

UNDERSTANDING THE EFFECTS OF THE HYDROGEN CONTENT OF ANODES ON HYDROGEN FLUORIDE EMISSIONS FROM ALUMINIUM CELLS.

E.C. Patterson¹, M.M. Hyland¹, V. Kielland² and B.J. Welch¹.

¹High Temperature Materials and Processing Group,
The University of Auckland, Private Bag 92019, Auckland, New Zealand.
²Hydro Aluminium, Technology Center Årdal (R&D), N-6884 Øvre Årdal, Norway.

Abstract

Recent reviews have pointed to the need to clarify the contribution of the identified sources of fluoride emissions from aluminium cells. Of all the sources investigated, the influence of the residual hydrogen content of prebaked carbon anodes is the least understood. This paper outlines both experimental and industrial results of such an investigation. In laboratory studies, HF generated from an experimental electrolysis cell was analysed using a FTIR spectrometer. It was found that the reaction of this hydrogen content (0.03 to 0.08 wt% of the anode) with the electrolyte was approximately 10% complete, resulting in a large HF generation from the anode surface. This was also seen in industrial measurements. In the in-plant studies it was found that if the emission was broken down into the variable alumina feeding contribution and a constant non alumina contribution, the anode hydrogen reaction contributes almost 10% of this non alumina emission. The unreacted H then could possibly add to the dissolved water generation and/or secondary HF generation. Hence, in an overall emission reduction scheme the effectiveness of the anode baking process contributes to an important portion of the total HF emissions.

Introduction

The importance of identifying the sources of hydrogen fluoride (HF) emissions in the aluminium smelting process has been proposed for many years now. In the past there has been a limited study of contribution sources, which reveal a limited breadth of understanding. Henry's [1] foundation study in 1963 highlighted the major sources and approximate contributions. Grjotheim *et al.* [2] then published a comprehensive review of the fundamental theory and studies in 1971. Further studies in the 1970's, most notably by Wahnsiedler *et al.* [3] in 1978, added to this understanding. All these studies identified the main sources of generation of HF being from the moisture of the alumina, the hydrogen content of the anode and a particulate hydrolysis contribution. However this data and the relative contributions of these sources differ for the present smelting technology, as most of these studies were prior to the widespread introduction of dry scrubbing technology and the use of more acidic electrolytes.

Furthermore, these past studies present overall generation results without a detailed consideration of some of the underlying formation sources. Only a general view was taken, with some contributions overlooked, or worse ignored. Of these, primary generation of hydrogen fluoride from hydrogen sources in the anode is perhaps the least understood. This paper aims to address some of the questions raised about the significance of this source, and how it affects the overall emissions reduction scheme of an aluminium smelter.

Background

This paper follows from a study of the alumina water reaction in the bath (refer to Patterson *et al.* [4]). Here it was proposed that only a certain amount of structural water reacts in the bath to form HF. It was also shown that the surface fluoride in secondary alumina was shock heated when added to point feeder holes due to the temperature change experienced. This causes a surface reaction which retains more than 90% of the fluoride on the alumina upon addition to the bath. Hyland *et al.* [5] provide a review of this study and a detailed summary of the other different sources of hydrogen fluoride from the smelting process.

Figure 1 highlights the major sources of these emissions. Essentially two forms of fluoride emissions, gaseous hydrogen fluoride and particulate fluoride are generated continuously from

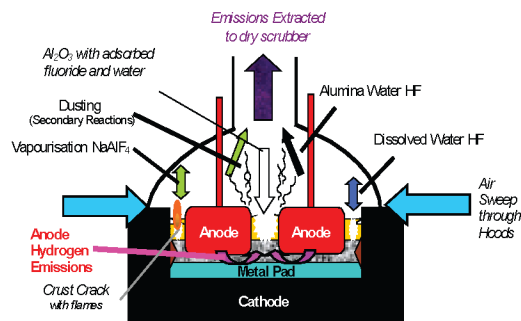


Figure 1: The important aspects of fluoride generation in an industrial aluminium smelting cell.

Table I Henrys [2] anode hydrogen HF evolution results.

