

The Complexity of PFC Generation in Alumina Reduction Cells

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<https://doi.org/10.71659/icsoba2024-al059>

Abstract

It is well known that off-gases from electrolytic production of aluminium contain perfluorocarbons (PFCs). Several studies have concluded with high emission figures for CF₄ and C₂F₆ during periods of anode effect (AE). Various methods for quantifying emissions have been launched, and the most widely used one today is the IPCC (2006) Tier 2 approach, which relies heavily on developed factors that have their basis in traditional measurements using FT-IR. However, the FT-IR method has limited sensitivity and is not ideal for analysis in potlines with low AE frequency. In the latter, questions have also been asked as to whether PFCs can be formed under operating conditions with no indication of AE. We have therefore extracted gas at the outlet of our stacks and from several electrolysis cells, without any sign of AE, to investigate the composition and level of PFCs in such off gases. The measurements showed surprising results and revealed the presence of several PFCs, and hydrofluorocarbons (HFCs) not reported before in primary aluminium production. In total, nine compounds were identified and quantified by using sophisticated sampling and analysis techniques. Hypothesis about their formation will be presented.

Keywords: Low voltage (LV)-PFC, HFC Formation, Sampling, Medusa-GC-MS.

1. Background

Recently the Norwegian Pollution Authorities challenged Hydro Aluminium to find a method for direct measurement of emitted perfluorinated compounds (PFC) from alumina reduction plants according to the Tier 3 method. As traditional spectroscopic methods have limited sensitivity, a more sensitive method based on a gas chromatograph equipped with a mass selective detector was regarded as a promising technique.

In 2022 Hydro Aluminium and Alcoa Norway contacted a research team at Norwegian Institute for Air Research (NILU) for testing their method for determination of PFCs in stack emissions. NILU has achieved a broad experience related to atmospheric monitoring of trace gases and is a partner of the worldwide Advanced Global Atmospheric Gases Experiment (AGAGE) project [1]. All participating laboratories in the AGAGE network are using instruments sensitive enough for detecting important halogenated gases at global background levels, including tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆).

NILU suggested a stack sampling setup based on a work conducted by CSIRO on Hydro's Kurri Kurri aluminium plant in Australia back in 2013 [2]. Since NILU and CSIRO are partners in the AGAGE program, NILU received all available data from the Kurri Kurri survey. An improved sampling strategy based on evacuated canisters followed by Medusa cryotrapping/cryodistillation

and finally gas analysis by gas chromatography with mass spectrometric detection using selective ion monitoring (GC-MS-SIM) was chosen.

When we received data from the analysis of our stack emission, two new components were added to the list of emitted fluorinated components. We therefore decided to study these findings in depth, and a program for a more detailed analysis of the off gas from stacks and individual electrolysis cell was initiated.

2. Experimental

2.1 Sampling

Sampling was conducted by using a 2 L evacuated stainless steel canister attached to the off-gas line through a stainless-steel sampling probe. The probe was equipped with a 4 cm³ alumina trap for preventing hydrofluoric acid entering the canisters. Smelter grade alumina from Alunorte was used as adsorbent.

The gas sampling period is flexible, but typically 2 h sampling period was used.

2.2 Sample Preparation and Chemical Analysis

2.2.1 Instrumentation

The cryogenic preconcentration gas chromatography-mass spectrometry (GC-MS: Agilent 6890-5973/5975) “Medusa” systems were used to measure PFC mole fractions in sampled emission gases at NILU laboratories, Norway. These instruments are part of the Advanced Global Atmospheric Gases Experiment (AGAGE) network [1].

The instrumentation is shown in figure 1. The GC-MS system represents the lower half of the picture, whilst the upper half represent the Medusa “Head”. The cryogenic unit is shown in the green square.



Figure 1. Medusa instrumentation.

The Medusa system is versatile and can be used in very different modes. This is important when looking for “new” compounds in a range that is covering gases from CF₄ all the way up to C₆F₁₄. In combination with stainless steel canisters, samples taken at stack or cell outflow will contain air for many consecutive analyses runs. Looking for the retention times of specific compounds which are yet not in the compound list, is easy to perform, and with very good sensitivity.

