FLUORIDE EMISSIONS MANAGEMENT GUIDE (FEMG)

Written by
LIGHT METALS RESEARCH CENTRE (LMRC)
Auckland UniServices Limited
The University of Auckland

Under invitation of
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1.0 Introduction & Theory

Generation of unwanted fluoride by-products from the aluminium smelting process is unfortunately unavoidable with today's state of technology. However, the release of fluorides into the surrounding environment can be reduced.

With careful management and control of both operations and maintenance practises around the plant, smelters are able to reduce the amount of fluorides they release into the environment, achieving levels demonstrated by the world's best practise.

1.1 Purpose of the Guide

Why has this guide been written?

The Fluoride Emission Management Guide (FEMG) has been written for all smelters in China, and for managers, engineers and operators alike, to:

1) Increase understanding of the factors that control fluoride evolution and emissions, and
2) Detail what operating, control and maintenance practises are required in order for smelters to control and reduce their fluoride emissions.

The guide focuses mainly on improvements to work and maintenance practises, as these are typically low cost and allow a smelter to maximise its environmental performance with its existing technology. Less emphasis is placed on technology improvements, which require higher capital investment.

Recommendations have been proven by world-class smelters and are based upon world's current best practises – if adopted; smelters stand to achieve significant improvement in their environmental performance.

The ultimate aim of the guide is to provide practical and technical information to help all smelters in China achieve significant reductions in fluoride emissions, reducing the overall environmental impact of the smelting industry in China.

The guide has been prepared by the Light Metals Research Centre (LMRC), the University of Auckland, on the invitation of the Australian Aluminium Council (AAC), under the Asia-Pacific Partnership (APP) on Clean Development and Climate.

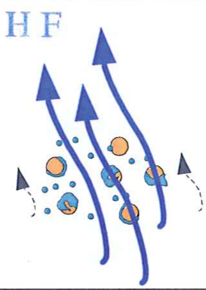
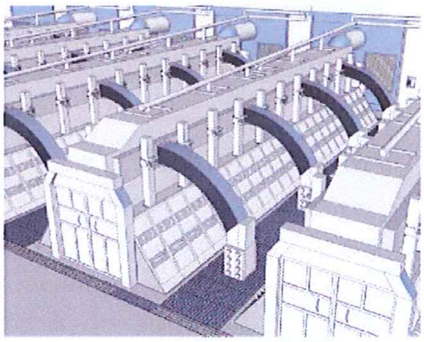
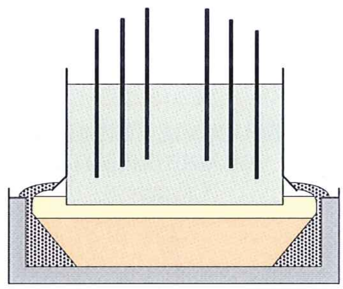
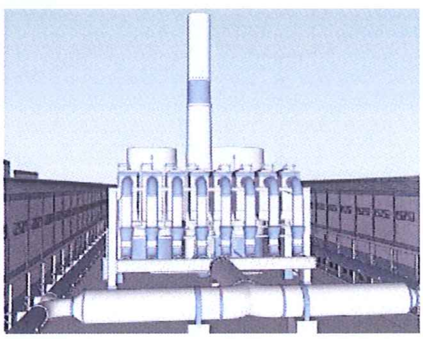
1.2 Scope of the Guide

What emissions & types of smelters are covered by the guide?

The FEMG covers fluoride emissions from primary aluminium smelters, concentrating on the potroom and gas treatment centre, as well as audits required and overall smelter systems that contribute to emissions.

The guide focuses on pre-bake, point-fed pot technologies and injection-type dry scrubbing technologies, which cover over 90% of all Chinese aluminium smelters. The full scope of the FEMG is illustrated in Table 1.1.

Table 1.1 - Scope of the FEMG.

Elements in the FEMG	**What <u>IS COVERED</u> In the FEMG?**	**What's <u>NOT covered</u> in the FEMG?**
Environmental Emission Type	**Fluoride emissions only**, including: • Gaseous fluorides, HF • Particulate fluorides  	**Non-fluoride emissions**, including: • SO_2, CO, CO_2 • Polycyclic Aromatic Hydrocarbons (PAH's) • Perfluorocarbons (PFC's), CF_4, C_2F_6
Potroom / Pot Design	• **Pre-bake** pot design • **Point-fed** 	• **Söderberg** pot design • **Bar-break / side-work** designs 
Gas Treatment Centre / Scrubber Design	• **Dry scrubbers**, with an **injection-type** reactor and bag-house 	• **Wet scrubbers** • Dry scrubbers, with alternate technology like Torroidal or fluidised bed

1.3 Structure of the Guide

What kind of information does the guide provide?

