but the evolution of both fluorocarbons was less than 0.1 ppm, i.e., undetectable until the anode effect occurred. Figure 2 shows the same data plotted on the expanded scale needed to illustrate the anode effect. The anode effect drove the CF_4 concentration to almost 4000 ppm before the electron multiplier could be switched off to protect it from overload.

Bench-Scale Experiments

According to thermodynamic equilibrium predictions (3), CF_4 and C_2F_6 should react with either alumina or water to produce AlF_3 or HF and CO or CO_2. If these reactions occurred at
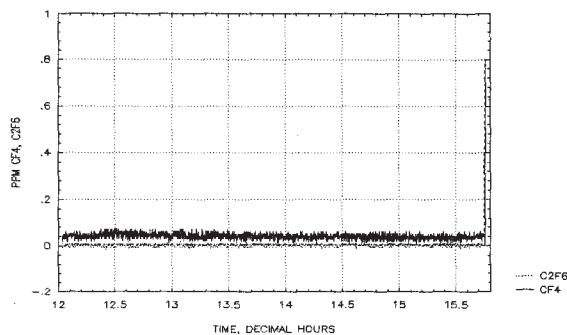

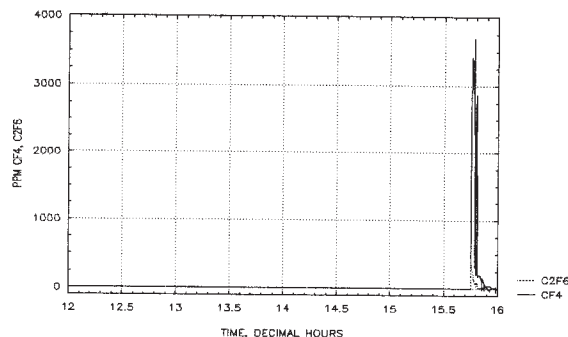Figure 1: Fluorocarbon evolution from pilot cell anode gas, 0-1 ppm scale.

Figure 2: Fluorocarbon evolution from pilot cell anode gas, 0-4000 ppm scale.

reactor temperatures, however, the fluorocarbons would be converted in dry scrubbers and would not be accumulating in the atmosphere.

In order to determine if these reactions occur to any extent at all in dry scrubbers, a mixture of CF_4 and C_2F_6 was passed through a bed of 10 grams of alumina contained in a stainless steel reactor 2.9 cm in diameter, which was heated in a laboratory furnace.

Calibration gases containing 100 ppm CF_4 in air and 100 ppm C_2F_6 in N_2, respectively, were metered with mass flow controllers to provide equal flows of the two gases, then mixed to reduce the concentration of each to 50 ppm. The mixture was passed through a preheating coil surrounding the reactor in the furnace, and then through the alumina bed. The gas was delivered at a velocity that produced full fluidization at room temperature, so the alumina is believed to have been fluidized at the reactor temperatures.

The gas mixture was sampled with the mass spectrometer before and after passing through the reactor to detect any change in concentration of either of the fluorocarbons. After the dry gas stream was tested, the mixed gases were routed through a vaporizing coil in an oven, into which water was being metered and vaporized at a rate calculated to yield an absolute humidity equal to 5% of the total gas stream by volume. The line carrying the humidified gas from the oven to the furnace was heated to maintain the stream above its dew point.

The gas stream was passed through the alumina, first dry and then with 5% water vapor, at temperatures of 100° and 300°C.

No change in concentration of either fluorocarbon was detected under any of these conditions, which extend well beyond the operating range of dry scrubbers.

Plant Tests

Sampling Layout at Plant

The sampling layout (Figure 3) included 41 pots exhausting into a common duct, which feeds four dry scrubbers. During the entire test period, one of the pots was out of service, so that 40 pots were actually monitored. Gas was drawn continuously from the duct or a reactor stack and transported across the courtyard, through a potroom and to a temporary building outside the potroom which housed the mass spectrometer. An air eductor was used to move the gas through each transfer line. The transfer lines were unheated, 1.9 cm I.D., semi-rigid PVC tubing.

The final sample was drawn out of the transfer line and into the mass spectrometer inlet by a second eductor. The inlet was connected to the high vacuum chamber by a fused silica capillary, which reduced the pressure of the sample as it passed into the analyzer.

Sampling Efficiency

The sample transfer lines were 1.9 cm I.D and initially of unknown length. Because of the length and volume of the transfer lines with relation to the capacity of the eductors, there was concern that the flow would not be fully turbulent, and that the anode effect peaks would be broadened so that the leading and trailing edges could be diluted beyond the detection limit by diffusion. Therefore, a series of tests of transfer efficiency was carried out.

