

# Light Metals 2011

## **ALUMINUM REDUCTION TECHNOLOGY**

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**ALUMINUM REDUCTION  
TECHNOLOGY**

**Enviroment- Emissions /  
Anode Effect I**

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## HF MEASUREMENTS INSIDE AN ALUMINIUM ELECTROLYSIS CELL

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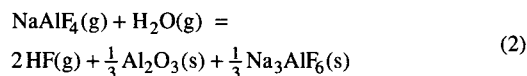
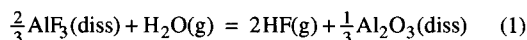
### Abstract

HF emissions to the working atmosphere may still be a problem for the aluminium industry. The objective in the present work was to study how the HF evolution is distributed between feeder holes, other openings in the crust, gases diffusing through the crust, fumes from the secondary alumina residing on top of the crust etc. A movable “gas sniffer” connected to a Tunable Diode Laser was used to measure the HF concentrations at the above mentioned locations. The stationary HF level in an open flaming feeder hole was approximately 9000 ppm, when measured a few cm above the bath surface. In comparison, when the probe was positioned 5-10 cm above a crust area with good integrity, the HF concentration was in the range 5-10 ppm. The results support the notion that most of the HF evolves from open feeder holes and the tapping hole.

### Introduction

HF emissions to the working atmosphere continues to be a problem, and new challenges concerning emissions to both internal and external atmosphere emerge as a consequence of the ongoing cell technology development. In this situation, it is important to know precisely which factors affect the formation of hydrogen fluoride, and where it evolves.

Hydrogen fluoride is generated when fluorides present in the bath or in the vapour phase react with moisture,



It has long been established that two of the main sources of water are the structural hydroxyl in the primary alumina and the moisture content in the air [1, 2, 3]. A certain amount of HF is also generated from electrochemical oxidation of hydrogen in the anodes. It is also a well known fact that the HF formation rate increases with increasing temperature, decreasing bath ratio, and decreasing alumina concentration [1, 2].

Quite a lot of industrial measurements and a few laboratory studies have been carried out during the recent years to quantify

the relative contributions to HF emission, and to locate the main HF generation sites. The industrial measurements have been carried out in the gas channel between individual cells and the main duct system. From such measurements, essential information regarding the importance of certain parameters such as crust integrity has been obtained [4]. Still, the fluoride concentration in the duct represents the average of the conditions at the top of the cell.

Useful and more direct information can be obtained by doing measurements locally on top of the cell. The main purpose of the present work was to gain knowledge about how the hydrogen fluoride evolution is distributed locally between the feeder holes, secondary alumina, openings in the crust, and gases diffusing through the crust as illustrated in Figure 1. To make measurements locally at the top of the cell, a portable sniffer based on online Tunable Diode Laser monitoring was constructed.

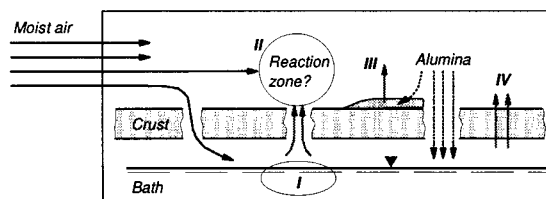


Figure 1. Schematic representation of water sources and possible HF-evolution sites (represented by the red arrows) in an aluminium electrolysis cell.

### Design Criteria for “HF-sniffer”

Based on the data from the literature [5], as well as calculations using the fluoride evolution model by Haupin and Kvande [2], the total fluoride evolution from a rather large modern cell, such as the cells in Hydro’s plant at Sunndalsøra (SU4), will be in the order of 30-40 kg F/t Al. Between half and two thirds of this is due to HF. Depending on the gas suction rate, the concentration of HF in the duct will be around 300 ppm (volume), or about 250 mgF/Nm<sup>3</sup>. This value represents the average situation on top of the cell. The maximum possible gas concentration can be estimated by assuming that all HF is formed in the bath and follows the cell gases out from below the crust. 20 kg HF/t Al then corresponds to about 3.4 vol% HF (24 000 mgF/Nm<sup>3</sup>) in the

