

## ALUMINA STRUCTURAL HYDROXYL AS A CONTINUOUS SOURCE OF HF

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## Abstract

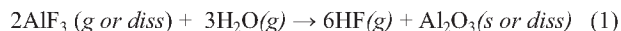
The link between moisture on alumina and HF generation in aluminium reduction cells has been long established. The assumption has usually been that the 'culprit' is the loosely bound adsorbed water, generating HF via bath hydrolysis as this surface water is flashed off during alumina feeding. Structural water, or more correctly, structural hydroxyl, also makes a significant contribution to HF generation. Laboratory experiments show that hydroxyl can dissolve in molten cryolitic electrolytes and gives rise to electrochemically generated HF. The electrochemically generated HF could be readily distinguished from HF generated via thermal hydrolysis.

Experiments with aluminas of varying combinations of high and low surface adsorbed moisture and structural hydroxyl (as measured by their LOI (20-300) and LOI (300-1000), respectively) confirmed the importance of electrochemically generated HF from structural hydroxyl. While some of the structural hydroxide reacts rapidly at the time of feeding, it also contributes to the steady state HF emission. From plant studies it was estimated that up to 8 kg F/tonne Al was generated from structural hydroxyl, for aluminas containing 0.4 wt % LOI (300-1000) and assuming 3wt% alumina in the bath. Structural hydroxyl is found in transition alumina phases in smelter grade aluminas. Their presence ensures that even conservative smelter specifications of surface areas of 60-80 m<sup>2</sup>/g can be met. Paradoxically, this surface area is specified to ensure that the HF adsorption capacity of the alumina is sufficient for scrubber requirements, but for reasons of both surface and structural water incorporation, having a high surface area also means that the alumina will generate more HF. This reopens the debate on the merits of high surface area aluminas.

## Introduction

Gaseous HF makes up roughly half of the total F emissions from aluminium reduction cells. Although HF and fluoride particulates evolved from the cell are captured with high efficiency in the dry scrubber, there is still reason for concern. Variability in HF evolution at the cell can affect cell chemistry, increase the demand on the dry scrubber and contribute to fugitive emissions. We have recently completed a major study of HF generation that examined the major mechanisms of formation in the cell and quantified the sources of HF [1,2,3].

It is generally assumed that HF is produced by the reaction of AlF<sub>3</sub> in the electrolyte or as a vapor with a source of H, as described by Equations 1 and 2.



The source of H may be

- Residual H in the anode
- Moisture in the air
- Water and hydroxyls in smelter grade alumina.

Quantification of duct HF levels in smelter studies showed that smelter grade alumina represents the largest single source of H for HF generation, Figure 1.

The bulk of the H in alumina is 'loosely bound' water that can be removed by heating alumina to 300°C. This consists of physio- and chemi-sorbed water and hydroxyl groups on the alumina surface plus some hydroxyl as gibbsite. LOI (20-300°C) values range between 0.6 – 2.0 wt%, but can change rapidly when surface water and hydroxyl are adsorbed or desorbed in response to changes in relative humidity [4]. A smaller fraction of H is incorporated into the crystal lattice of residual oxyhydroxides and transition aluminas. This 'structural hydroxyl' is driven off when smelter grade alumina is converted to α-alumina by heat treatment to 1000°C, and is measured as LOI (300-1000°C). Typical smelter

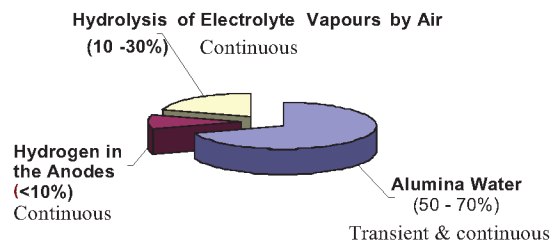


Figure 1: The relative contributions to total HF generation for the three major H sources.

