Light Metals 2003 *Edited by Paul N. Crepeau* ***TMS (The Minerals, Metals & Materials Society), 2003***

HF EMISSION FROM DUBAL'S ELECTROLYSIS CELL

N. Aljabri[1], Dr.K.G. Venkatasubramaniam, Y.A.M. AlFarsi
Dubai Aluminium Company Limited
Dubai, Jebel Ali
U.A.E

Abstract

The overall goal for this paper is to gain better understanding of the environmental aspect of the aluminium smelting cell. It encompasses a study of the relative contributions of operational practices, duct flow, alumina feeding and ambient conditions to the overall HF generation and the different categories of emission distribution between the recycle system, the pot room roof and the stack. DUBAL has examined the influence of humidity on HF emission during the summer period, when the ambient temperature was 20 to 45°C and humidity pH_2O = 1 to 4 kPa. This study was undertaken separately in the cell duct and the pot room roof through continuous HF emission monitoring on different cell technologies, operating amperages and correlated to operating practices flow rate etc.
.

Introduction

Aluminium Fluoride is the most important additive in the electrolysis cell. In order to achieve good current efficiency in the cell, the target aluminium fluoride level, typically 10-14 %, is required to be maintained. Aluminium fluoride is consumed within the electrolysis cell by four main processes. The reaction with impurities in alumina, the hydrolysis reactions that produce gaseous HF and particulate, vaporization, and entrained particulates [1]. Haupin and Kvande classified the fluoride emissions into gaseous and particulate categories. Fluoride particulates become solid at low temperature and are removed with the carbon dioxide gases. Primary HF is formed by reaction between AlF_3 and the water contained in alumina and with the anode hydrogen. Secondary HF is produced from the hydrolysis reactions between the cell gases and air humidity. Haupin and Kvande assumed that the AlF_3, rather than other components in the bath, reacts with water to produce HF gas, and also that it reacts with Cryolite to produce vaporized $NaAlF_4$ [2]. This paper studies the potline hydrogen fluoride emission through the duct as well as through roof during summer period. Trials were carried out to study the HF emission variations due to alumina feeding, humidity and hot weather at the smelter [2]. An increase of pH_2O from 1.5 to 3.5 kPa showed a 100% increase in the baseline emission. The HF emission was studied corresponding to different duct flow rate as presented in [1]. As one of the main components in fluoride cycles in aluminum smelter, the roof emission was monitored. The roof HF emission was analyzed using Boreal continuous analyzer installed at the potroom roof and data collected for about 3 months [4].

Fluoride Emission From the Electrolysis Cell

Haupin and Kvande classified the fluoride emissions into gaseous and particulate categories. Fluoride particulates become solid at low temperature and are removed with carbon dioxide gases. Primary HF is formed by reaction between
AlF_3 and the water contained in alumina and with the anode hydrogen. Secondary HF is produced from AlF_3, rather than other components in the bath. Equation 1 is applied to calculate the amount of primary gaseous HF, which is a function of water in alumina and hydrogen in anodes

$$F_{GB} = \beta * \left(\frac{W_{ore}}{25.96 + 1.237 * W_{ore}} + \frac{H_{an}}{17.72} \right)^{1/2} \qquad \textbf{(1)}$$

Where; W_{ore} is the amount of water (%) in the alumina ore, H_{an} is the amount of hydrogen (%) in anodes and β is a constant calculated from alumina, AlF_3 reactivity and HF vapor pressure.

To calculate the amount of secondary gaseous HF, which is a function of gas suction and air humidity, Equation 2 is applied.

$$F_{GP} = \mu * HBA * \left(P_{H2O}\right)^{1/2} \qquad \textbf{(2)}$$

Where *HBA* is a weighting factor function of gas suction and amperage, P_{H2O} is the water pressure in the air, μ is a constant calculated from bath temperature, barometric pressure and current efficiency.

HF Duct Emission Measurement

Measurement was carried out using an infrared SRI HF monitor to measure the emission from a DUBAL cell [3]. In later studies Boreal analyzer was used but these did not incorporate simultaneous measurement of P_{H2O} .

The equipment was set as in Figure 1 and HF monitor was installed to measure the emission of a single cell by measuring a path length through outlet duct.