cell gas coming up from, *e.g.*, an open feeder hole. This can be regarded as the maximum concentration that can be expected. Formation of 20 kg HF/tAl is equivalent with 0.48 wt% water in the alumina, if all water reacts to HF. The total amount of water in the alumina is normally much higher, which indicates that most of the water is not available for reaction to HF. Furthermore, the equilibrium in Eq. (1) is not completely displaced towards the right hand side. Figure 2 shows the concentration of HF and H<sub>2</sub>O in the cell gases at 960 °C (“normal” bath composition) as a function of the content of water in the alumina. In these calculations, it was assumed that all water is available for reaction with the bath.

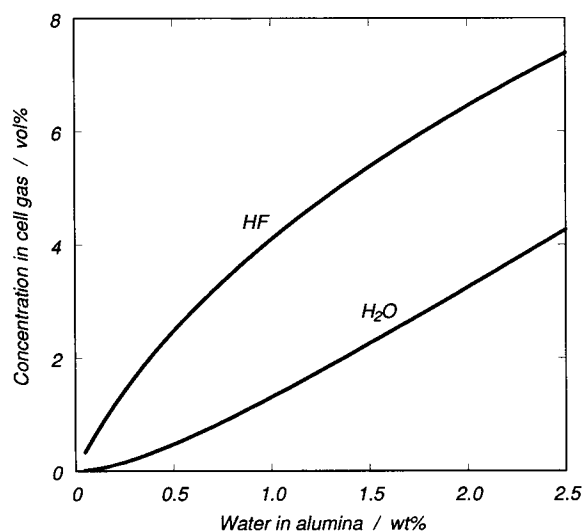


Figure 2. Equilibrium concentration (Eq. (1)) of H<sub>2</sub>O and HF in the cell gases as a function of the H<sub>2</sub>O-content in the alumina, assuming that all water in the alumina is available for reaction with the bath. 11.5 wt% AlF<sub>3</sub>, 4.5 wt% CaF<sub>2</sub>, 3.5 wt% Al<sub>2</sub>O<sub>3</sub>, 960 °C, 93 % current efficiency.

### Experimental Set Up and Procedure

The measurements were performed at an end cell at SU4 Hydro Sunndal in Norway during two campaigns, one in October 2008 and one in May 2010. The laser used in the 1<sup>st</sup> campaign had a more sensitive measuring range and was therefore suitable for measurements only at sites where the HF concentration was below 750 ppm, such as on top of the crust far away from any openings. The second campaign was performed with modified equipment. The measuring cell was covered with PTFE (Teflon<sup>®</sup>) to provide better protection towards HF than the steel used earlier. The cell was also made shorter. Furthermore, a sapphire glass window was used instead of fused silica. The shorter measuring cell resulted in a quicker dynamic response and contributed to a higher upper concentration limit since the physical principle utilized in TDL technology involves a correlation between concentration and optical path length. A pressure probe was placed in the measuring cell. This improved the instrument’s capability to handle underpressure, something which was essential

in this case, since it turned out that a certain minimum suction rate was necessary to get a good reading.

Figure 3 shows a principal sketch of the set-up. The instruments were placed on a table close to the wall by the emergency exit. It was then out of the way for all motorized traffic, and the magnetic field was moderate. The tunable diode laser (TDL) was a HF and H<sub>2</sub>O Lasergas II Single Gas monitor from Neo. The PFA tubings (diameter 1/4”) between the laser and the probe were approximately 20 m long and flexible. The probe could then be transferred manually from one measuring site to the next. Gas was sucked continuously through the probe and into the laser measuring cell with the help of a pump placed at the end of the line at a rate between 5 and 15 l/min. N<sub>2</sub> (g) was purged through the path of the laser beam between the emitter and the receiver outside the actual measuring cell to eliminate the effect of humidity in the ambient air that otherwise would be present. The laser was connected to a computer, and the values recorded every 10<sup>th</sup> second. During some of these measurements, a thermocouple (Pt-PtRh 10%, type S) was placed at the probe tip. The purpose of this was to document the vertical position of the probe. Figure 4 a shows a picture of the probe tip with the thermocouple, and Figure 4 b shows how the probe was inserted through a hole in the cover.

