Continuous Long Path Gaseous HF Monitoring in a Potroom Roof Vent

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Various continuous long path HF monitors were operated in a potline roof ridge ventilator at the Tomago Aluminium Smelter. The reliability, consistency and usefulness of the equipment was assessed during their period of operation in the roof ridge ventilator over 520 m. A cassette sampling method developed previously was used to assess the accuracy of the monitoring equipment over a range of concentrations of HF. An OPSIS continuous long path HF monitor was operated in a potline roof ventilator at the Aluminium Pechiney St Jean-de-Maurienne plant over 360 m. The equipment was compared with a cassette sampling method developed by Aluminium Pechiney's Laboratoire de Recherche des Fabrications.

1. INTRODUCTION

Gaseous hydrogen fluoride (HF) emissions are generated by the reduction cells in the Aluminium Smelting process. The bulk of these emissions are captured and treated in dry scrubbing centres, however fugitive emissions escape through the roof vents of the smelter buildings during anode changing, metal tapping, pot tending, etc. This is shown schematically in figure 1.

Figure 1 - Schematic Diagram - Potroom and Dry Scrubber
The fugitive emissions escape into the atmosphere without being treated. It is therefore of interest to quantify the concentration of these emissions in order to reduce them to the lowest practical level thereby minimising any impact.

Figure 2 shows the view inside the potroom along the catwalk located just below the roof ridge ventilator.

![Figure 2 - Potroom Roof Ventilator and Catwalk](image)

Tomago Aluminium, and Aluminium Pechiney in France have had experience using wet scrubbing and specific ion electrode measurement techniques (Tesscom and Bran and Luebbe brand fluoride analysers) for assessment of HF emissions on dry scrubber stacks. It was thought that these measurement devices, used in conjunction with USEPA Type 14 manifolds over a section of the roof vent area had the potential to quantify these emissions on a continuous basis, however disadvantages with this method, such as delays between measurement, retrieval and presentation of data, and slow instrument response times limited their usefulness as an on-line process control tool. Moreover, these instruments are labour intensive, require frequent calibration and verification of accuracy, and the measurement is restricted to the USEPA 14 Type manifold area which covers only 8% of the potroom roof vent area.

In Australia, to investigate the quantification of the fugitive emissions from the potroom roof vents on a continuous basis, Tomago Aluminium was selected through the Aluminium Development Council (now the Australian Aluminium Council) as the test site for evaluation of a long path monitor developed by the CSIRO. This work has been described previously.(1),(2).
Because potroom buildings can be of the order of 800 - 1000 m in length, and the cells are tended on an intermittent basis, measurement of the fugitive emissions from potroom roof vents has presented a challenge. Figure 3 shows part of the potroom roof ventilator.

![Figure 3 - Potroom Roof Ventilator](image)

In order to meet this challenge, Tomago Aluminium and Aluminium Pechiney have conducted further evaluations of means of measuring potroom roof vent emissions using continuous long path measurement techniques.

This was done by operating continuous long path HF monitors over potroom roof vent lengths of up to 520 m and comparing the results with a tedious labour intensive, accurate cassette sampling technique previously developed (1).

The purpose of this paper is to present the results obtained in Australia and France on the evaluations of various technologies for the continuous long path measurement of gaseous HF emissions from a potroom roof ventilator.
2. INITIAL COMPARISON BETWEEN HF MONITORING TECHNIQUES

Aluminium Pechiney’s Laboratoire de Recherche des Fabrications (LRF) at St Jean de Maurienne provided an initial comparison of various long path HF monitoring equipment. LRF reviewed the performance of different HF measurement techniques in terms of path length achievable, range of measurement, stated accuracy, stated detection limit, response time, possible interferences from other gases, calibration and maintenance requirements, portability, constraints and cost.

Table 1 summarises the information obtained.

At the same time, Tomago Aluminium was working with other Australasian Aluminium Smelters through the Australian Aluminium Council to trial a long path HF monitor being developed by the CSIRO in NSW, Australia. Tomago Aluminium was chosen as the site of the field trials for this instrument. Results of the testing from these trials have been presented at the 13th International Clean Air and Environment Conference, 1996 (1) and the TMS Conference, 1997 (2).

Subsequent to this development work, Tomago Aluminium independently purchased one continuous HF monitor; the commercial product which resulted from further development of the CSIRO long path HF monitor - now called the SBL HF monitor.

