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CORRELATION BETWEEN MOISTURE AND HF FORMATION IN THE ALUMINIUM PROCESS

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Abstract

Hydrogen fluoride (HF) emission to the working atmosphere is still a problem in the aluminium industry. Moisture in secondary alumina fed to the cell and humidity in the ambient air reacts with fluorides in the bath and fluoride vapours to form hydrogen fluoride. The relation between the various sources of water and the resulting HF emission is still not well understood. In this work, industrial measurements have been done to determine where HF escapes from the bath. The quantities of HF and moisture at the specific sites have also been determined. Measurements were done in the duct during normal operation as well as during anode change, above the feeder hole and above an open hole in the crust. A strong correlation between feed cycle and HF levels was measured. Increased HF emissions were also recorded during anode change.

Introduction

HF emissions to the environment have been reduced considerably since the introduction of the dry scrubber in the 1980s. However, emission to the working atmosphere is an issue that remains. Emissions to the working atmosphere mainly happen during work on the electrolysis cells, for example during changing of anodes, tapping, etc. when the covers are removed.

Generation of HF takes place when fluorides in the bath or in the vapour phase react with moisture according to Reactions 1 and 2 below [1],

$$\tfrac{2}{3}AlF_3(diss) + H_2O(g) = \tfrac{1}{3}Al_2O_3(diss) + 2HF(g) \qquad (1)$$

$$NaAlF_4(g) + H_2O(g) = \tfrac{1}{3}Al_2O_3(diss) + 2HF(g) + \tfrac{1}{3}Na_3AlF_6(g) \qquad (2)$$

This work has been done to establish knowledge about the different factors that affect the formation of HF and gain a better understanding of where it evolves in the cells. Different technologies for producing aluminium have different challenges concerning HF emissions, and it is therefore interesting to compare the different technologies. In this paper, it is distinguished between HF formation and emission in accordance with Haupin and Kvande [5]. Formation is the total HF formed by reaction with the different moisture sources. Emission is the amount of HF released to the atmosphere, from both the cell and the fume treatment plant. [2]

The work was carried out at Alcoa Mosjøen, Norway, in June 2010, to create a basis of comparison with the measurements already done at Hydro Sunndal SU4, Norway [3]. The objective of the work was to increase the knowledge concerning where hydrogen fluoride emissions escape from the bath, and the correlation with feed cycle of the cells. An HF/H_2O NEO Lasergas II Single gas monitor instrument was used to measure the concentrations of HF and H_2O in the cells. A portable "sniffer line" was used to suck gas from various positions in the electrolysis cell. These positions included inside the duct, above the crust, the feeder hole and an open hole in the crust. HF emissions as well as H_2O concentration were measured at all these positions. The main objective of this work was to obtain quantitative measurements of the HF levels above holes in the crust and inside the duct.

From the measurements in the duct, average values of HF are found. When measuring over the feeder hole and over other holes in the crust, more knowledge concerning how the hydrogen fluoride evolution is distributed over the cell is found. This way it can be established how moisture in the alumina fed to the cell affects the HF formation. Two main sources of water contribute to the HF formation. These sources are structural hydroxyl in the primary alumina and moisture in the air sucked into the cells [4,5,6].

Experimental Setup and Procedure

The experimental setup was similar to the one used at SU4, Hydro in May 2010 [3], except for the following adjustments: The drum-type gas flow meter and the cover near the junction between the probe and the tubing were eliminated. Figure 1 shows a sketch of the experimental setup [3]. It was possible to manually switch the ventilation system on the cell from normal to forced gas suction, and this way the ability to manipulate the suction rate on each cell was present. Measurements could be done in the duct on each individual cell relatively close to the crust itself. The magnetic field was moderate in this area of the pot room.

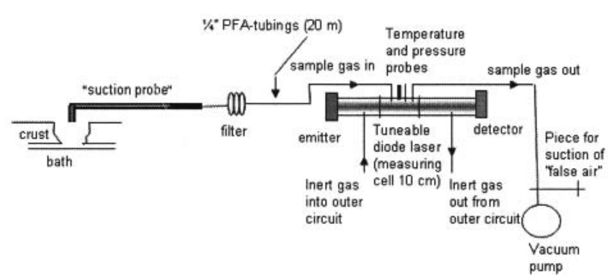

Figure 1: Experimental setup of the equipment used at Alcoa Mosjøen [3]

Earlier experience from measurements using the laser equipment showed that is sensitive to the magnetic field. If the magnetic field is too strong the unit will stop working. Hence, it should be placed in an area of moderate magnetic field. The computer used has a flash disk which makes it suited for bringing into a pot room with a magnetic field. The laser instrument is made to withstand a moderate magnetic field and still giving reliable results.