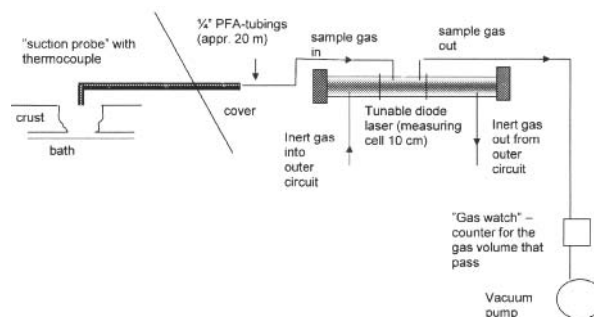


Figure 3. Gas sniffer, as it was used in the 2<sup>nd</sup> campaign. Improvements from 1<sup>st</sup> Campaign: New laser (higher upper limit), shorter measuring cell (shorter response time and higher upper limit), inside coated with PTFE, sapphire glass instead of fused silica, pressure probe installed, and thermocouple at the probe tip.

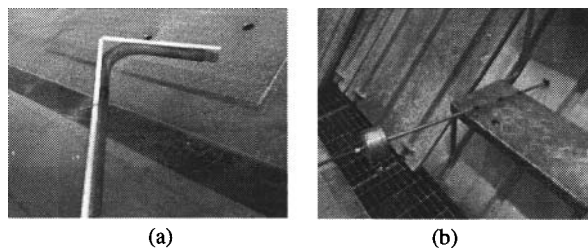


Figure 4. a) Probe tip with thermocouple. b) Probe inserted through a cell cover.

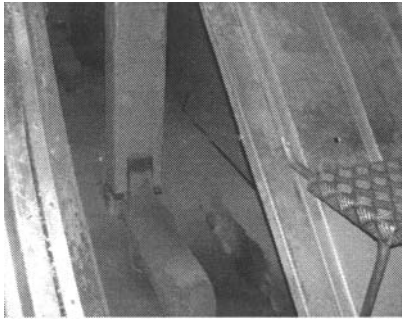


Figure 5. Probe positioned on top of the crust.

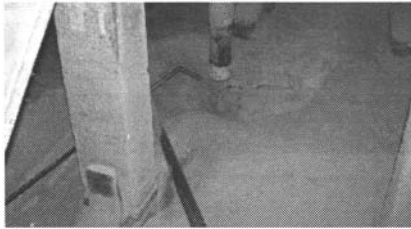


Figure 6. Probe positioned above feeder hole.

To verify the system, measurements were performed in the duct (the measuring site was located at a place close to the cell where only the off gas from one particular end cell is passing) where the expected concentration range could be calculated to be around 300 ppm as mentioned earlier. During one of these periods, a NaOH containing filter was placed at the end of the line. This was done to confirm that the online measurements were in consistency with the well established Sintalyzer fluoride analysis method.

Then the probe was placed on top of the crust as shown in Figure 5, and further hand held above an open tapping hole and above and inside an open flaming feeder hole. Figure 6 shows the probe placed above an open flaming feeder hole.

## Results

### 1<sup>st</sup> Campaign

**Duct Measurements.** A more convenient short measuring probe was used during the first duct measurements. This probe was kept in place over night for approximately 16 hours and 40 minutes while recording the HF and H<sub>2</sub>O concentrations continuously. To trap the HF passing through the laser, several filters soaked with NaOH were placed at the end of the line and kept there for about 16 hours and 13 minutes, that is, during almost the entire time period. The subsequent Syntalyzer analysis performed on the filters showed an average concentration of 213 mg/Nm<sup>3</sup> HF in the gas passing the laser during the measurement. The average HF concentration calculated from the laser measurements done at the same time interval was 253 ppm, which corresponds to 210 mg/Nm<sup>3</sup>.