An investigation commenced in March, 1998, to increase coverage of continuous long path HF monitoring to all potlines.

It was then decided to widen the investigation to evaluate various other technologies which might also meet Tomago Aluminium’s objectives of:

- cost effectiveness
- required path length
- adequate technical support
- usefulness
- reliability
- portability
- accuracy

At this time the original market study conducted by LRF was supplemented to include more recent emerging technologies.

Between May 1998 and August 1998 three additional technologies were investigated. Two of the three technologies; the Boreal Laser HF monitor, and another, which we do not have permission to identify, were practically evaluated in field trials at the Tomago Aluminium site at the same time as the existing SBL HF monitor. The third; an OPSIS HF monitor, requiring significantly higher installation costs, was not field tested at Tomago Aluminium, however this equipment has been tested by LRF at the Aluminium Pechiney St Jean-de-Maurienne plant (and has been operating there on a routine basis since 1996).
Information from the original market study by LRF together with that obtained by Tomago Aluminium is summarised in Table 1 below.

Table 1 - Long Path HF Monitor “Market Study”

| + | HYDRO ALUMINIUM | MIDAC | MDA FTR | OPSIS | LasIR | SBL | BOREAL |
|++|----------------|-------|---------|-------|-------|-----|--------|
| Principle of Operation | Fourier Transform Infrared | Fourier Transform Infrared | Fourier Transform Infrared | Differential Optical Absorption Spectrometry | Tunable Diode Infrared Spectrometer | HeNe laser Direct Absorption | Tunable Diode Infrared Spectrometry |
| Max. Path Length | ~270 m | 1000 m | 1000 m | 2000 m | 150 m | ~1000 m | ~1000 m |
| Other Gases | No | Yes | Yes | Yes | No | No | No |
| Equipment Weight | 20 kg | 40 kg | 75 kg | 320 kg | 12 kg | 65 kg | 10 kg |
| Multiplex Capability | - | - | - | Yes | Yes | No | No |
| Capital Cost | High | High | High | High | Medium | Medium | Low |
| Operating Cost Including Spares | - | - | - | Medium | Medium | Medium | Medium |
| Smelter Potroom Installations | * Hydro Aluminium Árdal Karm y | * Comalco Alcoa | * Hydro Aluminium H yanger Sundals r a | * Comalco Bell Bay | * Elkem Mosj en | * Aluminium Pechiney St Jean-de- Maurienne | * Alcoa Brazil | * Aluar Aluminio Argentino | * Alcan Grand Baie | * Tomago Aluminium | * Capral | * Comalco Bell Bay | * Tomago Aluminium |

+ Original table prepared May 1994, updated with information from Tomago Aluminium August 1998.
++ There are other technologies available. These are not presented here.
3. METHOD OF FIELD TESTING OF HF MONITORING EQUIPMENT

3.1 FIELD TESTING AT TOMAGO ALUMINIUM

The purpose of the field testing conducted over a 4 month period at Tomago Aluminium was to evaluate the reliability, consistency, accuracy and usefulness of the HF monitors as process control tools. The path length used was 520 m which equates to an optical path length of more than 1000 m each for the HF monitors tested.

3.1.1 RELIABILITY, CONSISTENCY, AND USEFULNESS

The continuous HF monitors were installed adjacent to one another and were used to measure potroom roof vent emissions over a 520 metre path length. The units were run continuously 24 hours per day, unless equipment problems prevented this.

Ease of installation, portability, technical support from the supplier, ease of alignment, alignment stability, calibration requirements and other parameters relating to the operation of the units were noted during this time. A comparison of these parameters is given in Section 4: Results and Discussion.

3.1.2 ACCURACY

During the initial testing of the CSIRO laser, sampling trains for measuring potline roof vent emissions over 400m had been developed at Tomago Aluminium using filter cassette methods.

The cassette sampling method which was developed is very labour intensive, but has been proven to be reliable for measuring gaseous hydrogen fluoride in a potroom roof ridge ventilator and for demonstrating the accuracy of other monitoring systems.

3.1.2 a) SAMPLING METHOD VALIDATION

Work done previously at Tomago Aluminium (1) had proven the cassette sampling method developed to be very reliable for comparison of continuous long path HF monitors. In order to further validate the method, four larger EPA compliance testing cassettes were used for the duration of some of the tests. Simultaneously, for some of the tests, four larger compliance testing cassettes were used over a 32 m length of the roof vent. These were then compared with the sample train cassettes over the same distance.