The laser used was an HF and H_2O Lasergas II Single Gas monitor from NEO. The PFA tubing between the laser and the probe was flexible and measurements could be done in different areas of the cell. The pump helped sucking the gas from the measuring site through the probe, the tubing and into the laser. The total volume flow through the measuring system was 10-20 L/h. Before entering the laser, the gas passed through a filter to prevent the laser measuring cell from being filled with dust. Nitrogen was purged through the laser measuring cell to eliminate humidity from the ambient air to affect the H_2O measurements. Measurements were recorded every ten seconds. The pump, probe, filter and nitrogen were standard equipment at Alcoa Mosjøen.

The laser instrument was calibrated in the laboratory before going to Alcoa Mosjøen. Known amounts of moisture entered the laser instrument and the moisture level recorded was compared with the theoretical value. The comparison showed good compliance with the theoretical and recorded values.

Measurements were done in the duct during constant feed rate with and without forced suction (open and closed damper). The duct measurements were partly done to verify the system. Subsequently measurements were carried out above the feeder hole and finally over an open hole in the crust.

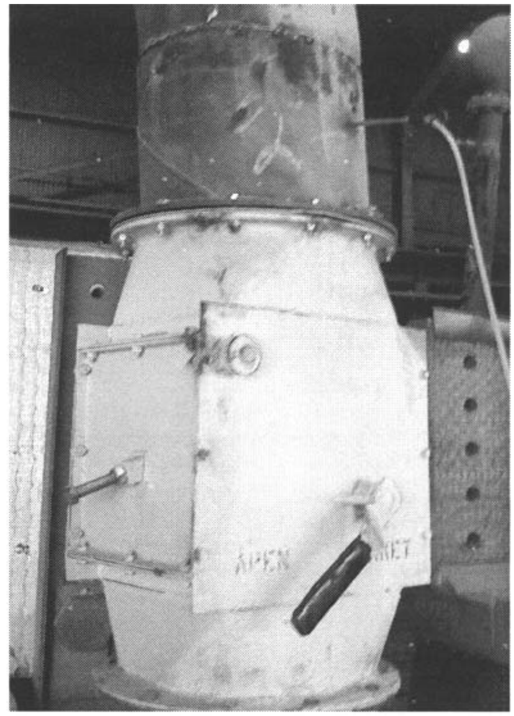

Figure 2: Probe inside the duct. Notice how the damper can be opened and closed manually.

Results

Duct Measurements

The probe was placed inside the duct as shown in Figure 2. It was made sure that there were no leakages in the system and that all valves and tubes were reliable. In Figure 2, also notice the possibility to manually open and close the damper while working on the cell. Measurements were done with forced suction (open damper) as well as without forced suction.

According to various literature data [4, 5], the hydrogen fluoride evolution rate is in the order of 20-35 kg F/t Al. Depending on the gas suction rate, this corresponds to an HF concentration in the duct in the range 200-400 ppm (volume). Figure 3 shows the results from the duct measurements.

A section of Figure 3 is enlarged in Figure 4 to show the correlation between moisture and HF, as well as the response in HF and H_2O concentrations after feeding of alumina.

Measurements in the duct were also done during anode change, and the results are shown in Figure 5. Measurements of HF concentrations in the pot room during the same time interval are shown in Figure 6.

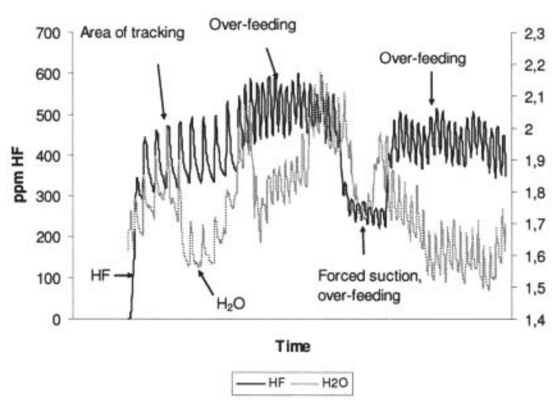

Figure 3: HF and H_2O measurements in the duct showing variations in the cell when the damper is open and closed. The lower points on the HF graph represents the time just before the feeder fed the cell.