Another advantage with the Medusa system is the fact that other gasses like light hydrocarbons and light aromatics and even some sulfur containing gases can be measured alongside the halogenated compounds. This is an important input when discussing processes at cell level.

2.2.2 Measurement

For each measurement, the condensables in a 2-l air sample are preconcentrated onto a micro-trap and then cryofocused onto a second micro-trap (both micro-traps are initially held at 160 °C and subsequently heated for desorption before injection onto a capillary column. The Medusa permits several stages of analyte purification and refocusing prior to GC-MS analysis.

The quadrupole MS is operated in selective ion mode (SIM). Additionally, only a defined number of species were measured in our experiments, as compared to the more than 50 species typically measured as part of the AGAGE network. Such a setup was chosen to minimize the number of acquired ions and further improve sample precisions.

2.2.3 Quality Control

To have access to the best available standard scale has high priority. Within the AGAGE network, a stock of standard gases is available. The Scripps laboratories at La Jolla, CA, USA is responsible for updating and maintaining their own “Standard Scale” for important halogenated gases in this network. As an additional quality control approach within this project, compounds like trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12) and sulfur hexafluoride are monitored. These compounds are always present in air within a close level to atmospheric background concentrations. They represent gases with high stability even within the harsh conditions present in the individual smelter cells. They represent useful references for correct calculations as well as serving as references for correct dilution of the samples. They are therefore used also as references for other halogenated compounds, which either undergo destruction within the cell or are produced within the cell due to specific reactions.

Differences in concentrations for the components in the analyzed samples between air entering the cell and leaving the cell will give valuable input to understand what processes take place within a cell at different processes conditions. The range of linearity is large from low ppt levels up to high ppb levels. The precision is exceptional, and for most compounds often lower than 2 %.

3. Results

The results from our investigation will be presented in two chapters. One chapter refers to stack investigation and another chapter will focus on cell emission. We will not discuss the emission of “common” PFCs in detail, because Hydro presented stack emission figures from Medusa measurements in 2023 [3].

3.1 Stack Measurements:

A recently published article [4] raises the concerns about potential emission of c-C₄F₈ from the aluminium cells as a source.

We have, for the first time, identified two new components in our stack emission from alumina reduction processes: octafluorocyclobutane (c-C₄F₈) and hexafluorobutane (C₄F₁₀).

The concentration of c-C₄F₈ in 16 stack samples varied between 3.5 ppt and 14 ppt, which is higher than the present atmospheric level of 2.2 ppt. The increasing trend of c-C₄F₈ in the atmosphere is illustrated in Figure 2 and represents data from seven laboratories located at defined sampling stations.

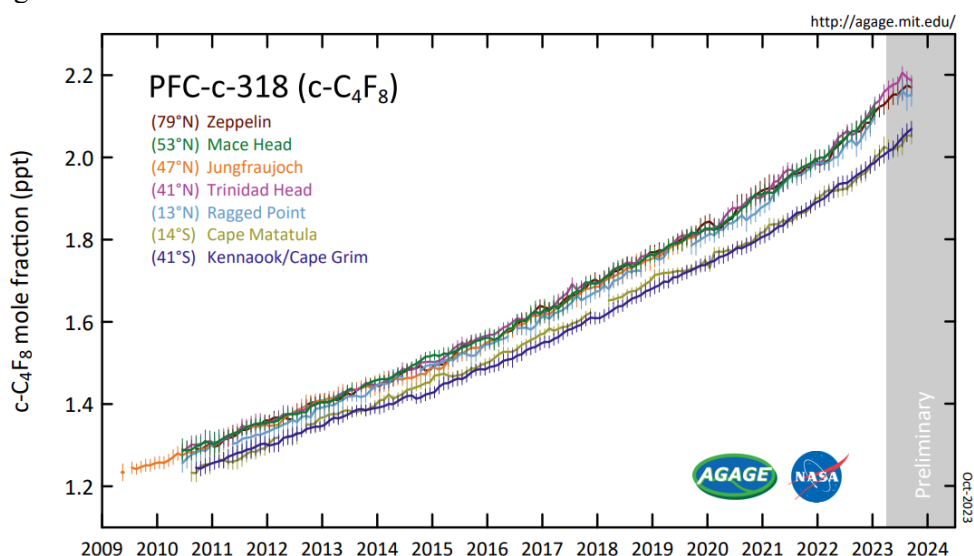


Figure 2. Atmospheric trend of PFC-318.