Transfer Line Transit Time, Volume and Length. Actual transfer line flow was measured with a thermal mass flow meter as 18 SLPM (at 0°C). Argon pulses were injected at known times into the transfer line at the duct wall through a valve teed into the line. The area medians of the resulting argon peaks detected at the mass spectrometer were measured, and the time of arrival of each peak median was determined. These gave median transit times averaging 1.72 minutes. From these data a transfer line length of 108 meters and volume of 31 liters were calculated.

Transfer Line Losses. In each of these tests a 5-liter gas bag was filled with 100 ppm CF_4 calibration standard, then connected to the valve and tee in the transfer line at the duct wall. The valve was opened rapidly, and the bag allowed to exhaust into the gas flowing in the transfer line. The resulting CF_4 peak detected by the mass spectrometer was integrated to give a total volume of CF_4 recovered; this volume was compared against the expected volume of 0.5 cm³. Recovery was 0.67 cm³ CF_4 in the first test; it is believed that the gas bag was over-pressurized. 0.50 cm³ CF_4 was recovered in the second test. In this case the bag was filled, then vented momentarily to atmosphere to equalize pressure. The maximum concentrations in the CF_4 peaks were 12-13 ppm. These tests indicate that there was no detectable loss of CF_4 in the sample transfer system.

Recovery of CF_4 through Hooding and Exhaust System. To check for losses of detectable sample in the total system, pure CF_4 was leaked into Pot #1, the most remote pot from the duct sampling port. The detected concentration was compared with the concentration expected after dilution, and the total amount recovered was compared with the amount injected. The operators placed all the pots on overfeed during this test to avoid interference from anode effects.

The expected concentration at the mass spectrometer, based on total flow in the duct and assuming 95% hooding efficiency, was 5.5 ppm. The maximum peak level detected was 5.8 ppm. The integrated concentrations recovered were 98% of the expected values, assuming 95% hooding efficiency. These tests indicate that recovery of CF_4 through the entire potroom exhaust and the
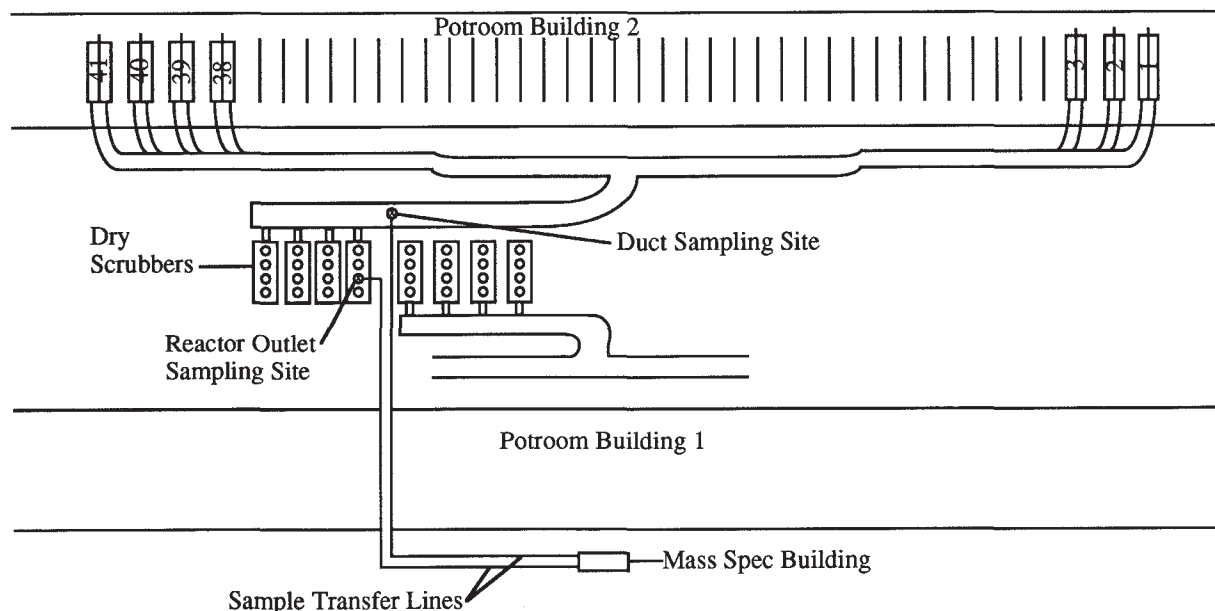