The FEMG covers 6 main sections for understanding and controlling fluoride emissions:

1. **Introduction & Theory** – Drivers behind reducing fluoride emissions, and background into how fluoride emissions are generated.
2. **Overall Fluoride Emission Management System** – Overall concept and approach for controlling and managing smelter fluoride emissions.
3. **Potroom Systems for Reducing Fluoride** – Key Process Indicators (KPI) and control points for operations/control & maintenance practises in the potroom.
4. **Gas Treatment Centre for Reducing Fluoride** – Key Process Indicators (KPI) and control points for operations/control & maintenance practises for the gas treatment centre.
5. **Smelter Systems Outside the Potroom and Gas Treatment Centre** – Key Process Indicators (KPI) and control points for other areas in the smelter that affect fluoride emissions.
6. **Fluoride Emission Measurements** – Standard and recommended smelter fluoride measurement methods.

Where possible in the guide, improvements to practises will be focused on over technology improvements, with recommendations ranked from requiring little/no capital investment to significant capital investment.

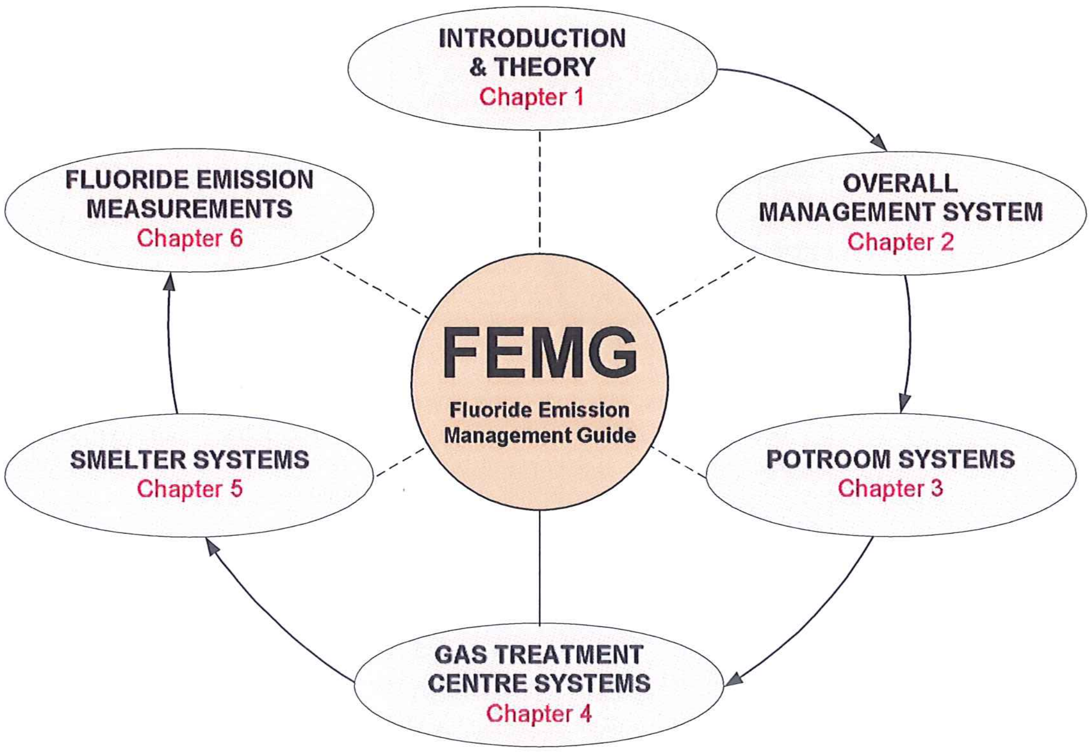


Figure 1.1 – Structure of the FEMG.

1.4 Drivers Behind Fluoride Emission Control

Why is controlling & reducing fluoride emissions important?

All aluminium smelters in the world, including those in China, are driven by the same factors for reducing the amount of fluorides they release into the environment. These factors are legal, health and environment, as well as operations or performance as illustrated by the chart below.

It is important to note that by implementing the best practices in this FEMG, each smelter has the potential to not only make significant improvements in environmental performance, but also significant improvements in the smelter's key operating performance measures, e.g. reductions in specific energy consumption, higher current efficiency, reductions in material losses, and so on.

