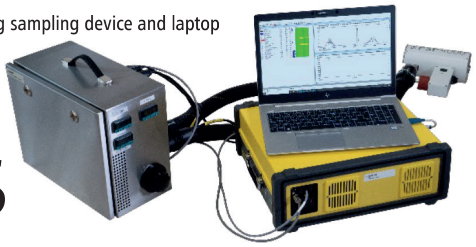

Fig 1. FTIR instrument showing sampling device and laptop

Perfluorocarbon Emissions Measurements by FTIR Spectroscopy

By **Luis Espinoza-Nava***

The aluminium industry is facing a challenge to reduce and/or eliminate its greenhouse gas emissions. The International Aluminium Institute (IAI) started an initiative to encourage its members to track and publicly report the greenhouse gas reduction efforts and progress to address climate change as part of the 2023 United Nations Climate Change Conference, known as COP28. Thirteen major aluminium producers supported the IAI initiative, and they have already published greenhouse gases reduction targets on different sources, which are categorised as scopes by 2030 and some of them want to be net zero emitters by 2050. These greenhouse emissions are either generated directly by aluminium production process (scope 1), generated by electricity purchased (scope 2) or generated by other indirect sources (scope 3).

Perfluorocarbons (PFC) gases that are emitted in aluminium production are mainly Tetrafluoromethane, CF4, and Hexafluoroethane, C2F4. These are potent greenhouse gases, which are linked to global warming due to their ability to efficiently trap infrared radiation. Both gases have long atmospheric lifetimes, estimated at 50,000 and 10,000 years, respectively. The global warming potentials (GWP) of these gases are reported as CO2 equivalents (GWP of CO_2 = 1). Every kilogramme of CF4 or C2F6 emitted is equivalent to 7380 kg CO_2 and 12400 kg CO_2, respectively. Both gases are undesired by-products of the reaction of carbon anode with sodium aluminium fluoride electrolyte. PFC emissions occur during a condition known as an anode effect (AE), which occurs when the alumina (Al_2O_3) ore concentration drops below ∼1 %, the pot voltage rises, and the bath and carbon anode(s) begin to react.

The International Panel of Climate Change (IPCC) has published a 2019 Refinement to the 2006 IPCC Guidelines to report PFC emissions. The refinement includes CF4 and C2F6 emissions coming from high voltage (HV), low voltage (LV) and pot start-up PFC emissions. It includes also updated values for Tier 1, Tier 2 and Tier 3 methods that can be used to calculate PFC emission factors that depend on pot technology. IAI has also published a PFC measurement guideline reviewing all methodologies to account for high-voltage PFC emissions, produced when the pot voltage is above 8 V, and low-voltage PFC emissions, produced when the pot voltage is below 8 V. Initially, the aluminium industry established a voltage threshold of 8 volts to record and report PFC emissions that were used by most smelters. Before 2010, it was thought that PFC emissions occur only during anode effects events. However, LV PFC emissions can occur during pot room operation activities such as anode changes, tapping, pot starts, underfeed periods, and high pot noise periods. A localised increase in pot voltage can induce PFC emissions from the pot. For example, during anode changes, LV PFC emissions can occur when anode current distribution is unbalanced, and the critical current density is reached on one or more of the anodes that have been subjected to alumina depletion.

Fig 2. Stack gas monitoring FTIR instrument

Fourier Transform InfraRed (FTIR) Spectroscopy is the best technique to measure and report GHG inventories as well as measure and manage PFC emissions to gain process improvements and target reductions. The FTIR method is based on the infrared absorption of chemical molecules by light exposure within an instrument called the spectrometer. It records light intensity response versus wavelength range, graph that is called a spectrum. Infrared absorption occurs due to changes in rotational and vibrational energy in the molecular bonds from the chemical gas compounds. The FTIR instrument consists of a light source, a gas cell compartment, a detector and signal processing electronics to convert the optical signal into a spectrum that displays wavelength range to absorbance values. It is very important to select the FTIR instrument configuration to detect low concentrations of PFC emissions.