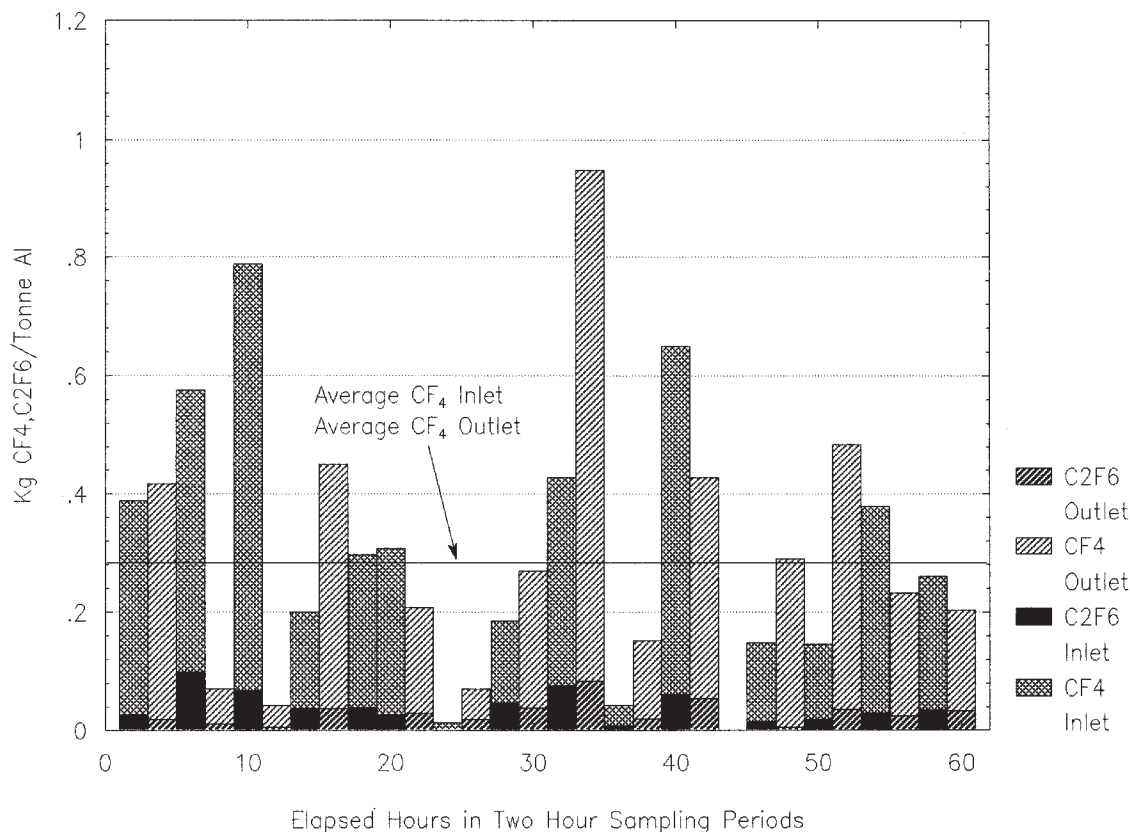Figure 3: Sampling arrangement from commercial potline.

Figure 4: Dry scrubber inlet and outlet data.

sampling system is nearly complete if the hooding efficiency is about 95%.

Limit of Detection. The practical limit of detection of the mass spectrometer is determined by the background noise, and is therefore dependent on the number of scans averaged. The band width of the CF_4 noise with no averaging is 0.15 ppm; averaging 10 scans, it is 0.1 ppm. All of the present investigation was done using no or 10-scan averaging, and 0.15 ppm was used as the integration threshold for CF_4. By the same rationale, C_2F_6 had an integration threshold of 0.05 ppm.

Plant Emission Data

Figure 4 presents the data obtained at the plant by switching between the pot exhaust duct and the dry scrubber outlet every 2 hours for a total of 58 hours. Because the process is so variable, it was impossible to make a direct comparison between inlet and outlet without having two analyzers operating simultaneously. However, the 2-hour emission averages from the outlet showed the same variation and the same range of fluorocarbon content as the 2-hour averages from the duct; and the overall average CF_4 content of each was the same, as shown by the horizontal line. These data confirm the conclusion drawn from the bench-scale reactor that at dry scrubber conditions the fluorocarbons pass through the reactor intact.

Figure 5 shows the hourly mean evolution rates of CF_4 and C_2F_6 during the 306 hours (510 pot days) in November and December of 1991, when sampling was conducted. The hour-to-hour and

day-to-day variability in evolution is evident. The ranges of the hourly emission rates were:

* 0.001-1.2 kg CF_4/tonne Al and
* 0.0005-0.1 kg C_2F_6/tonne Al.