Figure 4 shows a Tomago Aluminium EPA compliance testing cassette.
3.1.2 b) CASSETTE SAMPLING METHOD

The sampling method used to assess the accuracy of the HF monitors in the roof vent at Tomago Aluminium is described below.

A 0.8 micron pore size mixed cellulose ester membrane filter treated with citric acid was used for particulate removal. Gaseous fluoride was collected using a cellulose pad treated with sodium hydroxide. The cassette assembly is shown below in figure 5:

Eighty cassettes spaced at 5m intervals were supported using extendible poles made from PVC tubing. The poles were mounted from a catwalk just below the roof ridge ventilator of the potroom and covered a path length of approximately 520 m. Ten manifolds consisting of eight cassettes, nylon tubing, vacuum pump, vacuum gauge, pulsation dampener, thermometer and dry gas meter were used. The sampling train is shown in Figure 6.
Each sample train was leak checked before commencement of testing. The flowrate for each sample train was set at 16 litres per minute, i.e., 2 litres per minute for each cassette.

Results of comparison testing is given in Section 4 - Results and Discussion.
Figure 8 shows the view in the potroom just under the roof ventilator. EPA compliance cassettes, support poles, sampling cassettes and the USEPA 14 Type manifold are all visible in the photograph.

![Figure 8 - Sampling Systems in the Roof Vent Area](image)

3.2 FIELD TESTING AT ALUMINIUM PECHINEY, ST JEAN-DE-MAURIENNE

Two methods were used by Aluminium Pechiney’s LRF to compare with the OPSIS HF monitor measuring gaseous HF in the potroom roof ventilator over 360 m at St Jean-de-Maurienne:

(i) a Bran and Luebbe fluoride analyser used in conjunction with a USEPA 14 Type manifold over 35 m, and  

(ii) an array of cassettes placed in the roof ventilator measuring over a 360 m path

Only the second method is described in this paper, since a preliminary study showed that the cassettes were more suitable to represent the entire length of the potline.

An array of 12 cassettes was installed in the roof ventilator. Two manifolds consisting of six cassettes, tubing, vacuum pump, gas meter, etc were used.
Figure 9 shows the sampling train employed.

![Diagram of the sampling train](image)

Figure 9 - Cassette Sampling Train at St Jean-de-Maurienne

The spacing between cassettes was approximately 30 m, therefore each cassette spanned approximately 5 pots. The flowrate for each cassette was set at 1.5 litres per minute. The sampling period was 8 days, representing two full potroom work cycles.
4. RESULTS AND DISCUSSION

4.1 FIELD TESTING AT TOMAGO ALUMINIUM

4.1.1 RELIABILITY, CONSISTENCY AND USEFULNESS

A comparison of various parameters assessed during the operation of two of the three continuous HF monitors in the potroom roof ridge ventilator over a 520 m path length is given in Table 2. Each parameter was assessed against the criteria of: Good / OK / Poor. Permission was not given to present the results for one of the monitors.

Table 2: Comparison between two of the continuous long path HF monitors tested at Tomago Aluminium:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SBL HF Monitor</th>
<th>Boreal Laser HF Monitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ease of Installation</td>
<td>poor</td>
<td>good</td>
</tr>
<tr>
<td>Ease of alignment</td>
<td>ok</td>
<td>good</td>
</tr>
<tr>
<td>Ease of calibration</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Ease of operation</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Ability of hold alignment</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Ability to hold calibration</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Portability</td>
<td>poor</td>
<td>good</td>
</tr>
<tr>
<td>Reliability of operation</td>
<td><em>good</em></td>
<td>good</td>
</tr>
<tr>
<td>Technical support</td>
<td>poor</td>
<td>good</td>
</tr>
<tr>
<td>Graphical representation of data</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Duration of installation</td>
<td>12 months</td>
<td>2 months</td>
</tr>
</tbody>
</table>

* Reliability during the last 6 months has been good following a change in the manufacturer of laser tubes. Prior to that reliability was poor.

All of the equipment was found to be useful for providing continuous, real time feedback to the potline operator about potline roof vent emissions. In all cases the units were sensitive enough to distinguish various potroom operations, were easy to operate by an instrument technician, held alignment well in a potroom environment over 520 m and were able to display the data in a useful format.

