Fluoride Emissions Monitoring in Aluminum Smelters

OVERVIEW

Electrolytical reduction of Aluminum from its ores results in emissions of CO₂, CO, SO₂, and HF. During the operation of electrolytic baths an oxygen shortage may occur. This condition, known as an anode effect, changes the emissions drastically and leads to emissions of fluorides such as CF₄, CF₂=CF₂, SF₆, and SiF₄ until fresh aluminum ore containing oxygen is added to the process.

Aluminum smelters have to monitor the Sulfur Dioxide and Hydrogen Fluoride emissions, and there are typically emission limit values for these gases tied to the mass of Aluminum produced. In addition, Aluminum plants have greenhouse gas emissions, not only in the form of CO₂ emissions but also CF₄, CF₂=CF₂, and SF₆ emissions during the anode effect situations. While the emitted concentrations of perfluorocarbons and Sulfur Hexafluoride are small, their Global Warming Potential is great. Emitting one kilogram of CF₄ into the atmosphere has the same effect as emissions of 7,000 kilograms of Carbon Dioxide.

Continuous Emissions Monitoring from Aluminum Smelters is an ideal application for the In Situ FTIR Gas Analyser, which does not need extractive sample handling equipment.

The Gasmet FTIR gas analysers provide accurate analysis of all above mentioned gases both in permanently installed Continuous Emissions Monitoring applications and as portable instruments suitable for short-term measurement campaigns. While the duration of each anode effect can be measured from the process automation control system, the real-time concentration of perfluorocarbons, HF, and SF₆ may be measured continuously with high accuracy using the new In Situ FTIR Gas Analyser. Reporting greenhouse gas emissions based on real measured data instead of estimates ensures that the carbon credits are calculated correctly.

Short term and periodical measurements can be carried out with the portable analyzer and sampling system (above)
Case Study: **In Situ FTIR Emissions Monitoring at an aluminum plant**

A **Gasmet** In Situ FTIR Gas Analyzer has been used to monitor the emissions to air from a common ventilation stack of an aluminum production line, where compliance monitoring of HF and SO₂ was required. In addition to these inorganic species, perfluorocarbons and fluoride containing inorganic gases contributing to Global Warming were monitored. The graph at right highlights the emissions during an anode effect condition. Both CF₄ and perfluoroethylene concentrations rise measurably and in correlation with the anode effect detected from process data. During a ventilation fan interruption, the flow was reduced and concentrations of gases increased momentarily. In order to calculate the mass emissions correctly, the instruments must on one hand measure low concentrations in large flow accurately, but on the other hand they have to possess a large dynamical range to allow for the high concentration in low flow situations. A permanently installed on-line FTIR analyser provides accurate readings of hydrogen fluoride (HF) and sulfur dioxide (SO₂) concentrations, and gives an independent reading for the PFC emissions from anode effects.

**TYPICAL COMPONENTS FOR ALUMINUM SMELTER EMISSIONS MONITORING APPLICATIONS**

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Formula</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>0 - 5</td>
<td>vol-%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>0 – 20 000</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>0 – 1000</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>SO₂</td>
<td>0 – 400</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>COS</td>
<td>0 – 50</td>
<td>ppm</td>
</tr>
<tr>
<td>Hydrogen Fluoride</td>
<td>HF</td>
<td>0 – 15</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Carbon Tetrafluoride</td>
<td>CF₄</td>
<td>0 – 5</td>
<td>ppm</td>
</tr>
<tr>
<td>Perfluoroethylene</td>
<td>C₂F₆</td>
<td>0 – 5</td>
<td>ppm</td>
</tr>
<tr>
<td>Sulfur Hexafluoride</td>
<td>SF₆</td>
<td>0 – 5</td>
<td>ppm</td>
</tr>
<tr>
<td>Silicon Tetrafluoride</td>
<td>SiF₄</td>
<td>0 - 15</td>
<td>ppm</td>
</tr>
</tbody>
</table>

Other ranges and compounds available; please contact Gasmet Technologies for further details.

This application note is meant to be an informative example of typical application where Gasmet analyzers could be used. This is not a technical specification sheet. Information in this document is subject to change without prior notice. Optimal product configuration is application dependent, and exact application details such as detection limits, components included in the application, etc depend on process and/or measurement site details and may vary. Please, contact your local Gasmet sales representative to get information specific to your needs.