Overall average emissions were

* 0.2 kg CF_4/tonne Al (0.4 lb CF_4/ton Al) and
* 0.02 kg C_2F_6/tonne Al (0.04 lb C_2F_6/ton Al).

Figure 6 shows the fluorocarbon concentration peaks corresponding to anode effect events over an 8-hour time period. Table I lists the time above 8 volts for each event, the number of anode effects comprising the event and the total kilograms of each fluorocarbon evolved in each event. Events 3, 5 and 8 are multiple anode effects, while all the other events are recorded in the pot log as single anode effects. The potroom computer logs the time above 8 volts, but not the complete voltage profile for each anode effect. There was no detectable evolution between anode effects in this time period.

Discussion

The first objective of this investigation was to determine if there is an unavoidable continuous low-level production of fluorocarbons from aluminum smelting pots. The evidence from the pilot cell measurements in pure anode gas, as well as from the exhaust gas measurements from the 40 full scale pots, demonstrates that there is not. While investigators using
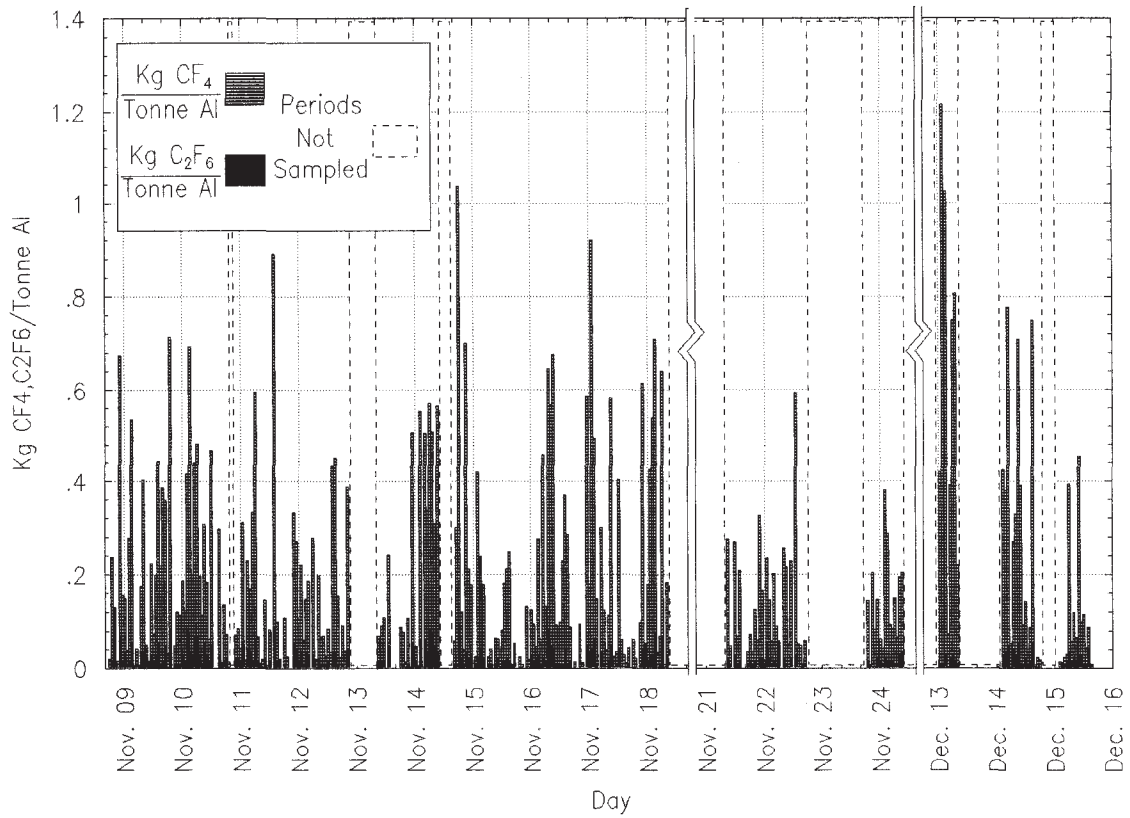
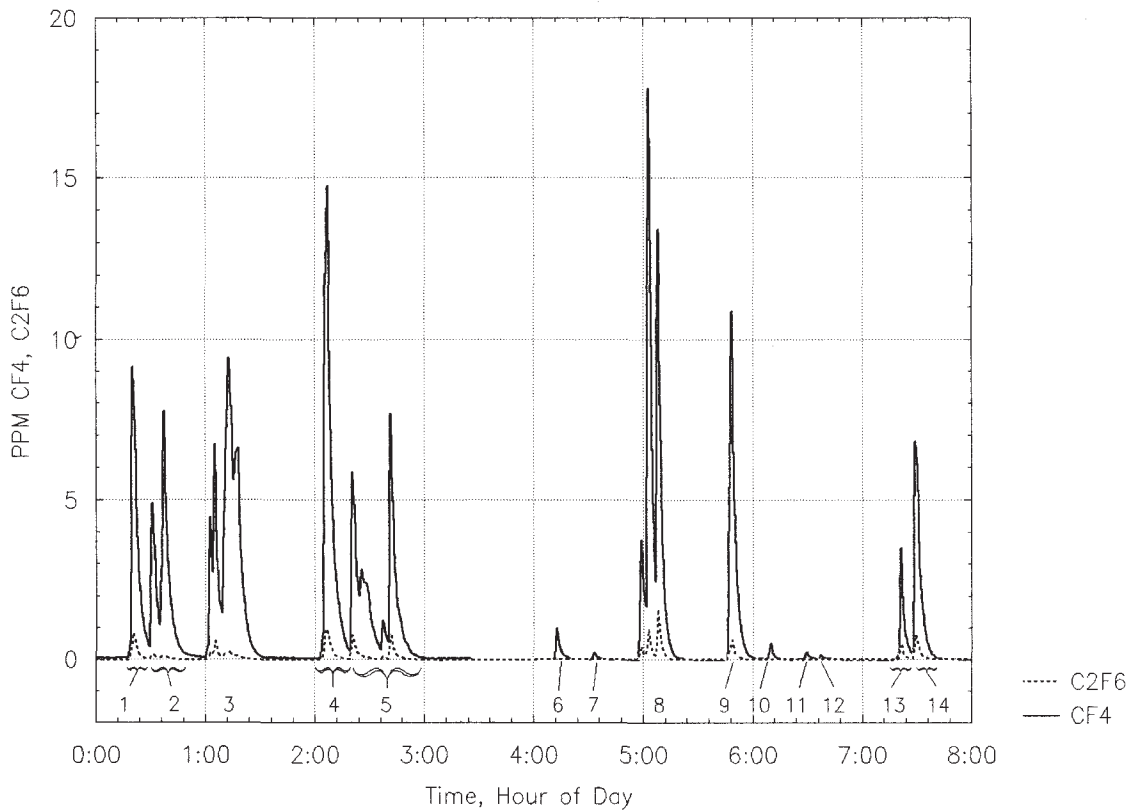Figure 5: CF_4 and C_2F_6 evolution from 40 pots in a commercial smelting plant.