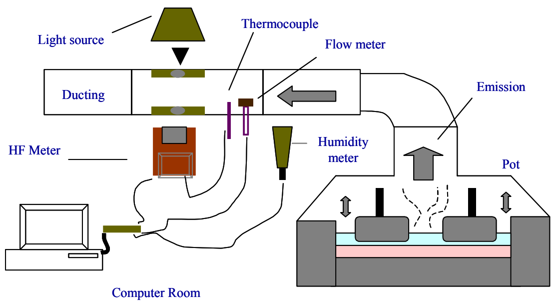

Figure 1: Equipment setup in cell duct

The monitoring system continuously monitored HF concentration, duct temperature, duct flow rate, ambient humidity and temperature. The alumina feeding, cell temperature, AlF_3 additions and metal tapped were also monitored.
The measurement was aimed at studying the effect of air humidity, gas suction flow rate and the alumina feed rate on HF emission. The impact of air humidity on HF emission was determined over periods characterized by different ambient humidity levels. The duct flow rate was varied from 6,000 to 11,000 Nm^3/h and the alumina feed rate from track window to over feed following the scenarios shown in Figure 2 [3]. The alumina trial was aimed to establish the effect of change of alumina feeding rate and bath concentration on the fluoride emission generation.

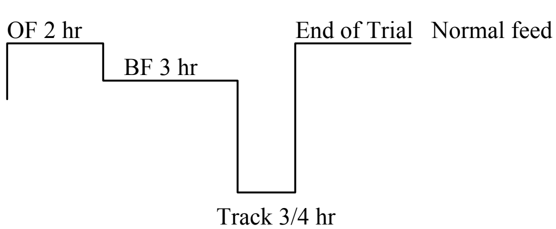

Figure 2: Demand feed trial

This attempted to find the effects of the dissolved water content in the bath during the track. A response curve should indicate the magnitude of this contribution. Alumina concentration was taken via bath samples to follow the decay of this content in the bath and was compared with the emission results. HF emission followed the same alumina feeding response pattern as shown in Figure 3.

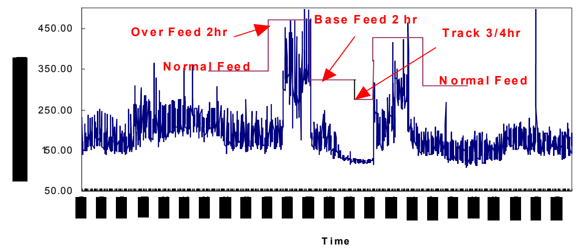

Figure 3: HF emission with Alumina Feeding

Varying the duct flow rate was tried. The HF emission increased by 20% corresponding to change of flow from 6000 to 11000 Nm^3/hr. The reason could likely be attributed to the thermal hydrolysis content of the cell's non-alumina emissions. The base measurements revealed that the alumina contribution was reasonably constant. As feeder hole state remained constant over the period of the trial and duct flow did not impinge on the alumina feeding rate, the alumina emission was unaffected by duct flow. This could be established, as the only other major contributor to the non-alumina was anode hydrogen generation. The main reason for this variation in HF emission due to the duct flow was the change in moisture content of the air flow for the estimated 40 ^oC, 40% relative humidity ambient conditions of that day as shown in Table 1.

Table 1: The results of the duct flow [3]

Duct Flow (Nm^3/hr)	HF (kg/tAl)	H_2O input decrease as compared to 11000 Nm^3 case, %
11000	36.96	0
11000	34.32	0
9000	34.56	18.18
7800	31.82	29.09
6000	22.08	45.45

Increasing the duct flow increases the moisture content entering in the cell. With constant vaporization rate, more water vapour enters the cell and reacts through the thermal hydrolysis.
The effect of the humidity could quite easily be seen on HF variations. This can be presented through equation (2). The trends were expected due to the thermal hydrolysis reactions of the non-alumina emission.

Roof HF Emission

The Boreal continuous analyzer was installed at the potroom roof and data collected for about 3 months. During this time, spot air velocity measurements were logged using a data-logging anemometer. The airflow data, combined with HF concentration, was used to estimate the HF emission data [4]. Figure 4 shows the HF emission average per day.