Differences exist however when comparing parameters such as portability, ease of calibration and ease of installation.
The SBL HF monitor is relatively difficult to install due to its size, compared with the other continuous HF monitors tested. It is therefore not portable. Although slightly more difficult to align than the other units tested, it has a very precise alignment mechanism and once aligned required no further adjustment. The unit has operated for 12 months without any realignment required. No on-site calibration is required for this monitor, however a reference is needed to correct for interference due to particulate matter. Since this reference had not yet been installed, the monitor was tested without it. Despite this, the instrument proved very useful as a process control tool.

The Boreal laser HF monitor had some initial commissioning problems and was therefore only included in two out of the four test runs. After the early problems (which were apparently due to condensation of moisture on the laser) were rectified, the equipment operated continuously for 2 months.

This instrument was found to be the easiest to install of the three operated at Tomago Aluminium and also the most portable. The instrument is very small and self-contained allowing it to be easily moved. It requires minimal technical skill to operate, does not require an external computer for operation and was precalibrated. Due to the limited testing period of this equipment it is difficult to comment on its long term reliability, although the unit has operated continuously, without intervention, for 2 months in the potline roof ridge ventilator.

Information from the continuous HF monitors which can be used for process control is shown in Figure 10.

![laser comparison 28/7/98](image)

**Figure 10** - Continuous HF Monitor Trends over 520 m for a 24 hour period

Although there is not exact agreement between different technologies, the trend is similar for the two HF monitors shown operating over 520 m in the potline roof ridge ventilator.
4.1.2 ACCURACY

4.1.2 a) SAMPLING METHOD VALIDATION

Results of the comparison between the cassette sampling method developed for testing long path HF monitors, and the traditional EPA compliance test method, over a 32 m path length are given in Table 3.

Table 3. Cassette Sampling Method Compared with EPA Compliance Cassette Method

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Date</th>
<th>Duration</th>
<th>Cassette Sampling Method for Long Path Monitors</th>
<th>EPA Compliance Cassette Method</th>
<th>R = Cassette long path cassette EPA compliance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28 Jul 98</td>
<td>2h 45min</td>
<td>1.11</td>
<td>1.01</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>29 Jul 98</td>
<td>5h 15min</td>
<td>0.12</td>
<td>0.12</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Comparison of the two cassette methods over a 32m path length shows good agreement between the two.

4.1.2 b) Cassette Sampling Method Comparison.

Results of the average HF emissions measured for each of the continuous HF monitors operating over 520 m are compared with the HF emissions measured by the sampling trains consisting of eighty cassettes spanning the same distance. The duration of each of the four tests was between 2 hours 45 minutes and 5 hours 15 minutes. Tests were conducted for a variety of potroom operations in order to measure the accuracy of the equipment over a range of HF emissions.
Table 4 shows the results of emission monitoring using the three continuous HF monitors compared with the cassette sampling method.

Table 4: Emissions Measured Using Continuous HF Monitors
Compared with Cassettes Over 520 m

<table>
<thead>
<tr>
<th>Test No</th>
<th>Date</th>
<th>Duration</th>
<th>Cassettes mg/Nm³</th>
<th>SBL mg/Nm³</th>
<th>Boreal mg/Nm³</th>
<th>( R_A = \frac{\text{Cassettes}}{\text{SBL}} )</th>
<th>( R_C = \frac{\text{Cassettes}}{\text{Boreal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16 Jun 98</td>
<td>3h 55min</td>
<td>0.37</td>
<td>0.58</td>
<td>Not tested</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>18 Jun 98</td>
<td>4h 15min</td>
<td>0.34</td>
<td>0.60</td>
<td>Not tested</td>
<td>0.57</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>28 Jul 98</td>
<td>2h 45min</td>
<td>0.62</td>
<td>0.78</td>
<td>0.53</td>
<td>0.79</td>
<td>1.16</td>
</tr>
<tr>
<td>4</td>
<td>29 Jul 98</td>
<td>5h 15min</td>
<td>0.09</td>
<td>0.17</td>
<td>0.09</td>
<td>0.53</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>s.d.</td>
<td>0.11</td>
</tr>
</tbody>
</table>

A scatter diagram is also given below to represent the results from Table 4

Figure 11 - Continuous HF Monitoring Measurement Plotted Against Cassette Measurement

An initial problem with the Boreal HF monitor prevented its inclusion in the first 2 tests. This problem was subsequently rectified and the unit ran continuously for two months without any further problems.