Figure 6: Individual anode effect events.

Table I. Fluorocarbon Evolution During
Individual Anode Effect Events

Event #	Seconds Above 8V	# of Anode Effects	kg CF_4 Evolved	kg C_2F_6 Evolved
1	100	1	0.57	0.07
2	120	1	0.72	0.02
3	440	3	1.65	0.09
4	160	1	1.04	0.09
5	320	5	1.11	0.13
6	20	1	0.04	0.004
7	10	1	0.004	0
8	350	5	1.55	0.18
9	130	1	0.56	0.05
10	10	1	0.01	0
11	20	1	0.004	0
12	10	1	0.004	0
13	40	1	0.14	0.03
14	80	1	0.41	0.06

infrared spectrometers have reported measuring CF_4 at part-per-million levels in both the anode gas (4) and the pot exhaust (5) between anode effects, we have demonstrated that it is not present at our detection limit, 0.1 ppm in either gas stream under steady low voltage conditions. This raises the question of whether there is a major bias in the infrared measurement, or if there have been improvements in pot control that allow steady-state operation below the threshold for CF_4 evolution.

The calculated reversible cell emf's for a series of possible electrochemical reactions in Hall cells are as follows (6):

$$-E^o \text{ at } 967°C$$

$$2/3 \ Al_2O_3 + 2 \ C = 4/3 \ Al + 2 \ CO \qquad 1.07 \ V$$

$$2/3 \ Al_2O_3 + C = 4/3 \ Al + CO_2 \qquad 1.19 \ V$$

$$1/3 \ Al_2O_3 + 2/3 \ Na_3AlF_6 + C = 4/3 \ Al + 2 \ NaF + COF_2 \qquad 1.87 \ V$$

$$4/9 \ Al_2O_3 + 4/9 \ Na_3AlF_6 + 4/3 \ C = 4/3 \ Al + 4/3 \ NaF + 4/3 \ CFO \qquad 2.22 \ V$$

$$4/3 \ Na_3AlF_6 + C = 4/3 \ Al + 4 \ NaF + CF_4 \qquad 2.55 \ V$$

$$4/3 \ Na_3AlF_6 + 4/3 \ C = 4/3 \ Al + 4 \ NaF + 2/3 \ C_2F_6 \qquad 2.77 \ V$$

The cell potential for the formation of CF_4 (2.55 V) is substantially higher than those for CO (1.07 V) and CO_2 (1.19 V); the potential for C_2F_6 is higher still (2.77 V).