grade aluminas have LOI (300-1000°C) values of 0.4-0.9 wt%. Of the total water/hydroxyl added with the alumina, only some 5 – 11% [1,5,6] reacts to form HF. Plant studies show that it reacts rapidly, giving spikes in the HF duct concentrations that correlate perfectly with alumina feeding cycles [1,7,8,9]. Because this is the largest source of HF in the cell, we were interested in understanding it better to develop strategies for its minimisation. Plant studies were carried out which improved our understanding, but also raised two important questions that were the motivation for the laboratory studies reported in this paper. First, we wanted to determine which type, the surface water/hydroxyl or structural hydroxyl was more important, and secondly whether hydrolysis of AlF<sub>3</sub>, or some other mechanism was responsible for the formation of HF.

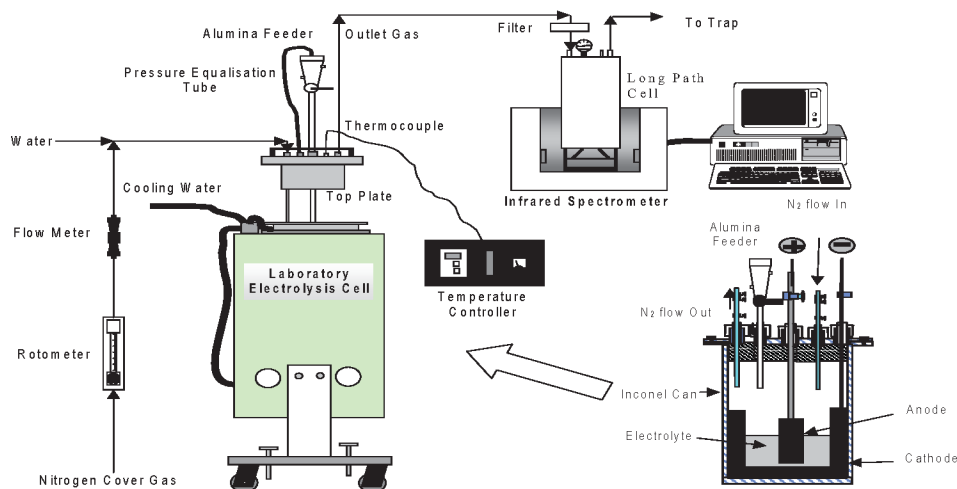


Figure 2: Schematic of the laboratory electrolysis cell and FTIR.

**Experimental**

A temperature controlled, laboratory scale electrolysis cell connected to a Biorad FTS-7 Fourier Transform Infrared (FTIR) spectrometer (Figure 2) was used to generate and monitor HF generation during electrolysis. The trials were conducted using an electrolyte with a composition of 10% excess  $\text{AlF}_3$ , 5%  $\text{CaF}_2$  and 3% or greater of highly calcined alumina and at a temperature of  $965^\circ\text{C}$ . Nitrogen cover gas was passed through the cell at a flow rate of 1.8 L/min, which carried the cell gases through to the FTIR. Electrolysis was conducted using a  $0.8 \text{ A/cm}^2$  current density, an anode-cathode distance (ACD) of 1.5 cm and a voltage set point of 4V. Graphite was used for both the cathode and the anode. In the latter case, graphite was selected to avoid HF generation from residual H in typical coke anodes. Current, voltage, HF adsorption peak intensity and gas flow rate were recorded for each 5 minute reading.

The exhaust gases from the cell were passed through a teflon filter to remove particulate before entering the long path gas cell of the FTIR. The transmittance in the near infrared range was measured at two HF peaks. These positions were chosen because of the low level of interference from water. The baseline transmittance was measured and subtracted from peak transmittance. Over the course of the experimental runs, the baseline degraded slightly, probably due to HF on the cell windows. For this reason, the peak intensities were not converted to HF concentrations. Nevertheless, the system was sensitive to changes in evolved HF throughout the course of the electrolysis, and the peak intensities are proportional to the HF concentration.