The values recorded by the laser varied from slightly below 200 ppm to slightly above 400 ppm, clearly correlating with the feeding cycles as would be expected.

**Above Crust and in Open Tap Hole and Feeder Hole.** When the probe was placed as shown in Figure 5, the HF stationary HF concentration varied between 5 and 10 ppm; see Figure 7.

When the probe was positioned above the feeder hole as shown in Figure 6, the concentration was in the range 100-200 ppm.

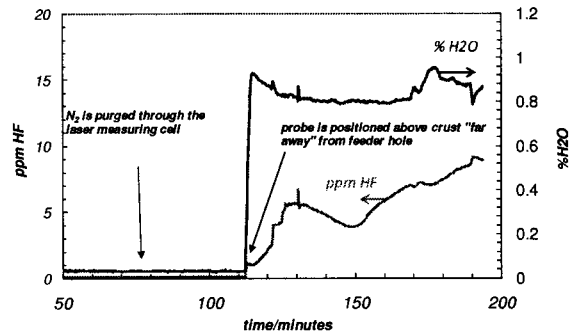


Figure 7. HF and H<sub>2</sub>O levels above crust (probe positioned as shown in Figure 5).

Figure 8 shows how the concentration varied as the probe was moved from above a blocked feeder hole to an open tap hole close to the bath surface. The probe was then flushed with N<sub>2</sub>, then placed in an open feeder hole close to the bath surface. Keeping the probe in the open tap hole or the open feeder hole made the concentration rise abruptly to above the measuring range of the instrument. It should be noted that the probe was positioned only a few centimeters above the bath surface, and not as shown in Figure 6. The flat signal when placed in the open tapping hole is simply a signal overload. The reason for the slightly stepwise increase when held above the open feeder hole is that the probe had to be yanked away every time the crust breaker came down before feeding. This resulted in a small dilution effect.

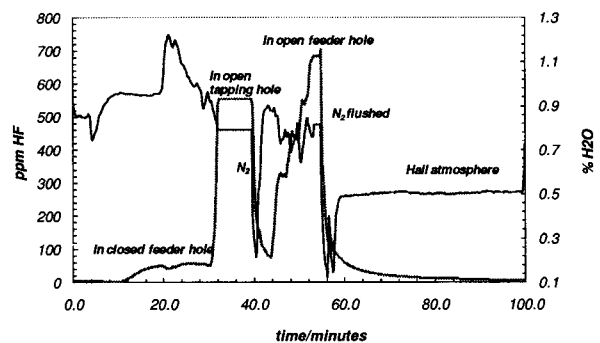


Figure 8. HF and H<sub>2</sub>O levels at various locations inside the cell.

### 2<sup>nd</sup> Campaign

The main purpose of this campaign was to obtain a quantitative value of the HF levels in the open feeder holes and tap holes.

**Duct Measurements.** As in the first campaign, to confirm that the system was without large leaks, and that the values obtained were reliable, various measurements were done in the duct. Figure 9 shows HF and H<sub>2</sub>O levels when a short probe and the long probe were placed in the duct with and without dust filter. As can be observed, when used with a dust filter, the long probe exhibited a larger response time than when used without the dust filter (after 4 minutes the measured value is still far below the expected stationary value). This was probably caused by the fact that a larger pressure drop is built up across the dust filter. When the dust filter was removed, it took about 4 minutes to obtain a “reasonable” value (approx. 300 ppm). The rest of the measurements were therefore conducted without using the dust filter.

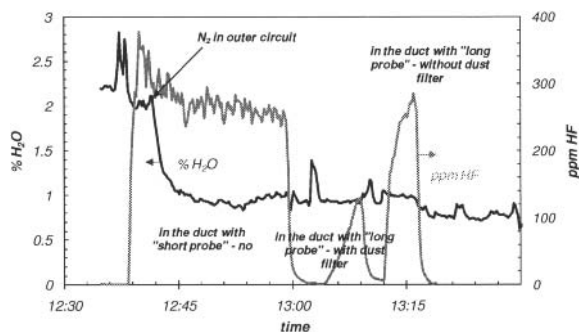


Figure 9. Measurements of HF and H<sub>2</sub>O in the duct.