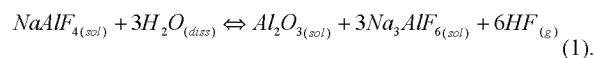
Type	Anode H (wt%)	Bath Ratio	Al ₂ O ₃ (wt%)	Calc*	Temp (°C)	Fluoride Emission (kg/tonne Al)		
						Gaseous	Particulate	Total
Carbon	0.06 – 0.08	1.48	4.23	4.3 – 5.7	976	3.9	15.1	19.0
Carbon	0.06 – 0.08	1.49	2.13	4.3 – 5.7	975	4.4	14.1	18.5
Graphite	0.01	1.46	3.09	0.72	971	2.0	10.4	12.4

*Calculated using equation 2 for the stated anode hydrogen contents.

the fluoride-based electrolyte of aluminium smelting cells. These fumes are extracted from the enclosed smelting cell to a dry scrubbing process and the fluoride content is recycled back to the cell via capture on the scrubbing (secondary) alumina.

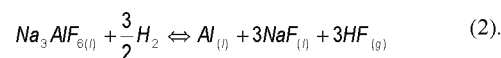
The *particulates* are generated via vapourisation processes from exposed electrolyte and also entrainment of particulate materials from the bath, alumina feed and crust during evolution of the gases. A significant portion of these leave with the cell gases (CO, CO₂) and burning of this hot gas-particulate mixture when it contacts air can result in thermal hydrolysis of some of the particulate fluoride with the formation of hydrogen fluoride. This source has been termed as *secondary generation* of hydrogen fluoride for this paper. This is HF generation outside the cell electrolyte.

HF generation from hydrogen within the anode and from water introduced to the electrolyte is associated with *primary generation* of *hydrogen fluoride*. This contribution can occur from a number of sources within the cell. With the modern low alpha aluminas which contain a hydrate or structural content, an equivalent water concentration can be present dissolved in the electrolyte. Such *dissolved water* could undergo a hydrolysis reaction with the aluminium fluoride (or more correctly, NaAlF₄) constituent of the electrolyte according to equation 1:



Similarly, while the cell is being fed, additional adsorbed water (adsorbed on the alumina surface from the surrounding atmosphere) may be released and undergo a similar hydrolysis reaction. Hyland et al. [9] suggests that this water content is loosely held on the surface and would be released when experiencing such a temperature change. Here the reacting phase would be gaseous and undoubtedly the residence time would be short. A past study has also suggests that part of the structural water content could undergo a similar process as a result of the alumina dissolution process[4].

A third source of primary hydrogen fluoride is from the hydrogen content of the anode (either from adsorbed hydrogen or hydrocarbon). Henry [1] demonstrated that the hydrogen of the anode gives rise to a significant amount of hydrogen fluoride in less acidic electrolytes. There is also undocumented but widely accepted evidence that the HF emission in Söderberg cells is higher due to this content [6]. This residual anode hydrogen content is thermodynamically fairly stable, since the anode has been baked to cell temperatures earlier. However since the anode has a potential of at least 1.5V, there are several possible oxidation reactions that this hydrogen can undergo. All these can be represented by the overall electrochemical HF formation reaction (2) which requires a voltage of ~ 1.28V:



Previously Grjotheim et al. [2] suggested that the hydrogen was initially oxidised by the anode carbon dioxide to form water, and this water subsequently hydrolysed the sodium tetrafluoroaluminate to form gaseous hydrogen fluoride. However one can not distinguish between any of the proposed mechanisms, because the anode is at a potential that enables both electrochemical oxidation of the hydrogen to water and the direct formation of hydrogen fluoride. While parallel reactions can occur (resulting in an incomplete fraction of hydrogen converted to hydrogen fluoride) kinetically and mechanically direct formation is a more feasible mechanism, since the concentration of the fluoride ions far exceeds those of oxide ions.

On the total amount of hydrogen converted, Hyland et al. [5] proposed that if equation 2 is used as a basis for calculation, then theoretically an anode containing 0.08wt% hydrogen could generate 5.7 kg/tonne Al of HF. However, there is doubt as to the fraction of this hydrogen content which reacts. This is seen in the results of the two previous studies.

The first significant study by Henry [1] in 1963 perhaps reveals the best information on the amount of fluoride evolved from the anode. Here a 10000 ampere experimental prebake anode reduction cell was used to generate the cell gases. Three different anodes were used. A graphite anode containing 0.01 wt% H, one under-baked at 960°C (0.08% H) and one baked at 1069°C (0.06% H). With respect to current technology the bath composition (a much lower AlF₃ content) and alumina used were quite different, with a different alpha content and structural water. Emissions were analysed from batch samples using chemical analysis of the emission extracted from below the crust, using a purpose built vent hole. The results are summarised in table I. Here the gaseous emissions increase, with a corresponding increase in the particulate emission with increasing anode hydrogen content.