The generation of HF during alumina feeding was of particular interest. A pressure equalisation tube between the feeder and the cell was used to minimise air and moisture entrainment during the feeding process, which could be a potential source of HF. Smelter grade alumina was pretreated to generate samples with a range of LOI (20-300°C) and LOI (300-1000°C). The alumina designations, their pretreatments and LOI values are summarised in Table I. Reagent grade sodium hydroxide that had been dried and fused was also used for one series of experiments.

Some data from plant studies of HF evolution from individual cells is also presented for comparison with the lab results. Details of the plant trials can be found in [1,2,3].

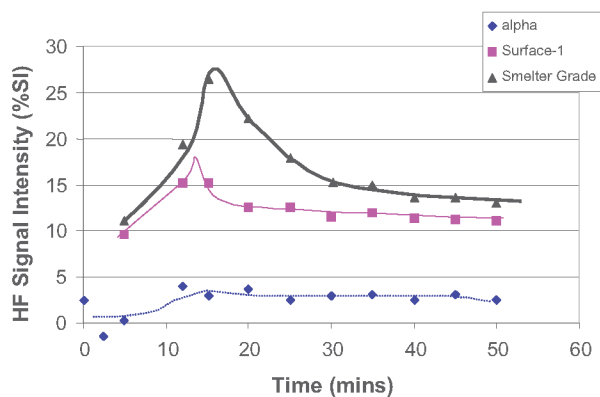
Table I: Alumina Samples Used to Generate HF

Description	Treatment	LOI (20 -300°C) wt %	LOI (300 -1000°) wt %
SG-1, Smelter grade alumina	Storage under ambient conditions	1.25	0.76
$\alpha$ -alumina	1000°C for 3 days, stored at 300°C.	0.46	0.0
Surface-1 alumina	1000°C for 1 day followed by storage at ambient humidity, 20°C	1.5	0.09
Surface-2 alumina	1000°C for 3 days followed by storage at 100%RH, 20°C for >4 days.	13	0.3
Structural-1 alumina	300°C for at least 3 days, then stored at 300°C until used.	0.15	1.2

**Results and Discussion**

Surface Hydroxyl/Water and Structural Hydroxyl

An initial series of experiments were carried out with three aluminas having increasing levels of total moisture. The results are shown in Figure 3. Electrolysis was allowed to reach a stable baseline HF emission prior to addition of alumina. The baseline HF emission was essentially zero, indicating that the graphite cathode and the highly calcined alumina already present in the electrolyte did not generate a significant level of HF. As each 10 g charge of alumina is fed to the cell, a measureable level of HF is recorded, peaking shortly after alumina addition and tailing away over the next 20-40 minutes (Figure 3). The results show the expected trend of increasing HF emission with increasing water/hydroxyl on the alumina, with the HF emission from  $\alpha$ -alumina barely rising above the baseline level. Comparing the Smelter grade and Surface-1, the larger and longer emission profile of Smelter grade alumina appears disproportionately larger than expected for its only 1/5 greater total LOI. Numerous repeats



**Figure 3 :** HF emissions after addition to the electrolysis cell of aluminas with varying surface and structural water/hydroxyl contents as measured by LOI (20- 300°C) and LOI (300-1000°C), respectively.

of this experiment gave the same relative HF emission levels. The biggest difference between this pair is in their LOI (300-1000°C) – SG-1 has an eight times greater structural hydroxyl content. This suggests that the structural hydroxyl plays the more important role in HF generation.

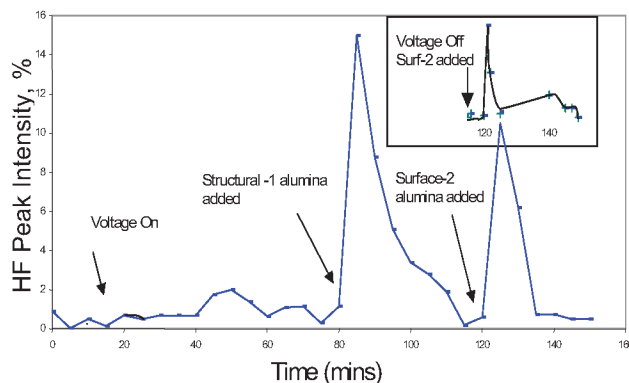
To explore this hypothesis further, two additional alumina samples were prepared with extremes of differences in their LOI (20-300°C) and LOI (300-1000°C). Surface-2 alumina was prepared with a very high surface water/hydroxyl level, and low LOI(300-1000), while Structural-1 was the reverse. It was not possible to prepare the samples with the same total LOI, but as the results show, this wasn't important.