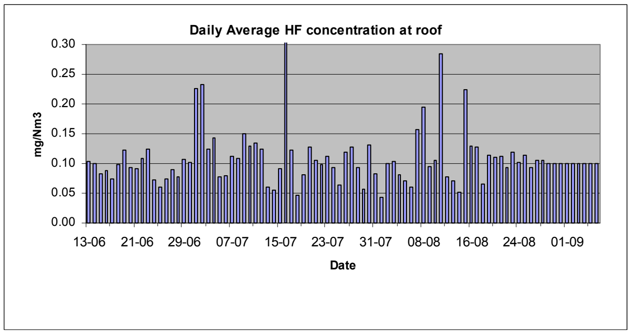

Figure 4: Daily variation of roof HF concentration

The grand average for the entire period was ~ 0.1 mg/Nm^3. The HF concentration was high on some days due to specific events such as shields opening, changing in suction rate, and breaking the crust for special measurements.
A typical daily graph of the HF concentration is shown in Figure 5. The individual events are marked on the graph for easy correlation.

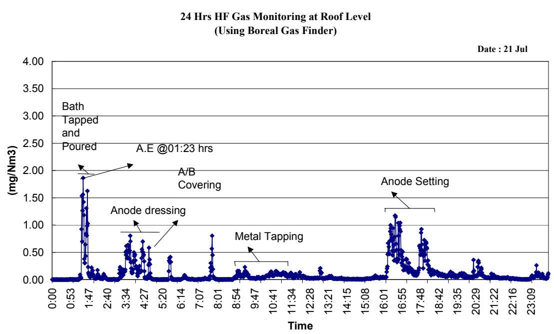

Figure 5: Daily HF roof emission

The contribution of daily operations, and special events, which can take place, is summarized in Figure 6.

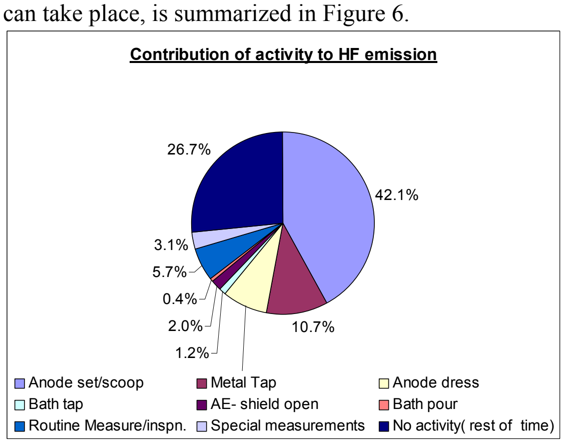

Figure 6: Contribution of Operation to HF emission

Anode setting and tapping are key contributors.

Though the average concentration of HF is low during idle periods, since the cell remains most of the period in this state, the contribution from this state is significant. This base level can be reduced by better quality of shielding, better maintenance practices for pot doors and shields, improved shield/ door designs, and higher gas off-take rate.
The importance of good pot shielding was amply demonstrated during the trial in which several pot shields were removed in quick succession. Approximately 0.1mg/Nm^3 increase was seen in the average per shield removed for the DUBAL cells studied .

Conclusion

The HF emission, which is generated inside the pot, is varying based on two components, namely the water contents in alumina, and the humidity of air. Both components are affecting the thermal hydrolysis rate to forward reactions.

The source of roof HF emissions are the hydrolysis reaction taking place in the bath (Primary HF) and the hydrolysis reactions of the fluoride particles (Secondary HF) but as a concluded in reference [5], is a function of hooding efficiency.
The roof emission is varying on daily basis depending on the operational practice and performance.

References

1. W. Haupin and H. Kvande, " Mathematical Model of Fluoride Evolution From Hall - Heroult Cell" Light Metals 1993, 257-263.

2. E. Patterson et al, " Understanding the Effect of the Hydrogen Content of Anodes on Hydrogen Fluoride Emission From Aluminum Cell", Light Metals 2001, 365-370.

3. E. Patterson, "Fluoride Emission From Aluminum Cells DUBAL's Industrials Trials", (Internal Report, Auckland University– Dubai Aluminum Company., September 2000).

4. Dr.K. G.Venkatasubramaniam, " Roof HF Emissions", (DUBAL internal report, 2002).

5. M. Hyland et al, "Changing Knowledge and Practices Towards Minimizing Fluoride and Sulfur Emission From Aluminum Reduction Cell" Light Metals 2000, 333-338.