The main advantage of FTIR spectroscopy is that almost all the smelter gases from the pot exhaust can be measured simultaneously because the entire infrared spectrum is scanned at once. Therefore, other emissions concentration gases like sulphur dioxide, SO_2 carbon monoxide, CO carbon dioxide, CO_2 and carbonyl sulphide, COS can be also measured and their emissions calculated. Furthermore, spectral data can be reprocessed to verify CF4 and C2F6 emissions at different ranges. FTIR requires extractive sampling with filters to avoid instrument intensity degradation, corrosion of internal optics, and might need maintenance during measurement campaigns. FTIR is a reliable technique, but it can drift over time and needs to be accurately calibrated in the low parts-per-billion (ppb) range.

Fig 1 shows a portable FTIR instrument commercially available which uses a 9.8-metre pathlength to measure various aluminium emission gases. The FTIR resolution is 8 cm-1, which provides enough sensitivity to detect up to 10 ppb CF4 and 20 ppb C2F6.

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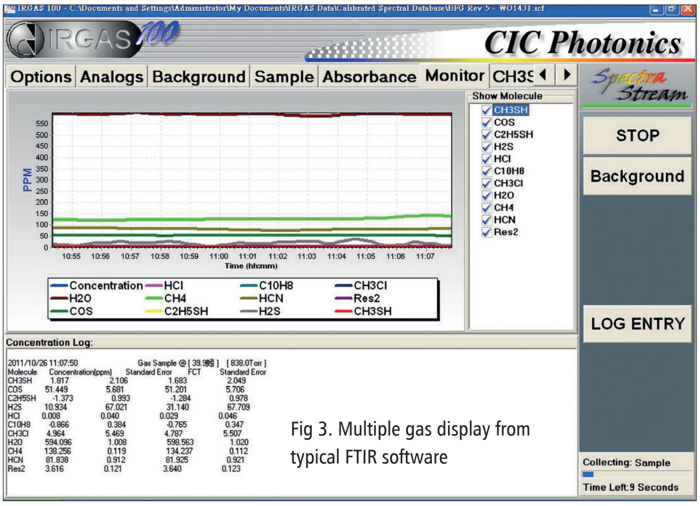

Concentration Log:

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2011/10/26 11:07:50              Gas Sample @ [ 39.9蚓 ]   [ 838.0Torr ]
Molecule   Concentration(ppm)   Standard Error    FCT     Standard Error
CH3SH      1.817            2.106            1.683          2.049
COS        51.449           5.681            51.201         5.706
C2H5SH     -1.373           0.993            -1.284         0.978
H2S        10.934           67.021           31.140         67.709
HCl        0.008            0.040            0.029          0.046
C10H8      -0.866           0.384            -0.765         0.347
CH3Cl      4.964            5.469            4.787          5.507
H2O        594.096          1.008            598.563        1.020
CH4        138.256          0.119            134.237        0.112
HCN        81.838           0.912            81.925         0.921
Res2       3.616            0.121            3.640          0.123
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Fig 3. Multiple gas display from typical FTIR software

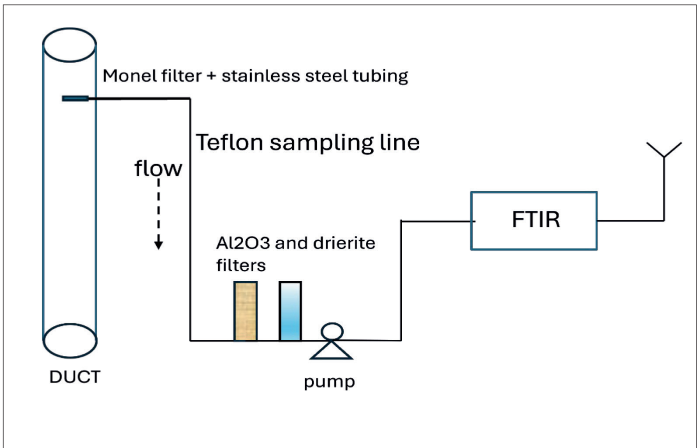

Fig 4. PFC sampling layout (not to scale)

Fig 2 shows another commercially available FTIR instrument in a NEMA enclosure that can be used as stack gas emission monitoring permanent system. This high-performance spectrometer features a double pivot MB 3000 Michelson Interferometer and built-in health monitoring capability. The MB3000 has a lower resolution (down to 0.5, 1.0 or 2 cm-1), allowing a more defined spectrum in case interference compounds are present. It has a lower detection limit for both CF4 and C2F6. It offers also a 50,000:1 signal to noise RMS, and a spectral range of 485 to 8,500 cm-1.