Figure 4 shows the resulting HF emissions when these aluminas were added sequentially to the operating electrolysis cell. For the same weight of fed alumina, Surface-2 alumina consistently gave lower intensity HF emissions and of shorter duration compared to Structural-1. This is remarkable, given that Surface-2 has roughly ten times greater total LOI. The difference is clearly due to the greater structural hydroxyl content Structural-1, which has an LOI (300-1000°C) of 1.2 wt% compared to 0.3 wt% for the Surface-2 alumina.

Table II: HF emissions for normal and hydrated alumina fed to a commercial Al reduction cell.

	LOI (20-300°C), wt%	LOI (300-1000°C), wt%	Ave HF emission, kg/tonne Al
Primary alumina	1.58	0.67	17.98
Hydrated Primary alumina	4.46	0.72	17.73

The more minor role of surface hydroxyl/water was also reflected in plant studies. There was no significant difference in the quantity of HF evolved when feeding alumina that had been hydrated by exposure to high relative humidity compared to the



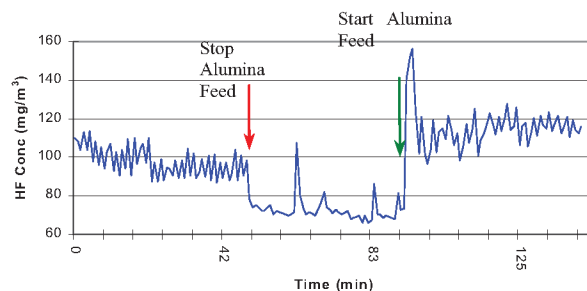
**Figure 4 :** HF emissions after addition to the electrolysis cell of aluminas with varying surface and structural water/hydroxyl contents as measured by LOI (20- 300°C) and LOI (300-1000°C), respectively. The inset shows the HF emission when Surface 1 alumina is added to the cell The same axes apply.

conventional smelter grade alumina. The results of this trial are summarised in Table II.

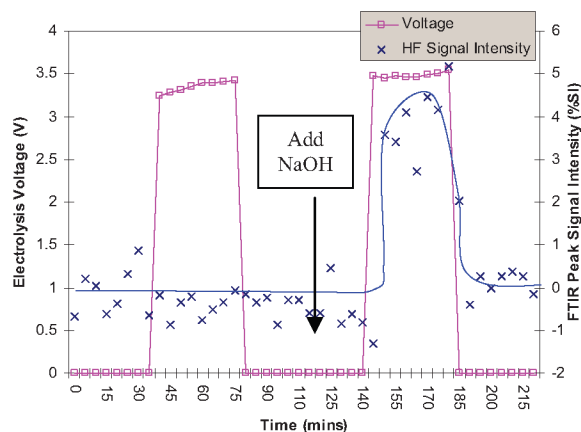
The surface water/hydroxyl is expected to be rapidly flashed off as the alumina is fed into the cell. As it is flashed off it may hydrolyse  $AlF_3$ , or  $NaAlF_4$  vapour forming HF by Equations 1 and 2, above or below the crust.

Thermodynamic calculations [1] show that these hydrolysis reactions will generate significant quantities of HF only if the temperature is above 400°C. In other words, the water vapourised from alumina will only generate measureable HF while it is under the crust or in the flame since these are the regions where the temperature will be high enough. If it is carried away from the hot zones quickly, very little HF will be formed by the surface water/hydroxyl via hydrolysis (Eqns 1,2). Structural hydroxide, on the other hand is more slowly released as the alumina dissolves in the electrolyte. In this way, it is more efficient in generating HF because it can enter the electrolyte, ensuring better contact with dissolved  $AlF_3$  and for a longer time.