Another interesting observation has occurred when we interpret the results further. There is good correlation between C₄F₁₀ and C₃F₈ in our stacks measurements. As mentioned above, C₄F₁₀ has never been reported before, but the concentration is much higher than the atmospheric background of 0.22 ppt. Background concentration of C₃F₈ is 0.75 ppt [1]. Attempt to correlate CF₄ and C₂F₆ with either C₃F₈ or C₄F₁₀ was not successful.

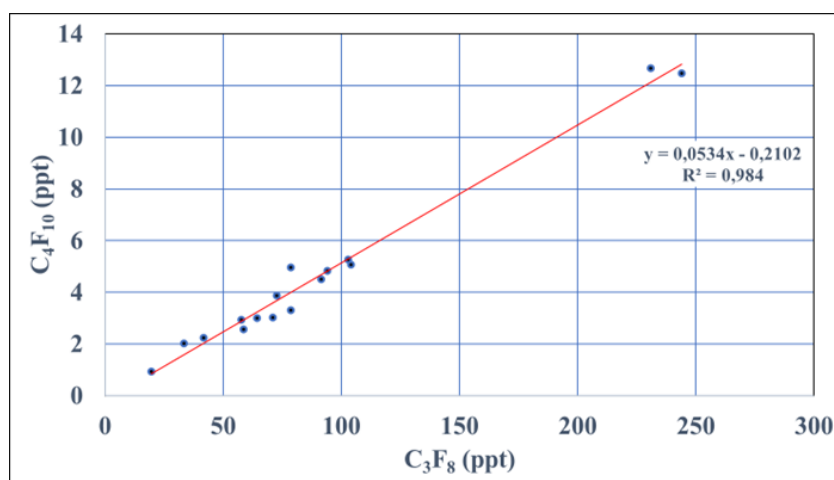


Figure 3. Correlation between C₃F₈ and C₄F₁₀.

3.2 Cell Measurements

A complete list of PFCs and HFCs found in our cell emission off gases is listed in table 1. Note that concentration figures are not included in the list, but details will be presented below. Important data such as Chemical Abstracts numbers and Global Warming Potential (GWP) are included.

To summarize: nine new chemical structures labelled from #4 -#12 can be added to our list of fluorine containing organic gases emitted from the alumina reduction process. Further information of physical and chemical properties of the gases is available in references [5, 6].

Table 1. Identified PFCs and HFCs in emission gas samples.

#	Chemical name	Formula	CAS Number	Synonyms	GWP [9]
1	Tetrafluoromethane	CF ₄	75-73-0	PFC-14	7380
2	Hexafluoroethane	C ₂ F ₆	76-16-4	PFC-116	12 400
3	Octafluoropropane	C ₃ F ₈	76-19-7	PFC-218	9290
4	Decafluorobutane	C ₄ F ₁₀	355-25-9	PFC-31-10	10 000
5	Dodcafluoropentane	C ₅ F ₁₂	678-26-2	PFC-41-12	9220
6	Octafluorocyclobutane	c-C ₄ F ₈	115-25-3	PFC-318	10 200
7	Trifluoromethane	CHF ₃	75-46-7	HFC-23	14 600
8	Pentafluoroethane	C ₂ HF ₅	354-33-6	HFC-125	3750
9	Trifluoroethene	C ₂ HF ₃	359-11-5	HFC-1123	0.005
10	Tetrafluoroethene	C ₂ F ₄	116-14-3	PFC-1114	0.004
11	Hexafluoropropene	C ₃ F ₆	116-15-4	PFC-1216	0.09
12	Octafluorobutene	C ₄ F ₈	357-26-6		0.102