Henry concluded the anode hydrogen fluoride emission was a significant HF generation source. He did not explain his results in terms of its overall contribution or give a qualifying mechanism scheme. However Grjotheim et al. [2] noted that if the graphite generation is taken as a zero basis, then it can be calculated that hydrogen in the anode is responsible for approximately 48 to 52% of the HF emission or 10 to 12 % of the overall generation. Using the theoretical reacted amounts (in the calculated column of table I) this amounts to approximately 50% of the H in the anode reacting.

Wahnsiedler et al. [3] studied fluoride evolution from a 170 kA prebake cell that had an anode hydrogen content of 0.093%. Hydrogen fluoride was measured using the Alcoa gaseous fluoride analyser (a semi continuous in situ chemical analysis

method) above the crust. Using the regression coefficients from some measurement sets and a few assumptions, the breakdown of the hydrogen sources generation was presented as shown in table II.

Table II Wahnsiedler et al. [3] hydrogen source evolution results

Source	Total (H)	Fraction Converted (%)	Evolution Rate (kg F/t Al)
Alumina Water	46 g/min	8.6	9.63
Anode H ₂	0.093%	8.7	0.76
Air Sweep	871 g/min	0.26	5.47

Due to the broad nature of each study it is questionable whether an accurate measure of the anode hydrogen contribution has been gauged. However, the use of these figures is widespread. Even Haupin and Kvande's [7] evolution model uses Wahnsiedler et al.'s [3] H reaction figure of 8% in their model when predicting the overall HF emission.

Therefore, the practical question is how much hydrogen in the anode is converted to the hydrogen fluoride in electrolytes used today? Other questions linked with the primary hydrogen fluoride evolution revolve around the proportion formed from gaseous versus dissolved water. Kinetically the contribution from both sources is expected to increase as the aluminium fluoride concentration increases (refer to equation 1). All sources are interlinked, and gauging the amount of one contribution sheds information on the relative contributions of the others.

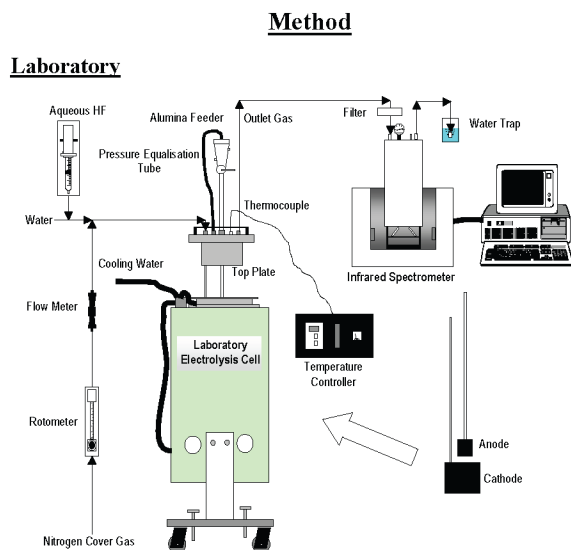


Figure 2: The experimental laboratory apparatus.

Laboratory studies of the anode HF generation potential were performed using a laboratory scale electrolysis cell connected to a FTIR spectrometer to monitor the hydrogen fluoride emissions generated from electrolysis (refer to figure 2). The IR adsorption peak at 4073.9 cm⁻¹ was monitored. For the trials, the cell with bath composition 10% excess AlF₃, 5% CaF₂ and 3% or greater alumina was heated to 962°C. The flow rate of the nitrogen cover gas was monitored to gauge a duct gas velocity.

Three different anodes were used in electrolysis (0.8 A/cm² current density):

- Low hydrogen anode – baked at 1200°C
- High hydrogen anode – baked at 900°C
- Graphite anode

The hydrogen content of each anode is presented in table III:

Anode	Bake Temp (°C)	Hydrogen Content (%)
High Hydrogen	900	0.094
Low Hydrogen	1200	0.042
Graphite	---	0.003

Over the trial period 10 g of alumina was fed per hour to replenish the alumina content of the bath. Alpha alumina was fed for the first two cycles, followed by a single feed of smelter grade alumina. All responses were recorded.