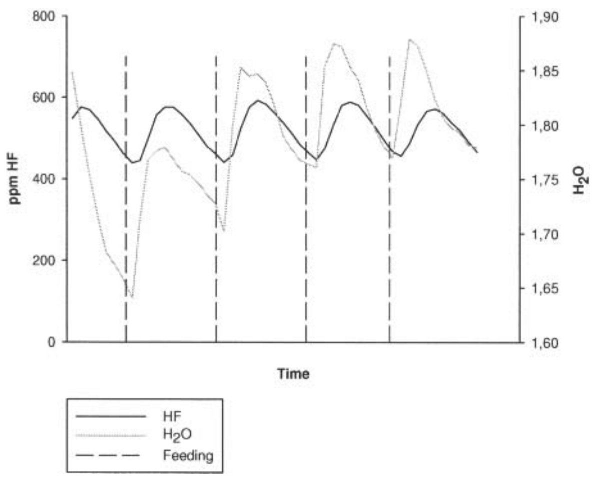

Figure 4: A section of Figure 3. This shows how the concentrations of HF and H_2O vary with feeding of alumina. The dashed lines indicate when feeding of the cell took place.

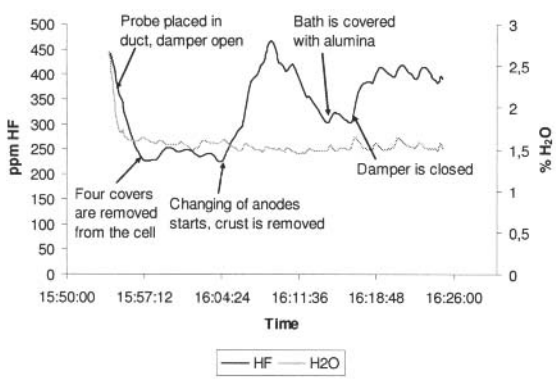

Figure 5: Effect of anode change.

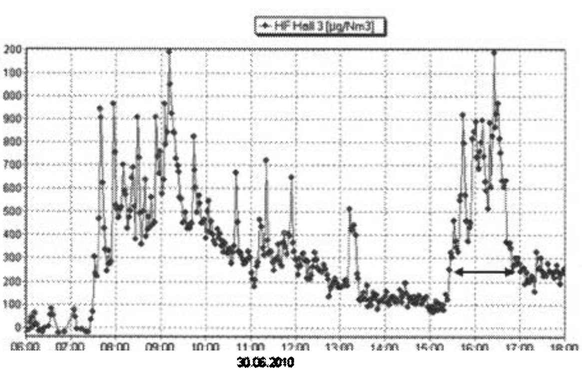

Figure 6: Data given by Alcoa Mosjøen of HF emissions to the pot room the 30th of June 2010. There is an apparent peak of HF emission at approximately 16.00-17.00 (this time interval is pointed out by the black arrow) showing that more HF is emitted to the pot room during anode change.

Measurements above the Feeder Hole

The results from the measurements above the feeder hole are shown in Figure 7, and a photo of the feeder hole is placed in Figure 8.

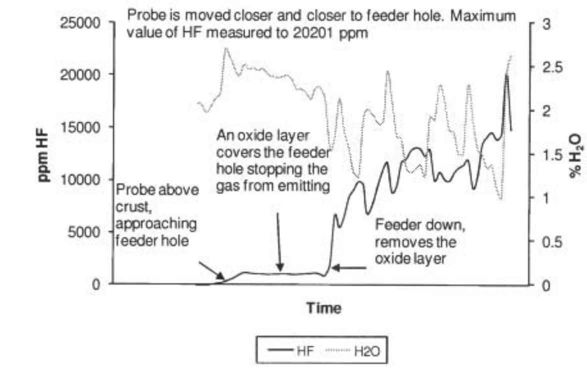

Figure 7: Measurements done above the feeder hole

Figure 8: Feeder hole.