Figure 11 indicates the SBL HF monitor showed a difference from the cassette sampling method, although the response was reasonably linear, decreasing with increasing emissions. This instrument was operating without a reference to correct for interference due to particulate matter and this is thought to be the reason for the error becoming less significant with higher gaseous HF emissions.
4.2 FIELD TESTING AT ALUMINIUM PECHINEY ST JEAN-DE-MAURIENNE

The results of the comparison between the OPSIS HF monitor and cassette sampling trains over 360 m at the St Jean-de-Maurienne plant are given in Table 5 below.

Table 5. Comparison Between OPSIS HF Monitor and Cassettes

<table>
<thead>
<tr>
<th>Test No</th>
<th>Commencement Date</th>
<th>Duration</th>
<th>Cassettes (mg/Nm$^3$)</th>
<th>OPSIS (mg/Nm$^3$)</th>
<th>$R_o = \text{Cassettes/OPSIS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25/07/95</td>
<td>192h</td>
<td>0.31</td>
<td>0.21</td>
<td>1.48</td>
</tr>
<tr>
<td>2</td>
<td>3/08/95</td>
<td>192h</td>
<td>0.33</td>
<td>0.32</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>17/08/95</td>
<td>192h</td>
<td>0.37</td>
<td>0.39</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>30/08/95</td>
<td>192h</td>
<td>0.22</td>
<td>0.27</td>
<td>0.81</td>
</tr>
<tr>
<td>5</td>
<td>7/09/95</td>
<td>192h</td>
<td>0.25</td>
<td>0.33</td>
<td>0.76</td>
</tr>
<tr>
<td>6</td>
<td>18/09/95</td>
<td>192h</td>
<td>0.22</td>
<td>0.12</td>
<td>1.83</td>
</tr>
<tr>
<td>7</td>
<td>27/09/95</td>
<td>192h</td>
<td>0.24</td>
<td>0.15</td>
<td>1.60</td>
</tr>
<tr>
<td>8</td>
<td>5/10/95</td>
<td>192h</td>
<td>0.23</td>
<td>0.16</td>
<td>1.44</td>
</tr>
<tr>
<td>9</td>
<td>17/10/95</td>
<td>192h</td>
<td>0.17</td>
<td>0.26</td>
<td>0.65</td>
</tr>
<tr>
<td>10</td>
<td>31/10/95</td>
<td>192h</td>
<td>0.17</td>
<td>0.25</td>
<td>0.68</td>
</tr>
<tr>
<td>11</td>
<td>16/11/95</td>
<td>192h</td>
<td>0.17</td>
<td>0.24</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Average 1.09  
s.d. 0.42

Despite a certain amount of dispersion due to the spacing of the cassettes, gaseous HF roof vent emissions measured by the OPSIS were in fair agreement with those measured using the cassette method.
Results of the comparison testing of the OPSIS are also plotted in Figure 12.

![Figure 12 - OPSIS HF monitor plotted against cassettes.](image)

CONCLUSION

Sampling trains previously developed for measurement of gaseous HF proved once again to be effective for comparison of long path gaseous HF monitors in a potroom roof ridge ventilator.

The continuous HF monitors assessed over a 520 m path in the potroom roof ridge ventilator at Tomago Aluminium and over a 360 m path at St Jean-de-Maurienne were useful for providing real-time trending of fugitive emissions from the potline roof vent. All of the equipment tested at Tomago Aluminium was easily operated by an equipment technician and maintained alignment without the need for intervention.

Although some of the equipment appears useful for the purpose of process control, the results from the testing at Tomago Aluminium shows that attention to calibration on a regular basis and comparison testing over the measurement path would be required in order to have confidence that there is no drift in the quantitative results. Where this is not practical, it would be advisable to compare the continuous HF monitor over a proportion of the path length, such as an EPA 14 Type manifold section, with a second measurement method. Based on some of the results of the testing at Tomago Aluminium it does not seem appropriate to consider the use of these instruments as compliance monitoring tools without quite a lot of further development.
Tomago Aluminium recognises that assessment of long path HF monitoring equipment is only part of the strategy for minimising fugitive emissions from the potlines. Acceptance and utilisation of the equipment by the operator is also necessary for the equipment to be of use as a process control tool.

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