Industrial

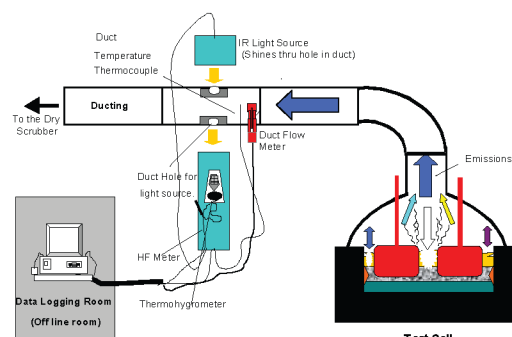


Figure 3: The in-plant study equipment.

In-plant fluoride measurements in the cell duct were recorded using an infrared based adsorption HF meter (refer to [8] for details) in the configuration shown in figure 3. Here the outlet (duct) HF concentration of a point fed, 170 kA cell (with an average anode hydrogen content of 0.044 wt%) was measured continuously and was correlated with continuous measurements of ambient temperature, humidity, duct gas flow, duct temperature, feeder hole state, crust integrity and amount of alumina fed.

To establish the various contributions, the study used comparative analysis of emissions produced under process changes compared to baseline 'normal' emissions. The baseline was established to be emissions without interference. Alumina feed, bath chemistry, and crust cover were varied and the responses measured.

Results

Laboratory

Figure 4 compares the three emission results for the three different anode types. The high hydrogen emission shows the typical profile changes. During bath heating (0<t<20min) virtually zero emission was observed. The anode was then

immersed into the bath and electrolysis started. This causes a slow rise in the HF emission as gas generation begins and the anode starts to be consumed. This will eventually reach a steady state emission level (here SI= 9.5% at 45 minutes). To avoid anode effects, alpha alumina was added after 40 minutes of electrolysis. Here a slight rise in emissions is seen due to the residual water content of the alumina, and possibly some hydrolysis effects from the feed air moisture. This then decays back to a second steady state level (SI = 10.9%). SG-alumina (smelter grade) was then added after 2 hours. This has a higher peak due to the higher water content of this alumina. Due to experimental limitations the peak of this curve was not recorded. It is likely that the actual peak is higher than this. After maximum emission the HF level decays back to the final steady state emission level (SI = 12.0%). For each run the three steady state levels and their calibrated emission levels (using an approximate calibration curve for the signal intensities) are presented in table IV.

Anode	Emission (mg/m ³)		
	SI	Emission	Difference
<i>High Hydrogen</i>			
Steady State 1	9.5	116.0	0
Steady State 2	10.9	143.8	27.8
Steady State 3	12.0	170.3	26.5
<i>Low Hydrogen</i>			
Steady State 1	5.0	58.1	0
Steady State 2	7.5	85.3	27.0
Steady State 3	9.4	114.2	28.9
<i>Graphite</i>			
Steady State 1	2.9	42.0	0
Steady State 2	6	67.7	25.7
Steady State 3	8.3	96.4	28.7

Clearly all three runs have an obvious difference in each steady state level generation (refer to table IV). Here the high hydrogen anode has higher HF emission, than the low hydrogen anode, which has a higher emission than the graphite anode. It is proposed that the difference in steady state levels is an alumina effect related to the alumina equilibrium with a dissolved water content in the bath (refer to equation 1). Hence the greater the alumina concentration in the bath the greater the amount of

dissolved water associated with this content (i.e. it is in equilibrium with this content).

Hence when more alumina is added, the steady state level to which the emission decays, will be higher. This is seen in the difference between the steady state levels in table IV. This difference for the 10g addition is consistently 27 mg/m³. This equates to an emission contribution of 11 mg/m³ per alumina wt% in the bath. Hence for this trial the graphite emission is effectively measuring the dissolved water emission, as its anode hydrogen content is negligible (in light of the proceeding results).

Hence the graphite run can be used as a basis to calculate the average H in the anode emission for the high and low anode emissions. This can be converted to an approximate reaction efficiency using equation 2 to calculate the possible generation level of HF from each hydrogen content (refer to table V).