**Measurements in Open Holes** After the duct measurements, a thermocouple was attached to the tip of the probe. The probe was transferred to an open tap hole, and then to a flaming open feeder hole. The measurements are shown in Figures 10 and 11. The figures represent the same time period, i.e. the same events, but presented somewhat differently. Experience from the last campaign had shown that there was a big concentration gradient above the open holes. Therefore, to get as high a reading as possible, the probe was held only a few centimetres above the bath surface. However, since the crust breaker regularly came down (every 2-3 minutes), the probe had to be pulled up and away from the path of the crust breaker. This to a certain extent contributed to dilution of the gas sucked into the probe.

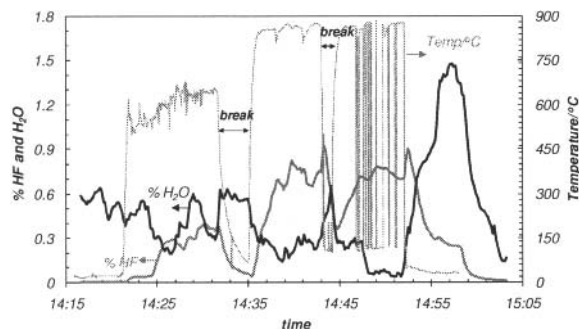


Figure 10. HF and H<sub>2</sub>O levels in an open tap hole (14:20-14:30) and in an open feeder hole (14:34-14:52) plotted together with the temperature measured.

As shown in Figure 10, the highest temperature (approximately 876°C) was measured inside the open feeder hole, a few centimetres above the bath surface. The bath temperature at 14:00 was measured to be 954 °C. When held in the open tap hole, the bath surface could not actually be observed visually. The temperature being “only” between 600 and 700 °C, might indicate that the probe was further away from the bath surface than when held in the open feeder hole, or it might indicate that the temperature above the bath is higher in a flaming hole due to the oxidation of CO.

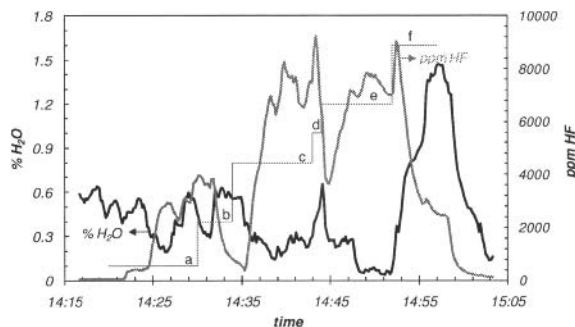


Figure 11. HF and H<sub>2</sub>O levels in an open tap hole and in an open feeder hole plotted together with the course of events. a) 14:20-14:30: in open tap hole, b) 14:30-14:34: break, c) 14:34-14:43: in open flaming feeder hole d) 14:43-14:44: break e) 14:44-14:52: back in open feeder hole, f) 14:52: break

The highest HF value measured was more than 9000 ppm (0.9%), and this was obtained when the probe was held in an open feeder hole (periods c and e in Figure 11). During the same periods, the water vapour level reached a low value when the HF values were high. This suggests that a large part of the moisture is converted to HF according to Eq. (2) at the prevailing conditions; high content of fluoride vapour and high temperature. When the probe was removed from the open feeder hole, the concentration of water vapour rose to a higher level. This is especially pronounced in period f in Figure 11. Why the concentration exceeds its original background level is uncertain.

**Dynamic Response Time.** The dynamic response time is here defined as the time between an imposed change on the system and the first response recorded. The thermocouple has a very fast dynamic response compared to the HF and H<sub>2</sub>O signal (and is also logged every two seconds), so its dynamic response could be used as a time basis for calculating the response in the other recorded items. In this way, the dynamic response time for the HF and H<sub>2</sub>O signals are estimated from Figure 12 to be 21-33 seconds and 10-11 seconds respectively; the probe is taken out from an open feeder hole at 13:36:18 and the measured HF concentration starts to decline between 13:36:40 and 13:36:51. H<sub>2</sub>O starts to increase between 13:36:18 and 13:36:51. The probe is put back in at 13:38:46 and the HF concentration starts to increase between 13:39:05 and 13:39:17. The onset of water level decrease is between 13:38:44 and 13:38:54.