Measurements above an Open Hole in the Crust

Measurements were done above an open hole in the crust, and Figure 9 shows a photo of the probe above this open hole. Figure 10 shows the results from the measurements over the open hole in the crust. Four vertical lines indicate when the feeder went down into the bath.

Figure 9: Probe held above an open hole in the crust.

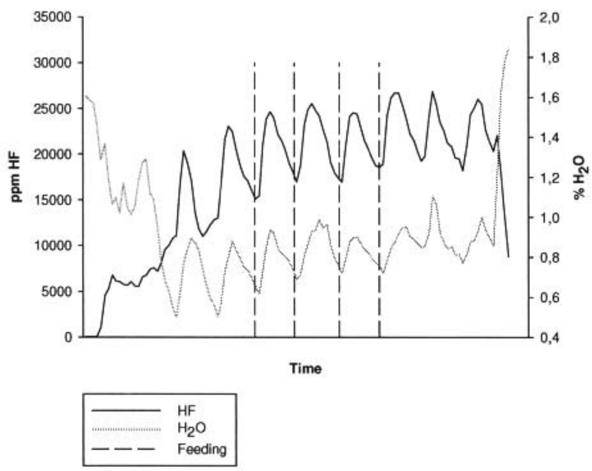

Figure 10: Results from measurements done above the open hole in the crust. The vertical lines indicate feeding of the cell.

Discussion

Duct Measurements

Measurements in the duct were performed to create a basis for understanding how feed rate, feeder cycle, anode changes and various air suction rates affect the HF concentration in the cell.

The measurements in the duct demonstrated a clear correlation between HF evolution and feeding of alumina. The results from the duct measurements are shown in Figure 3. The figure shows time intervals of different feed rate and with and without forced suction. It is worth noting that the concentration of HF decreased when the suction rate increased due to increased dilution of the raw gas. In Figure 3, the time intervals of tracking and over-feeding are shown. Tracking of the cell means that the cell is underfed. At over-feeding the concentration of HF increased. When the damper was closed the measured levels of HF was as high as 590 ppm. This is a higher value than earlier reported [4,5,6]. However, since the gas suction rate inside the duct was not measured, the dilution factor is not known, so the measured and earlier reported values are not directly comparable. Different plants have different technologies and routines, and this might lead to the deviation in predicted value of HF. When operating under forced suction, the gas becomes more diluted and the concentration of HF drops.

Also in Figure 3, a correlation between feeding of alumina and HF and H_2O levels are shown. A pattern of "peaks" and "valleys" is observed. The "valleys" in the HF graph occur just before the cell was fed with alumina. After feeding the cell the concentration of HF increased considerably, reaching a maximum value (a peak) and then started decreasing. This is shown in more detail in Figure 4. There is a short response time before the concentrations of HF and H_2O start increasing after feeding of the cell. This response time is most likely due to delay in the laser instrument, due to the time it takes to move the gas through the probe and the tubing into the laser and/or due to the reaction rate between moisture and AlF_3 in the bath. Hence, the formation of HF is almost immediate after the feeding of the cell.

Figure 5 shows the results from the measurements during anode change. These measurements were done to verify what happens with the duct concentrations of HF during anode change. In these measurements forced suction was introduced (by the operators as part of their anode change routine), cell covers were removed. When the anodes are removed a large surface area of the bath is exposed to the ambient air. When the covers are removed, part of the HF escapes into the pot room (as shown in Figure 6), without reaching the duct and hence the dry scrubbers. Also, when the crust is removed more HF is formed by hydrolysis due to the large surface area of the bath being exposed to ambient humidity. When the bath is covered with alumina to create a crust and the damper is closed, the cell returns to normal. The HF concentration increases in the duct and also in the pot room.