Anode	Emission (mg/m ³)		
	Ave HF	Calculated	% Reacted
High Hydrogen	75	510	14.7
Low Hydrogen	17	230	7.4

Note that the difference in the values is due to the assumption that the dissolved water content at the start of all three runs is the same. Due to possible differences in heating conditions and dissolved water retention on start up this may not be the case. Overall an average hydrogen conversion factor of 10% can be estimated. These are approximate values as there were calibration difficulties encountered for the FTIR instrument. However looking at the rough estimates of the percentage of H reacted shows that these values agree with the previous figure published by Wahnsiedler et al. [3] (8%). It does not agree with the 50% reaction value calculated by Grjotheim et al.[2] from Henry's results. It must be noted again that the conditions used by Henry differ vastly from those studied here.

This partial reaction of the anode hydrogen follows the trends proposed by the other past studies. As Wahnsiedler et al. [3] suspected, this is likely due to the rate at which CO and CO₂ are produced and emitted. The conversion of C to these species is an order of magnitude greater than that of H to HF. This results in a

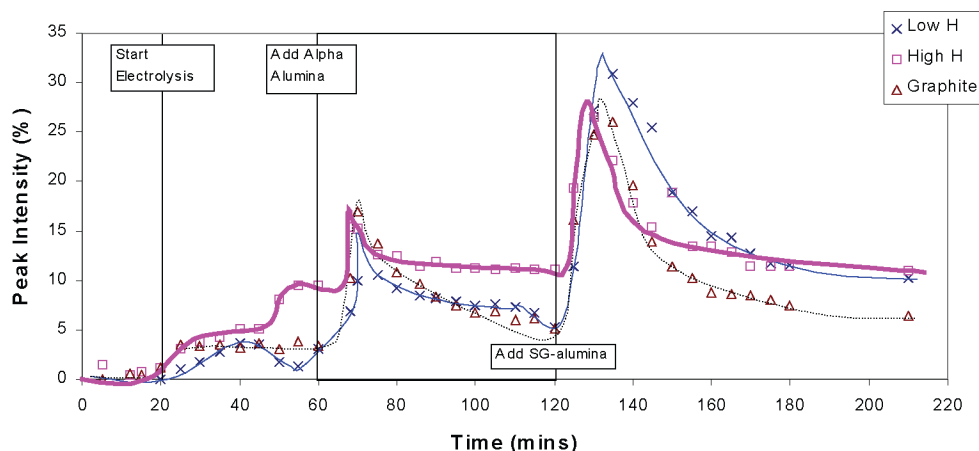


Figure 4: Emissions from different anode materials used during laboratory electrolysis.

large amount of gas being evolved from the same surface as the HF reaction is initiated. Hence, not all of the hydrogen in the carbon will contact the electrolyte and not all will react with this either, given the reaction kinetics. Obviously the higher the hydrogen content, the greater the probability that some will react. Interestingly the remainder of this H is likely to either form part of the dissolved water content of the bath (refer to [2]), or if swept away in the anode gases it could be carried to the extraction system with the other fumes through the crust. Depending on the crust integrity this content will contribute to secondary HF generation (thermal hydrolysis of the particulates at the vents).

Another interesting point is when alumina is added to all runs, the same spike response in the emission is seen. In the high hydrogen anode the addition of SG-alumina results in approximately 6000 mg/Nm³ extra HF generation at the peak. This results from rapid primary generation from the evolved alumina water. Patterson et al. [4] showed this may be caused by the structural water in the alumina. Here 10g of alumina was added. It has approximately 0.8% wt structural water, which is equivalent to ~1600mg HF total (if AlF₃ is assumed to react with H₂O to form Al₂O₃ and HF). This suggests like the results of past studies [3, 4] a fraction of the structural water reacts. Here approximately 20% of the structural water (~320mg) could be calculated to react over the 50min SG-alumina emission period. Once this water has reacted, the response decays down to the steady state level. Again the unreacted water could provide moisture for secondary HF generation at the crust/air interface. Even the alpha alumina used in these runs has a minor amount of water. Furthermore, the greater the structural water content, the higher the spike is, as the smelter grade alumina addition vs. the alpha alumina response illustrates. The spike heights should be directly proportional to the structural water content and fraction of the water reacted with the bath. This is an additive effect, where the alumina water HF emission adds on top of a constant non alumina steady state emission (here attributed to anode hydrogen and dissolved water content). This is also seen in the industrial measurements and results in a decoupling calculation, which simplifies emission analysis.