Indirect evidence for the importance of structural hydroxyl also came from analysis of HF evolution from commercial reduction cells. Figure 5 shows that when feeding is stopped, the HF level



**Figure 5:** Decay in HF evolution from a commercial cell during a non-feed period.



**Figure 6:** HF evolution following addition of NaOH to lab electrolysis cell.

decreases at a rate comparable to the alumina dissolution rate [2]. Others have noted a similar decay [7,9]. It is reasonable to assume that this is related to the release of structural hydroxyl from transition aluminas in the smelter grade feed.

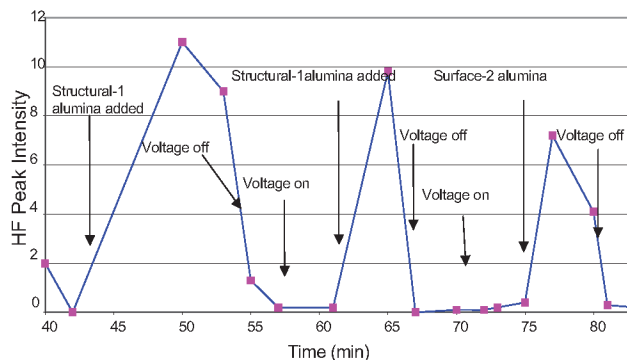
Further evidence for the importance of hydroxyl was demonstrated in experiments in which NaOH was fed to the electrolysis cell. Because NaOH is hygroscopic, it was heat treated prior to addition to remove water and avoid complication from HF that may be formed when the water is released. Figure 6 shows the results. Prior to the addition of NaOH, the baseline HF signal is essentially zero. The alumina present in the electrolyte was highly calcined so did not contribute HF. After addition of NaOH significant quantities of HF are produced.

The possibility of a dissolved water or hydroxyl species in cryolite electrolytes was postulated by Grjotheim et al [10] when considering Henry’s early studies of HF generation [5]. They suggested that water could be dissolved as hydroxyl, given the similarity in size, charge and polarizability of hydroxide and fluoride, hydroxide often substitutes for fluoride. The results represented here confirm that hydroxide, whether from NaOH or from structural hydroxyl in smelter grade alumina, can enter the electrolyte and give rise to HF formation.

HF Generation by Electrolysis or Hydrolysis

Having clearly established that the structural hydroxyl in alumina is the more important generator of HF, it was important to determine whether it also produced HF by hydrolysis, as described by Eqn 1, or by some other reaction scheme. If hydrolysis is the mechanism, then HF will be generated irrespective of whether or not there is an applied voltage on the electrolysis cell.

In Figure 6, NaOH was added at 120 minutes, with no applied voltage on the cell. No HF is generated until the voltage (4V) is re-applied at 140 minutes. When the voltage is returned to zero, (180 minutes) the HF evolution ceases. Evidently, the reaction between hydroxide and electrolyte is not a simple thermal hydrolysis, but is an electrolytic process. Cutting the voltage also terminates HF evolution when the source of the hydroxide is alumina.



**Figure 7:** Influence of applied voltage on HF evolution.

The same phenomenon could be reproduced with alumina additions. Figure 7 shows an experimental run in which Structural-1 and Surface-2 aluminas were added to the lab cell and the voltage terminated and reapplied at various points during the experiment. Sample additions of 10 g of were made, after which for Structural-1 normally took 25-30 minutes for the HF signal to return to the baseline. When the voltage is cut, the HF evolution is likewise terminated, the FTIR signal returning to the baseline 12 minutes and 5 minutes, after the first and second Structural-1 additions. HF generation after addition of the Surface-2 sample was also terminated early when the applied voltage was set to zero. Interestingly, HF evolution does not re-commence once the voltage is restored.