**Stationary Response Time.** The stationary response time is here defined as the time it takes for the system to obtain a new stationary value (where this is expected) after a change has been

imposed. For HF, this was estimated from the duct measurements to be approximately 4 minutes for increasing concentrations and approximately 2 minutes for decreasing concentrations. For H<sub>2</sub>O, the current data do not provide enough information to estimate the stationary response time.

The response time of the laser itself is believed to be around one second, so the discussion above refers to the whole system.

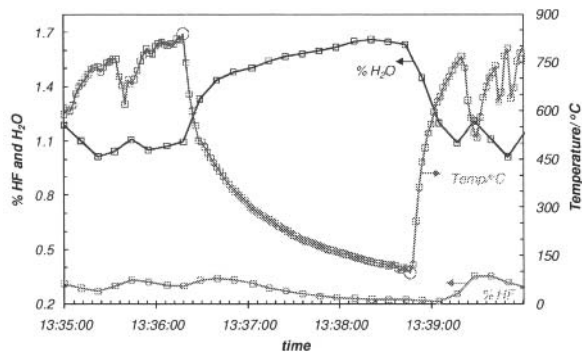


Figure 12. Close up of HF and H<sub>2</sub>O levels as they change when the probe is taken out from an open feeder hole and put back in.

### Summary and Discussion

Table I shows a summary of the HF levels measured at the various sites. It seems rather clear that the HF gas generated exits almost entirely through the crust openings. Keeping the probe above a blocked feeder hole gave no indication of HF desorption from secondary alumina. The fact that surface adsorbed fluoride does not re-evolve during ore feeds to the pot, has also been reported by others [4, 6].

Table I. Summary of HF levels.

Location	Range	Comments
Above crust ("far" away from feeder hole)	5-10 ppm	October 2008
Above open feeder hole	5-200 ppm	October 2008
Duct	200-400 ppm, fluctuate according to feeding cycle	October 2008
Above blocked feeder hole	50 ppm	October 2008
Just above bath, open tap hole	3000-5000 ppm	May 2010
In open feeder hole just above bath	0.90-1.0 %	May 2010

If the suction rate during the duct measurements is approximately 7000 Nm<sup>3</sup>/h (it was not measured accurately for the actual cell during the campaign), the HF generation rate can be calculated to be around 27 kg HF/ton Al. If the raw gas that exits the feeder hole were to be completely undiluted, the HF concentration would

be around 4.5 %, more than four times as much as the actually recorded amount. This may indicate that even though there, in principle, would be overpressure and a gas flow directed upwards in the open flaming feeder holes due to the gas evolved underneath the anodes, air may be sucked into the holes and possibly also underneath the crust. Possibly, this can be related to waves and splashing at the bath surface. The observation made in this work, that there is a large difference in HF concentration when measured "above" the hole as opposed to "inside" the hole also supports this. A follow up on the present work was later done at Alcoa Mosjøen, where levels up to 2.6 % HF were detected in crust openings; this is reported elsewhere [7]. The feeder holes at Alcoa Mosjøen had a smaller diameter and were more cylindrically shaped than the ones observed at Hydro Sunndal.

### Conclusions

The stationary HF level in an open flaming feeder hole was approximately 9000 ppm, when measured a few cm above the bath surface. In comparison, when the probe was positioned 5-10 cm above a crust area with good integrity, the HF concentration was in the range 5-10 ppm. The results support the notion that most of the HF evolution emits at the open flaming feeder holes and tapping hole. The gas sniffer equipment worked according to the purpose, and this method has proven a useful tool for these types of measurements. Future campaigns will be carried out, both at other smelters but also with respect to other kinds

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