Measurements above the Feeder Hole

The results from the measurements above the feeder hole are shown in Figure 7. The figure shows maximum values of HF of about 20000 ppm. At Hydro Sunndal the maximum values of HF measured above the feeder hole was only approximately 10000 ppm[2]. One problem of measuring over a feeder hole is that the probe has to be removed from the hole every time the feeder feeds the cell. Variations in HF levels according to feed rate are not obvious from Figure 7 in the same way as it was observed in the duct. The photo in Figure 8 shows that the feeder hole is very narrow with only a small surface area of the bath exposed to ambient air. When comparing the measured HF levels at Alcoa Mosjøen with the measured levels at Hydro Sunndal, it is obvious that the measured level at Mosjøen was significantly higher than at Sunndal. One reason might be the different shapes of the feeder holes at the two plants. At Mosjøen the feeder holes are narrow, giving a very concentrated flux of gas upwards from the hole. At Sunndal the feeder holes are more open and less narrow, giving a gas that is quickly diluted with the ambient air. This makes it difficult to "pick up" the HF gas at Sunndal with the probe used during the measurements, and prevents an exact comparison of the real variations between the different plants. Further studies of the effect of physically changing the feeder hole geometry in one cell may be useful for determining the reliability of the feeder hole measurements. This was not done in this work.

Measurements above an Open Hole in the Crust

Measurements were also done over an open hole in the crust. An advantage of measuring above an open hole versus the feeder hole is that it was not necessary to remove the probe every time the feeder fed the cell. In this way it was possible to determine whether or not it was necessary to be close to the feeder hole to detect any correlation between HF, moisture and feeding rate.

The results given in Figure 10 show clear indication of the variations in HF and H_2O concentrations during feeding of the cell. This is regardless of where the probe is located as long as it is above an open hole in the crust. The maximum level for HF was measured to be almost 27000 ppm which was significantly higher than the maximum value measured over the feeder hole. The fact that it was not necessary to remove the probe from the hole every time feeding took place, is believed to contribute to the higher maximum value measured. Another observation made was a change in flame colour in the hole during the cycle between every feeding. After feeding, the flame became bluish, turning more and more yellow until a new feeding was done.

Moisture Measurements and Moisture Importance

An observation that is worth noting is that the water level in the cell in general follows the HF levels. This is found both when measuring in the duct and above the open hole in the crust. However, this is not the case for the measurements done over the feeder hole as shown in Figure 7. In these measurements the moisture and the HF graphs show a negative correlation. This has to do with the fact that every time the feeder went down, the probe had to be removed from the hole. Also the feeder generated a lot of dust and this might give the apparent "drying" after feeding of the cell.

The measurements indicate that the moisture content of the alumina is an important factor contributing to the HF formation. Also, it seems likely that the HF adsorbed on the alumina in the dry scrubber, is released during feeding. This may, however, be determined by comparing primary alumina feeding with secondary alumina feeding.

Discussion of the Method

A filter was used to prevent dust from the crust and the bath to reach the measuring cell of the laser device. The laser instrument needs a transmission above 70 % and dust in the measuring cell will rapidly decrease the transmission. When measuring at Alcoa Mosjøen, the filter was changed several times. It was not possible to know exactly when the filter needed changing on site. An issue that has been considered, but not investigated is the possibility of the filter to adsorb HF. Tests on this matter can be a source of further work.

Summary of the Measurements

Table 1 gives a summary of the measured HF levels, both at Alcoa Mosjøen and at Hydro Sunndal.

Conclusion

In these measurements it has been established a strong correlation between feed cycle and HF evolution from the bath. It can be concluded that most of the HF evolution happen through open holes in the crust, both feeder holes and other holes in the crust. A maximum value of about 27000 ppm of HF was measured through an open hole in the crust. It can also be established a correlation between moisture and HF levels and they follow each other like "mirrors". The results indicate that the shape and diameter of the feeder holes can be a factor that decides how much HF it is possible to measure with this method.

Table 1: Summary of the results found in the different measuring campaigns.

Location	Range	Comments	Reference
Above crust, far away from feeder hole	5-10 ppm*	Oct 2008, SU4	[1]
Above open feeder hole	5-200 ppm*	Oct 2008, SU4	[1]
Duct	200-400 ppm*	Oct 2008, SU4	[1]
Above closed feeder hole	50 ppm	Oct 2008, SU4	[1]
Just above bath, open tap hole	3000-5000 ppm*	May 2010, SU4	[1]
In open feeder hole just above bath	9000-10000 ppm*	May 2010, SU4	[1]
Above open feeder hole	10000-20000 ppm*	June 2010, Mosjøen	This work
Above open hole in crust	15000-26000 ppm*	June 2010, Mosjøen	This work
Duct (open damper)	300-500 ppm*	June 2010, Mosjøen	This work
Duct (closed damper)	400-600 ppm*	June 2010, Mosjøen	This work

* Fluctuates according to feed cycle

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