These equations provide the thermodynamic basis for a voltage threshold below which one would not expect any fluorocarbon formation; this is in agreement with our experimental results, and supports the hypothesis that fluorocarbon evolution could be avoided entirely by operating the cells in an appropriate voltage range and eliminating anode effects.

A possible problem with that hypothesis is that formation of the compound COF_2 is predicted at a considerably lower potential than CF_4. If unstable, COF_2 could disproportionate to form CF_4:

$$2 \ COF_2 = CO_2 + CF_4$$
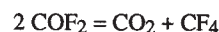
Nordmo and Thonstad (6) have also considered the possible reactions occurring at anode effect, and have analyzed the gaseous products from a closed laboratory cell, as well as anode gas from a full-scale pot. They report that COF_2 was not detected as a product of anode effect.

We incorporated COF_2 into the mass spectrometer analysis of anode gas. As no calibration gases were readily available, we used values from the NIST mass spectral library to simulate calibration. This enabled us to identify any concentrations of COF_2 above an arbitrary background level, but not to quantify them. If COF_2 were formed, it should have been detectable in the anode gas as the cell went on anode effect; however, only slight perturbations in the background were observed, indicating that the reaction forming COF_2, while thermodynamically possible, does not occur to a measurable extent.

The second objective of the present study was to determine the fate of CF_4 and C_2F_6 in dry scrubbers. It has been reported (7) that fluorocarbons are quantitatively decomposed over alumina in the presence of water vapor at 1000 to 1100°C. One purpose of these tests was to find out if such a decomposition might occur to some lesser extent at temperatures and humidities that might be encountered in dry scrubbers. The data from both the bench-scale model experiment and the full-scale reactor tests demonstrate conclusively that there is neither removal nor decomposition of the fluorocarbons at dry scrubber conditions.

The implication of this result is that the most practical way to reduce fluorocarbon emissions is to avoid producing them in the first place. Even if a means of removing them from the exhaust gas could be identified, the cost of adding additional waste gas treatment systems to remove species that are generated in such low concentrations by transient and irregular events would be prohibitive; whereas reducing fluorocarbon emissions by eliminating or limiting anode effects would enhance the productivity of the smelting process.

The third objective was to estimate the total emission rate of fluorocarbons from a typical pre-bake smelter. This program was the first known effort to get enough real-time data to begin to characterize the variability of the phenomenon of anode effects. Forty (40) pots were monitored for nearly 2 weeks out of a 2-month period or over 500 pot-days. The data were collected every 79 seconds, yielding detailed characterization of individual anode effects. Data were logged, transferred and processed electronically, with manual checks on the accuracy of the processing. Enough information was obtained to permit a statistical evaluation of the responses.

Statistical Analysis of Emission Data

The CF_4 and C_2F_6 emission data, expressed as kilograms per tonne of Al, were averaged for each of the 290 hours of the test period. Based on these 290 observations, an attempt was made to determine an appropriate probability distribution to describe

the random behavior of the emissions rates. Figures 7 and 8 are histograms of the observed hourly emission rates for CF$_4$ and C$_2$F$_6$ respectively. Both histograms exhibit significantly skewed behavior which precludes the use of symmetric distributions such as the normal distribution.

The shapes of the histograms in Figures 7 and 8 are consistent with the general shape of the exponential probability density function:

$$f(x) = \lambda e^{-\lambda x}, \text{ for } x \geq 0, \text{ and } 0 \text{ otherwise.}$$

Using the 290 observations, an exponential parameter was estimated for CF$_4$ and for C$_2$F$_6$; the estimates were 5.15 tonne Al/kg and 55.40 tonne Al/kg, respectively. The solid curves overlaid on the histograms in Figures 7 and 8 are exponential probability density functions with the estimated λ parameters; the qualitative assessment of the fit is very good. The following two tables contain the sample estimates of population parameters for an exponential distribution, and also theoretical estimates based upon the assumption of an exponential distribution; the units are kg/tonne Al, except the CV, which is dimensionless.