The rate of HF evolution from structural hydroxide was measured using the plant data collected during non-feed periods for two different cell technologies (as in Figure 5). The linear decay correlated well with calculated and measured alumina concentrations. Total HF emissions during this linear decay period indicates that this slow generation of HF can contribute between 2.5 – 8.6 kg HF/tonne Al, Table III.

Table III: HF Emission from structural hydroxyl, during linear decay period.

Cell Technology	Alumina consumption (kg.min)	HF decay rate, kgF/tonneAl/min	HF Emission KgF/tonne Al
I	1.7	$3.35 \times 10^{-2}$	2.5
II	2.6	$1.14 \times 10^{-1}$	8.6

The large variation between the two technologies is not surprising. Although both were point-fed prebake cells, there were notable differences in the crust quality and cover practices, and in the alumina specifications. A number of factors will affect the measured HF evolution from each cell, including:

- Structural hydroxyl content, as measured by LOI (300-1000°C): Technology II had a 30% greater LOI (300-1000°);
- Alumina dissolution rate;
- Kinetics of the electrolytic HF generation which are expected to be affected by cell chemistry, voltage and current;
- Capture of HF by the crust. The crust can scrub HF and the efficiency for scrubbing will be determined by crust conditions, number of holes etc.

While structural hydroxyl apparently reacts primarily by an electrolytic reaction, some thermal hydrolysis also occurs. The extent of thermal hydrolysis was tested by adding aluminas to the

cell, with the voltage set to zero, thus eliminating any contribution for electrolytic HF generation. The inset in Figure 4 show the measured HF when alumina is added to the lab cell when the voltage is zero. The level of HF generated for Surface-2 alumina is approximately 80% lower than when the voltage is at its usual 4 V setting. A similarly small emission was measured for Structural-1 additions without electrolysis. At this stage it is not possible to say whether this is hydrolysis of surface water/hydroxyl or structural hydroxyl.

In summary, approximately 5-11% of the total water/hydroxyl on alumina reacts to generate HF. Most of this is structural hydroxyl, i.e. hydroxyl groups incorporated into the crystal lattice of partially calcined transition aluminas in smelter grade alumina and measured as LOI (300-1000°C). It reacts with electrolyte to form HF via an electrolytic process, though a small proportion may also hydrolyse. The evolution of HF from structural hydroxyl closely tracks the dissolution rate of alumina, because it is the dissolution process which releases hydroxide ions into the electrolyte. Thus, there is initial rapid generation of HF when alumina is fed, but HF continues to be generated for some period after feeding.

Surface water/hydroxyl is rapidly desorbed. Its HF generating capacity is limited by the residence time in hot zones of the cell (i.e. under the cover and in flames) where it may hydrolyse  $\text{AlF}_3$  or  $\text{NaAlF}_4$  vapour.

#### Implications for Smelters

The generation of HF is clearly linked with the LOI (300-1000°C) content of the feed alumina. Its reaction with electrolyte will give peaks in emissions at feed, but also contributes to the baseline generation of HF as slowly dissolving alumina continues to release hydroxyl. There will be variations between technologies and even between cells in the efficiency of HF generation from structural hydroxide, which is expected to depend on voltage, current, cell chemistry and factors such as superheat which affect alumina dissolution rate. Furthermore, HF duct concentrations will depend on those factors that affect the mass transfer of HF from the cell, the main factor being crust integrity. A number of plant studies [1,7,8] have confirmed that poor crust condition and presence of holes is correlated with higher HF emissions from the cell. While some of this is due to exposure of electrolyte vapours to cell draft and its consequent hydrolysis, results presented by Slaugenhaupt *et al.* show that the holes affect the scrubbing capability of the crust [7]. HF produced from structural hydroxyl under the crust will be channeled out through holes instead of diffusing through the crust where it can be captured.