Both FTIR instruments have been used in aluminium smelters in North America, Europe, South America, the Middle East and Australia successfully. Each software is easy to use, and environmental personnel can be trained to maintain the instrument over several years allowing the smelter to perform their own PFC measurements.

Fig 3 shows typical software features showing multiple displays to record concentration results for almost all smelting exhaust gases and measurement parameters such as background, absorbance of each spectrum, gas cell length, gas pressure and gas temperature.

A sampling line configuration for PFC measurement is shown in **Fig 4**. The sampling probe is placed either in the inlet or outlet duct of a dry scrubber for a series of pots or at the duct of one individual pot. Pumps are used to extract gases to the internal FTIR gas cell.

Historical anode Effect Frequency (AEF), anode effect duration (AED), and anode effect minutes (AEM) are evaluated to decide the number of measurement days in a section of smelter pots. For example, a 5-day measurement time, to collect PFC emissions from 100 pots, will provide 50 anode effects with AEF=0.1. A chart of anode effects distribution during the measurement will be compared with typical plant anode effect duration distribution to evaluate if the sampling is representative and to calculate both CF4 and C2F6 emissions factors, low voltage PFC emissions and PFC emissions from pot startups. FTIR can scan at a fast rate, 10 interferometer scans each second, and therefore short anode effects are effectively detected.

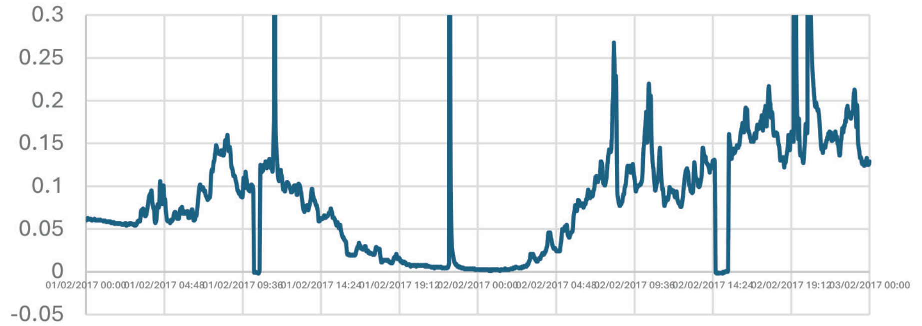

Fig 5. Results showing both high voltage and low voltage CF4 emissions

Fig 5 shows CF4 concentration emission results in parts-per-million over a measurement period of 2 days. The display was capped at 0.3 ppm in the y-axis to show the zero baseline. Note that only four anode effects (time above 8 volts) were recorded in 2 days from a section of 120 pots. Furthermore, low voltage CF4 emission concentrations are significant and reach as high as 0.27 ppm. The data collection parameters are usually set at 10–30 seconds/scan and 2.0 cm-1 or 8 cm-1 resolution. The FTIR instrument was zeroed twice with nitrogen gas for a short period of time. The nitrogen is also used as reference spectrum to calculate absorbance spectra from single-beam FTIR files. It is also important that the entire sampling line is vacuum checked prior to the start of sampling to ensure that there were no leaks in the sampling line during the measurement period. The FTIR gas cell is heated to approximately 80–120 °C to minimise condensation on internal optics.

The instrument is calibrated from low parts-per-billion (ppb) to parts-per-million (ppm) CF4 and C2F6, which can occur from emissions from single-pot or a section of several pot exhausts. The calibration files are stored electronically, and their spectra can be visually compared to measured spectra to validate concentration results. It is also important to certify primary gas standards within 2 or 5 % accuracy. Secondary standards are necessary to verify primary calibrations and to dilute concentrations to low ppb concentrations. A certificate of analysis for the gases used in the CF4 and C2F6 calibrations should be provided.

The aluminium industry has the challenge of reducing PFC emissions or eliminating them. Smelters can reduce the frequency and duration of high voltage PFC emission but can also avoid or minimise the generation of low voltage PFC emissions. Therefore, smelters should use instruments to have the ability to measure their emissions as well as predict the conditions that lead to these emissions. The capital investment of FTIR and sampling equipment may be paid off by process improvements that can be obtained by reducing PFC emissions. Therefore, more metal can be produced by avoiding the generation of LV PFC emissions during anode changes, feeding improvements, or avoiding any pot instability that will lead to better pot performance. ■

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