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Fluoride Emissions
from Aluminium Electrolysis Cells

by
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Abstract.

Modern aluminium electrolysis cells generate between 15 to 40 kg fluoride per tonne of aluminium fluoride produced. This represent a large material recycle load, of which over 99% of this fluoride content is returned to the cell via a dry scrubbing system. Most past research has concentrated on increasing the efficiency of this end scrubbing system, neglecting the actual cause of the fluoride emissions. Lower emissions would reduce this loading, resulting in smaller scrubbing systems, and ultimately lower capital costs. Fluoride emissions also contribute to the changes in heat balance in the cell. The fluoride evolved represents a material loss that requires to be replaced with AlF_3. The addition of this species is a major variable in cell heat balance instability [1]. Overall a better understanding of the contributors to fluoride generation in an aluminium cell would benefit the operation and economics of an aluminium smelter.

Past studies [2-6] have identified most of the important emission contributors to hydrogen fluoride (HF) generation. Two sources were shown to be significant. The most studied source was primary HF generation. This is HF generation from electrolytic reactions between constituents of the fluoride based electrolyte and water from the fed alumina and hydrogen in the anode. Overlooked in some studies were generation reactions outside the electrolyte - defined in this study as secondary HF generation. This source was found to occur mainly from hydrolysis reactions with the generated particulate fluorides. However the results and the relative contributions from these studies are not strictly applicable to the current generation scenario. The present smelting practices and technology, dry scrubbing technology and raw material specifications differ substantially from those used during the period of each past investigation. The present study was designed to identify and quantify emission sources for the current smelter technology and practices. This used controlled laboratory based studies of the individual generation sources complemented by in plant studies analysing the HF emission from production aluminium electrolysis cells.

It was shown that the main contributor to primary HF generation is the addition of water to the electrolyte from the feed alumina. This results in the cyclic short term variations in HF emission, which correlate to the rate of alumina addition to the cell. Laboratory and industrial studies show that only a fraction of the added water reacts. The water reacted is likely the structural water of the alumina. The adsorbed water is thought to be flashed off before addition to the bath. Depending on feeding technology and crust integrity, between 10 to 50% of this water can react. This produces 7 to 14

kgF/tonneAl. This makes it the most significant emission component. The remainder of this structural water is either entrained in the anode gases or forms part of the electrolyte dissolved water content.

Dissolved water generation is the second most significant primary generation contributor, and third most significant emission component. Dissolved water is in equilibrium with the alumina content of the bath. It represents a constant emission source. Depending on feeding technology and cell design, the emission can vary between 3 to 10 kgF/tonneAl.

The final primary HF emission contributor results from electrolytic generation of the hydrogen content of the anode. Laboratory studies found the emission to have a reaction efficiency of approximately 10%. This results in a small emission, of 2 – 5 kg/tonneAl. The remainder of the hydrogen content is expected to be entrained in the anode gases, as the generation of this CO/CO_2 mixture is an order of magnitude greater than the HF generation reaction.

Secondary generation of hydrogen fluoride is also a significant HF emission source. In an industrial cell this results from mainly thermal hydrolysis of the particulate fluoride emissions at the crust–air interface. Laboratory studies have shown that other identified secondary emission sources are unlikely due to the ambient conditions and feeding practices in a modern prebake aluminium electrolysis cell. Hence previously proposed generation from hydrolysis of the particulates in the ducts and desorption of the surface fluoride from the fed secondary alumina, have been found to be insignificant compared to the main HF generation sources.

The thermal hydrolysis emission contributor is the only significant secondary generation emission component. Industrial measurements show that it varies with ambient humidity and crust integrity, two parameters which vary constantly in a modern prebake anode cell. Measurements show that the emission from this source is responsible for 2 to 8 kgF/tonneAl. This makes it the second highest HF emission component. Control of the crust condition and feeder hole states reduces this component significantly.

Hence in a modern prebake aluminium cell, the most significant operational factors affecting emission are related mainly to secondary generation. Industrial measurements show that the long term variations in an emission result from changes in the ambient humidity and the cells crust cover. Control of the crust integrity is thus paramount in reducing such variations. This relates both to normal operation and batch operations. Reduction of all other sources of emission are a material composition problem. Simply reducing the water content (LOI(300) and LOI(1000)) and reducing the hydrogen content of the anodes will reduce the emission. However material considerations affect other aspects of cell operation and hence these factors are not as simple to adjust.

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We all know that three and a bit years brings so many people into ones work and life. Of the countless I have missed in this little note - I thank you whole heartedly.

I can't think a better place to start than with those who have guided me the whole way. Margaret and Barry I'm indebted for you help through all patches, even the rather rough one at the end. Its been fun – and what else is life about. Never fear, I'm glad I've done this and it's finished now ☺.

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To my Family. Mum, Dad, T and Darrell (and those attention grabbing cats). Thanks for the love and support, where would I be without that sort of foundation.

What else – well I'll end on this – we all need self commentary!!

Its had its ups and downs and side tracks a many
But who could ask for more than this….
Three years of fun, friends, rewards and heartbreak.
But its time to move on now way from all that,
Up and on and flying into the future
With a sprinkling that special nova dust,
Mixed in with sweat and tears.

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T	= Temperature	(K)
T_b	= Bath Temperature	(^{O}C)
P	= Absolute Pressure	(kPa)
p_{H2O}	= Partial pressure of water in the air at a fixed T and P	(kPa)
ΔG	= Gibbs Free Energy	(J)
K	= Equilibrium Constant	(---)
CR	= Cryolite Ratio	(---)
r	= Reaction rate	
k	= Rate constant	
k'	= Pseudo rate constant	
U	= Underfeed HF emission	(kg/h).
O	= Overfeed HF Emission	(kg/h).
A	= OF alumina feed rate	(kg/min).
a	= UF alumina feed rate	(kg/min).
B	= Non alumina emission	(kg/h).
D	$= U – O = D_{feeding}$	(kg/h).
d	$= A - \alpha$	(kg/min).
α	= Difference between alumina feed normalised overfeeding and underfeeding emission rates	(---).
τ	= Time constant for structural water dissolution	(s).
t	= Time	(s).
A, B, C	= Derived constants for step response analysis.	
a, b, c	= Derived constants for step response analysis.	
F	= Total primary fluoride evolution	(kg/tonne Al)
W	= Bath weight ratio.	
AW	= Alumina water content	(%)
BA	= Bath Alumina content	(%)
CF	= Bath calcium fluoride content	(%)
AE	= Anode effect.	
TR	= Track.	
AF	= Hand fluoride addition.	
HC	= Average hydrogen content of the anodes	(%)
ftc	= Feeding technology coefficient	
OFH	= Open Feeder hole percentage	(%)
P_B	= Ambient Pressure	(kPa)
%CE	= Current Efficiency	(%)
P_{NaF}	= Vapour Pressure of NaF above Bath	(kPa)
R_b	= Weight Ratio NaF/AlF_3 in bath	(---)
HBA	= Hydrolysis by air factor.	