Table II: Parameter Estimates for CF$_4$

Parameter	Sample Estimate	Theoretical Estimate
Mean	0.1941	0.1941
Standard Deviation	0.2269	0.1941
Median	0.0992	0.1346
Mode	0.0	0.0
CV	1.17	1.0

Table III: Parameter Estimates for C$_2$F$_6$

Parameter	Sample Estimate	Theoretical Estimate
Mean	0.0181	0.0181
Standard Deviation	0.0203	0.0181
Median	0.0108	0.0125
Mode	0.0	0.0
CV	1.12	1.0

A comparison of the sample and hypothesized values from the two tables supports the assumption that an exponential
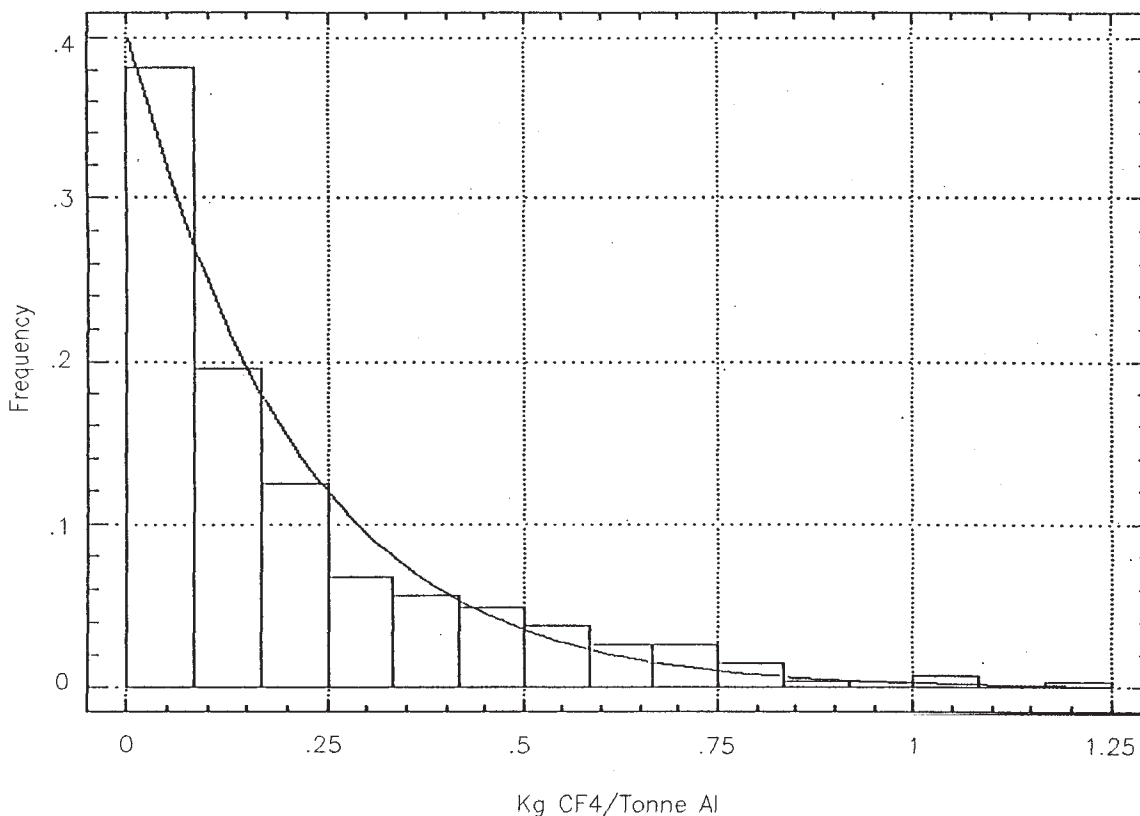