The obvious role of structural hydroxide in HF generation prompts a re-examination of the specifications of smelter grade aluminas. BET surface area is usually specified in the range of 45 – 80  $\text{m}^2/\text{g}$  to ensure a high efficiency of HF capture in the dry scrubber. High surface area is achieved by ensuring that the alumina is not too highly calcined: fully calcined  $\alpha$ -alumina has a very low surface area, it is the less calcined transition alumina phases which contribute most to the surface area. Unfortunately, higher surface area will be accompanied by higher LOI (300-1000°C). On the other hand, reducing LOI (300-1000°C), while lowering the surface area, will also reduce the amount of HF generated, reducing the load on the dry scrubbers. It may be possible to strike a balance between LOI (300-1000°C) which

gives reduced HF generation and still meets the performance requirements of the dry scrubbing system.

#### **Conclusions**

Structural hydroxyl, present in smelter grade alumina in the transition alumina phases, and measured as LOI (300-1000°C) has a much more significant role in generating HF than surface adsorbed water/hydroxyl (LOI (0-300°C)). Structural hydroxyl has a longer residence time, being released as the alumina dissolves. Furthermore, it produces HF by an electrolytic process, not by simple thermal hydrolysis as has long been assumed. Its reaction with electrolyte will give peaks in emissions at feed, but also contributes to the baseline generation of HF as slowly dissolving alumina continues to release hydroxyl. Reducing cell emissions may be achieved by using aluminas with a lower LOI (300-1000°C). Although this will also reduce the alumina scrubbing capacity, the HF loading on the scrubber is also reduced. Ensuring good cover condition will also reduce the amount of the generated HF which can leave the cell, by enhancing the amount of HF which is scrubbed by the crust.

#### **References**

1. E. Patterson, M. Hyland, B. Moxnes and B. Welch, 'Reducing hydrogen fluoride emissions from aluminium electrolysis cells.' Proceedings of the Seventh Australasian Smelting Technology Conference and Workshop, Nov. 11-16, Melbourne Australia, 92-105, 2001.
2. E. Patterson, M. Hyland, V. Kielland and B.J. Welch, 'Understanding the effects of the hydrogen content of anodes on hydrogen fluoride emissions from aluminum cells.' *Light Metals* 2001, 365-370.
3. E. Patterson, 'Hydrogen Fluoride Emissions from Aluminium Electrolysis Cells.' (PhD thesis, The University of Auckland, 2001).
4. M.M. Hyland, A.R. Gillespie and J.B. Metson, "Predicting moisture content on smelter grade alumina from measurement of the water adsorption isotherm." *Light Metals* 1997, 113-117.
5. J.L. Henry, 'A study of the factors affecting fluoride emission from 10,000 ampere experimental aluminum reduction cell.' In *Extractive Metallurgy of Aluminum*, vol. 2, G. Gerard, Ed. Interscience, New York, 67-81, 1963.
6. W.E. Wahnsiedler, R.S. Danchik, W.E. Haupin, D.L. Brackenstose and J.W. Colpitts, 'Factors affecting fluoride evolution from Hall-Heroult smelting cells.' *Light Metals* 1978, 407-424.
7. M.L. Slaugenhaupt, J.N. Bruggeman, G.P. Tarcy and N.R. Dando, 'Effect of open holes in the crust on gaseous fluoride evolution from pots.' *Light Metals* 2003, 199-204.
8. E. Sum, C. Beeby, S. Campbell and K. Gadsby, 'The effects of cell condition and operations on hydrogen fluoride evolution in an industrial cell.' Proceedings of the Seventh Australasian Smelting Technology Conference and Workshop, Nov. 11-16, Melbourne Australia, 67-78, 2001.

9. N. Aljabri, K. Venkatasubramaniam and Y.A.M. AlFarsi, 'HF Emission from Dubal's electrolysis cell.' *Light Metals* 2003, 487-489.
10. K. Grjotheim, H. Kvande, K. Motzfeldt and B.J. Welch, 'The formation and composition of the fluoride emissions from aluminium cells.' *Canadian Metallurgical Quarterly*, **11(4)** (1972) 585-599.