Industrial

Unlike the controlled conditions of the laboratory studies, it is difficult to isolate all the contributions generating HF from an industrial cell. Past studies [3] have used regression factors to find the contributions. These have given numerical approximations to the contributions, but not fitted the mechanisms to complete satisfaction. This study has taken a different approach to simplify the analysis. Here a distinction has been drawn between the *alumina feeding contribution* and a *non alumina feeding contribution*. If figure 5 is examined, the alumina feeding contribution causes the overfeed and underfeed variations in the industrial emission. Conversely the *non alumina feeding* emission is a constant emission for normal cell operations (i.e. not during anode change or tapping) which primarily consists of the anode hydrogen content, a thermal hydrolysis proportion and (as the laboratory results show) a dissolved water contribution. The additive effect of the alumina emission in the laboratory results confirm that this simple separation can be taken as accurate to a first approximation, given the overwhelming effect of the structural water. Other effects such as crust integrity also become important for industrial analysis though.

Using this theory the two separate contributions can be calculated using the following Δ correlation:

$$\Delta = \frac{O}{A} - \frac{U}{\alpha} = \frac{-Bd}{(\alpha + d)\alpha} \tag{3}$$

$$\therefore B = -\frac{\Delta\alpha}{d}$$

Where:

- U = Underfeed HF emission (kg/h).
- O = Overfeed HF Emission (kg/h).
- A = OF alumina feed rate (kg/min).
- α = UF alumina feed rate (kg/min).
- B = Non alumina feeding emission (kg/h).
- D = O - U.
- d = A - α .

Hence, this correlation can be used to calculate the constant non alumina feeding emission to which the anode hydrogen emission contributes. Figure 5 illustrates a representative measurement of the HF emission during a forced zero feed period. Here the fed goes from an underfeed period to zero alumina fed. Hence the primary HF generation contribution of the alumina is removed and the emission quickly decays to the non alumina emission level. Once alumina feeding was re-established at an overfeed level, the emission rises as the alumina water HF generation contribution adds to the HF emission once again.

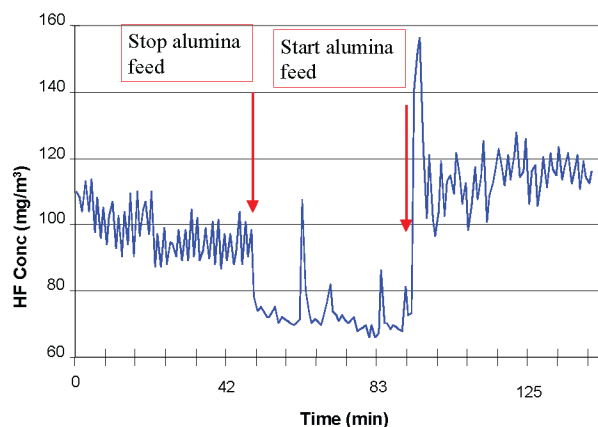


Figure 5: HF response during a zero feeding period in an industrial cell.

The emission levels at zero fed serve as a cross check for the validity of the Δ correlation. The value calculated from it should match the non alumina fed value of 0.557, and 0.540 kg/min. Therefore from the Δ correlation (with an overfeed of 2.65 kg/min and underfeed of 1.15 kg/min) the non alumina HF generation can be calculated as 0.543 kg/min. This compares well with the measured average zero feed HF values. This gives a non alumina HF contribution of 0.602 kg/tonne Al for that cell.

Breaking down this factor is more difficult. For the anode hydrogen emission it can be estimated that 10% of the anode hydrogen is converted to HF from the conversion factor found in the laboratory section. Using a version of the Haupin - Kvande model [7] it can be calculated that this amounts to 10% of the non alumina emission, though for a particular cell this will depend on

the amount of hydrolysis occurring (i.e. the state of the crust and ambient air conditions) and the alumina concentration in the bath.

The dissolved water content of the emission can be worked out from the track. Closer inspection of this track region shows that the emission still decreases over time. This can be shown to correspond to alumina content depletion at track. By fitting a linear curve to this portion it can be calculated that approximately 0.8kgF/tonneAl/wt%Alumina results from the dissolved water generation. For a typical cell alumina concentration (2.5%) this amounts to 2 kgF/tonneAl, or 16% of a total emission of 12 kgF/tonneAl. However this contribution could be bath chemistry and alumina quality dependent and therefore these figures should be taken as being indicative and not absolute.