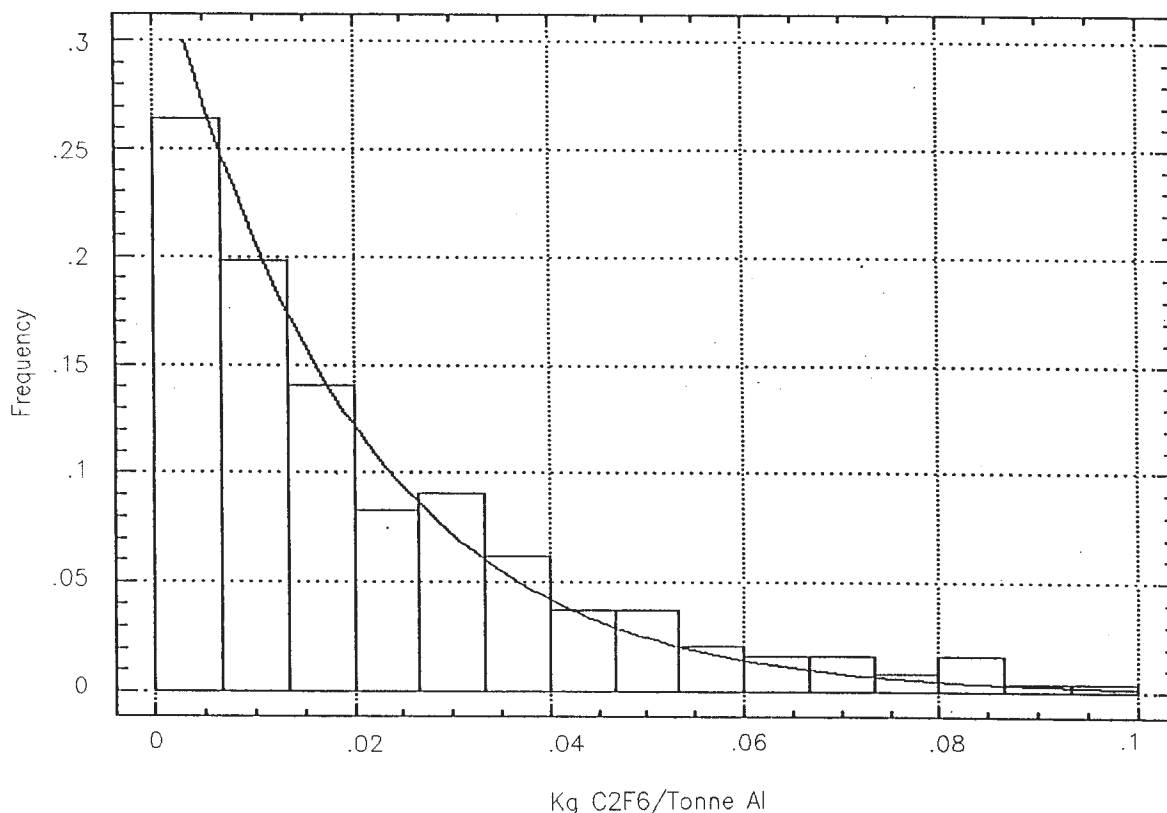Figure 7: Histogram for 290 CF$_4$ observations.

Figure 8: Histogram for 290 C_2F_6 observations.

distribution is a good approximation to the emission data; i.e., there are no significant discrepancies between the sample parameter estimates and the theoretical estimates based upon an exponential distribution.

Conclusion

In addition to a quantitative estimate of fluorocarbon evolution rates, this study has provided an improved understanding of the anode effect phenomenon. Perhaps the most significant thing we have learned, however, is the necessity for real-time data in characterizing a highly variable process. The frequency and duration of anode effects strongly influence the overall specific emission rates of CF_4 and C_2F_6 in aluminum production.

Acknowledgments

The authors would like to acknowledge the technical support of M. Todd Raines, Keith R. McCutcheon and Craig A. Soich in carrying out this study.

References

1. Ciccerone, R. J., "Atmospheric Carbon Tetrafluoride: A Nearly Inert Gas," Science, 206 (1979), 59-60.

2. Khalil, M. A. K. and Rasmussen, R. A., "Atmospheric Carbon Tetrafluoride (CF4): Sources and Trends," Geophysical Research Letters, 12 (1985), 671-672.

3. Cochran, C. N., "Global Warming Emissions in the Production of Aluminum," Alcoa Technical Report, 1990-06-03 (1990).

4. Kozarek, R. L. and Sharkins, A. J., "CF4 Evolution from Badin Hall Cells," Alcoa Internal Report, 1980-06-16 (1980).

5. Eller, M. E., "Measurement of Carbon Tetrafluoride in Pot Off Gas and A-398 Reactor," Alcoa Internal Report 93-84-006 (1984).

6. Nordmo, F. and Thonstad, J., "On the Anode Effect in Cryolite-Alumina Melts IV. Gas Composition and Faradaic Efficiency," Electrochemica Acta, 30 (1985), 741-745.

7. Somiya, Takayuki and Konishi, Yukio, "Carbon Fluorides in the Anode Gas of the Reduction Furnace of Alumina. I," Kogakuin Dagaiku Kenkyu Hokoku, 30 (1971), 72-78.