Emission figures of PFCs and HFCs from different cells are given in Table 2 and Table 3. Due to limited data material, correlation as shown above is not obtained from cell off gas, but it is worth mentioning that the C₄F₁₀ concentration from the C098#1 are extremely high and considerably higher than the C₃F₈ concentration. However, we are still working with data interpretation from our analysis of this cell, and exact figures related to concentrations will be published later. It is also important to notice that some cells, with optimum alumina feeding, emit surprisingly low CF₄ concentrations, slightly above the present level in the ambient atmosphere at 89 ppt. Alumina feeding at C098#2 was maintained at a minimum without forcing the cell to enter an anode effect (AE). However, minor local AE was measured, and the concentration of CF₄ is considerably higher from this cell compared with same cell operated with optimal alumina feeding. The concentration of c-C₄F₈ is relatively high in all samples.

Table 2. PFCs from cell emission samples. All concentrations are given in ppt.

Cell I.D.	CF ₄	C ₂ F ₆	C ₃ F ₈	c-C ₄ F ₈
C098#1	649	337	8.5	39695
C098#2	67416	3542	968	1947
C099#1	6389	262	11.1	5468
C099#2	134	40	0	1322
C102 #1	696	24	3.3	2635
C102 #2	122	217	6.2	28441
C103	418	12	2.6	167

It is also important to pay attention to the more detailed and extended investigation of gases collected from C098#1 as shown in Table 3. The concentration of C₄F₁₀ is surprisingly high, and the ratio C₄F₁₀/C₃F₈ differs if we compare with the stack measurements. We have also identified three HFCs in this sample.

Table 3. Results from C098#1, extended analysis.

Chemical	Concentration (ppt)	Relative to atmosphere
CF ₄	649	7.3 x
C ₂ F ₆	337	60 x
C ₃ F ₈	8.5	12 x
C ₄ F ₁₀	1224	5564 x
c-C ₄ F ₈	39695	18043 x
CHF ₃	194	6 x
CH ₂ F ₂	53	1.5 x
C ₂ HF ₅	336	8 x

4. Discussion

Several of the compounds detected in our investigations may originate from a reactive divalent fluorine compound, difluorocarbene (:CF₂). The role of :CF₂ in the synthesis of various organofluoride compounds including C₂F₄ is well studied in the organic fluorine research and details can be found in [7, 8] and references therein. It is not possible to isolate and analyse this compound in our processes since the compound undergo fast transformation to other more stable components. However, it is likely that :CF₂ participate in chemical reactions that lead to many of the components we have isolated and analysed in our off gas. As an example, a simplified reaction pathway for the formation of C₂F₄ and structures derived thereof is given in Figure 4. Note that C₂F₄, C₃F₆ and c-C₄F₈ are drawn in a more detailed manner. It is also important to be aware of the role of the temperature in the gas mixture environment, but this remains to be explored.

more complex. We have presented a list of 9 new components in the off gas from individual cells. Most of them are regarded as gases with a high GWP. Special attention about the formation of $c\text{-C}_4\text{F}_8$ and C_2F_4 is addressed because these are key components in the formation and degradation studies of fluoropolymers.

When considering our findings, all attempts to use factor-based calculation for reporting PFC emission during low voltage conditions are meaningless, because the composition from cells operating at such conditions seems to be dominated by $c\text{-C}_4\text{F}_8$ and not CF_4 .

We are still in an early stage in our research on what is happening inside individual cells. There are still more open questions than answers. And nearly every new sample opens for new findings and more questions arise. We hope that our study may inspire to more research to obtain a better understanding of how PFC and HFC compounds are formed. Such studies must involve teams with a depth knowledge of organic fluorine chemistry in addition to have access to advanced instruments for chemical analysis. Our results are based on a system which makes the advantages of cryogenic pre concentration and distillation of sampled gas followed by gas chromatographic separation of individual gases and finally identified and quantified with mass spectrometry. We also believe that it is possible to simplify the Medusa system and adopt it to the needs of our industry. Such an effort should be addressed in a joint venture program with financial support from the global aluminium industry.

6. References

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