Secondary generation from thermal hydrolysis of the cell gases at the crust cracks is also a factor in the generation of the non alumina emission. Past research [2,7] has attributed approximately 75% of this non alumina contribution to thermal hydrolysis. It must be noted that this does depend on the feeder hole state (open is conducive to excess thermal hydrolysis) and crust integrity. Though this is a reasonable figure when compared to the figure quoted above. Given this the HF in the anode can be noted to contribute at least 0.8 kg/tonne Al or 7% of a total emission of 12 kg/tonne Al. This is less than one fifth that found by Henry's study (50% of the emission could be attributed to the anodes), though his study used a test cell with completely different current, alumina and electrolyte conditions. These can not be directly compared.

This is a large emission, but not as large as Henry[1] suggested. Still, the anode hydrogen is an important contributor to the overall hydrogen fluoride emission. This content produces a large amount of HF by primary reaction at the anode, from which the unreacted H may add to the a constant electrolyte dissolved water reaction and/or secondary generation (thermal hydrolysis) at the crust vents. As these are three important HF sources, any reduction of the hydrogen content in the anode should lead to a direct reduction in the overall emission.

Conclusions

Hydrogen in the anode is the least understood HF generation source. This study has shown that the Wahnsiedler low Hydrogen reaction figure to be accurate, with up to 10% of the hydrogen in the anode reacting to form HF. This makes up around 8% of the total emission of the industrial cell studied. The remainder of the unreacted hydrogen either forms part of the dissolved water content in the bath, or is transported to the extraction system via the crust vents where it could aid in secondary HF generation. In both cases this hydrogen source adds to the emission as the dissolved water forms about a 16% of the emission and the thermal hydrolysis portion forms 30% of the emission of the studied cell. Hence all three generation sources are important components of the non alumina emission. Reduction of this content amounts to measurable reductions in the overall emission. Control of this and the crust integrity will lead to some reductions in the overall HF emission. Hence, in an emission reduction scheme, the effectiveness of the anode baking process contributes to a portion of the total HF emissions.

Acknowledgements

The authors would like to acknowledge the co-operation received from all the staff at Hydro Aluminium a.s Technology Center Årdal in Norway and Halvor Kvande for advice and guidance in all aspects of this study. They would also like to thank Dr. Frank Hiltmann and SGL Carbon for their invaluable assistance in providing the anode hydrogen analysis.

References

1. J. L. Henry, "A study of factors affecting fluoride emissions from 10,000 ampere experimental aluminium reduction cell," *Extractive Metallurgy of Aluminum*, (New York: Interscience, 1963), (2) 67 - 81.
2. K. Grjotheim, B. J. Welch, H. Kvande, and K. Motzfeldt, "The formation and Composition of the fluoride emissions from aluminium cells," *Canadian Metallurgical Quarterly*, (11) (1972) 585 - 599.
3. W. E. Wahnsiedler et al, "Factors affecting fluoride evolution from Hall-Heroult smelting cells.," *Light Metals 1978*, (2) (1978) 407 - 424.
4. E. C. Patterson et al., "Gaining a realistic view of fluoride generation from aluminium electrolysis cells," (Paper presented at the 2nd Australasian environmental research event, Sydney, Australia, November 1999).
5. M. M. Hyland, B. J. Welch, and J. B. Metson, "Changing knowledge and practices towards minimising fluoride and sulphur emissions from aluminium reduction cells," *Light Metals 2000*, (2000) 333 - 338.
6. K. Grjotheim et al., *Aluminium Electrolysis. Fundamentals of the Hall-Heroult Process*. (Düsseldorf, Germany: Aluminium-Verlag, 1982), 369.
7. W. E. Haupin and H. Kvande, "Mathematical model of fluoride evolution from Hall-Heroult cells," *Light Metals 1993* (1993) 257 - 263.
8. T. Foosnaes, V. Hjelle, and M. Karlsen, "Continuous monitoring of gaseous fluoride emissions," *Light Metals 1993*, (1993) 407 - 411.
9. M. M. Hyland et al. "Predicting moisture content on smelter grade alumina from measurements of the water isotherm," *Light Metals 1997*, (1997) 113 - 117.