The Complexity of PFC Generation in Alumina Reduction Cells

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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 CF_4 and C_2F_6 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 sophisticate 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 (CF_4) and hexafluoroethane (C_2F_6).

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 cm^3 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.

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-C_4F_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-C_4F_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

1. Advanced Global Atmospheric Gases Experiment AGAGE - Advanced Global Atmospheric Gases Experiment (nasa.gov) https://agage.mit.edu/, (accessed on 14 July 2024).
2. Paul Fraser, Paul Steele and Mark Cooksey, PFC and carbon dioxide emissions from an Australian aluminium smelter using time-integrated stack sampling and GC-MS, GC-FID analysis, *Light Metals* 2013, 871-876.
3. Henrik Åsheim et al., Determination of PFC with Canister Sampling and Medusa GC–MS Analysis in Comparison to General IPCC Estimation Methods, *Light Metals* 2023, 653–661.
4. Jens Mühle et al.: Perfluorocyclobutane (PFC-318, c-C_4F_8) in the global atmosphere, *Atmos. Chem. Phys.*, 19 (15), 2019, 10335–10359. ACP - Perfluorocyclobutane (PFC-318, c-C4F8) in the global atmosphere (copernicus.org)
5. National Institute of Standard and Technology (NIST), U.S Department of Commerce, NIST Chemical Webbook 69, revision 2023.
6. PubChem Open chemistry database at the National Institutes of Health (NIH), USA, 2024.
7. Richard D. Chambers, *Fluorine in Organic Chemistry* 2nd Edition, Wiley Blackwell; CRC Press 2004. ISBN 10-1405107871.
8. Junli Wang et al., Critical Review of Thermal Decomposition of Per- and Polyfluoroalkyl Substances: Mechanisms and Implications for Thermal Treatment Processes, *Environmental Science & Technology* 2022 56 (9), 5355-5370. https://doi.org/10.1021/acs.est.2c02251.
9. IPCC Global Warming Potential Values, https://ghgprotocol.org/sites/default/files/2024-08/Global-Warming-Potential-Values%20%28August%202024%29.pdf (accessed on 30 September 2024).