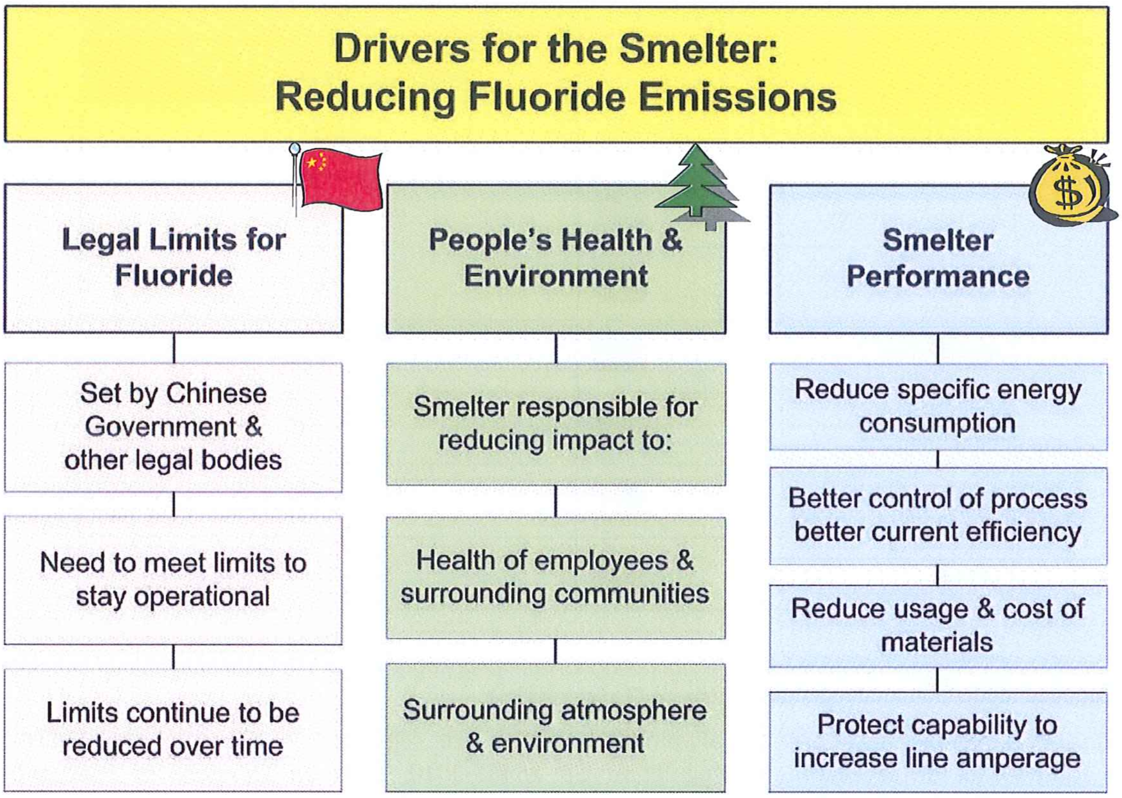


Figure 1.2 – Chart showing why smelters need to make practical steps to reduce its fluoride emissions.

What are the legal limits for fluoride emissions?

Best Practises & Legal Requirements for Fluoride Emissions

All smelters worldwide, including those in China, operate under strict limits for fluoride emissions. Smelters which cannot meet these limits stand to lose their operating license and may be required to stop production or shut down.

These regulatory emission limits are typically benchmarked by what can be achieved by the best performing smelters of a particular technology, i.e. for pre-baked, point fed pot technologies. The table below shows a comparison of production-based regulatory limits for primary aluminium smelters for different regions in the world, including the current world's best practise.

Table 1.2 – Comparison of production based regulatory limits and the current world's best practise for total (stack + fugitive) airborne fluoride emissions.

Region	Regulated Airborne Emission Limits Total Fluorides (kg F / t Al)
World Benchmark[1,2]	0.2
Europe – Iceland[3]	0.35
Europe – OSPAR[4]	0.6
Middle East	0.6[5]-1.25[6]
Australia[7]	0.6-1.0
USA – EPA[8]	0.6-1.5
China[9]	*To Be Advised*

Meeting Regulations from the Chinese Government

Fluoride emissions from primary aluminium smelters are regulated in China by the Ministry of Environmental Protection, under Regulation *GB 25465-2010, Emission Standard of Pollutants for Aluminium Industry for 2010.* The relevant regulatory limits for atmospheric fluoride emissions are presented in the Table 1.3.

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[1] Lindsay, S.J. (2004) *TMS Alumina Short Course*

[2] Lindsay, S.J. (2007) Effective Techniques to Control Fluoride Emissions, *TMS Light Metals.*

[3] Moras A., et. al (2010) Modern Potline Gas Treatment Technology for High Amperage Pots – The Alcoa Fjardaal Experience, *TMS Light Metals.*

[4] Emission targets for 2010. OSPAR Recommendation 98/2 on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants. www.ospar.org

[5] Royal Commission for Yubail and Yanbu, Kingdom of Saudi Arabia. Royal Commission Environmental Regulations 2004. Note that the figure of 0.6 kg F/ t Al is for potroom (i.e. fugitive) emission sources only.

[6] Emission limits for Bahrain. Figure of 1.25 kg F/t Al is for both potroom fugitive + stack emissions.

[7] NSW Government, Australia. Protection of the Environment Operations (Clean Air) Regulation 2010.

[8] US EPA (1997) *40 CFR Parts 9, 60, and 63.* Final Rule.

[9] Chinese National Standards, GB 25465-2010. *Emission Standard of Pollutants for Aluminium Industry* for 2010.

Work Practices
(Operating, Control &
Maintenance)
covered in the FEMG

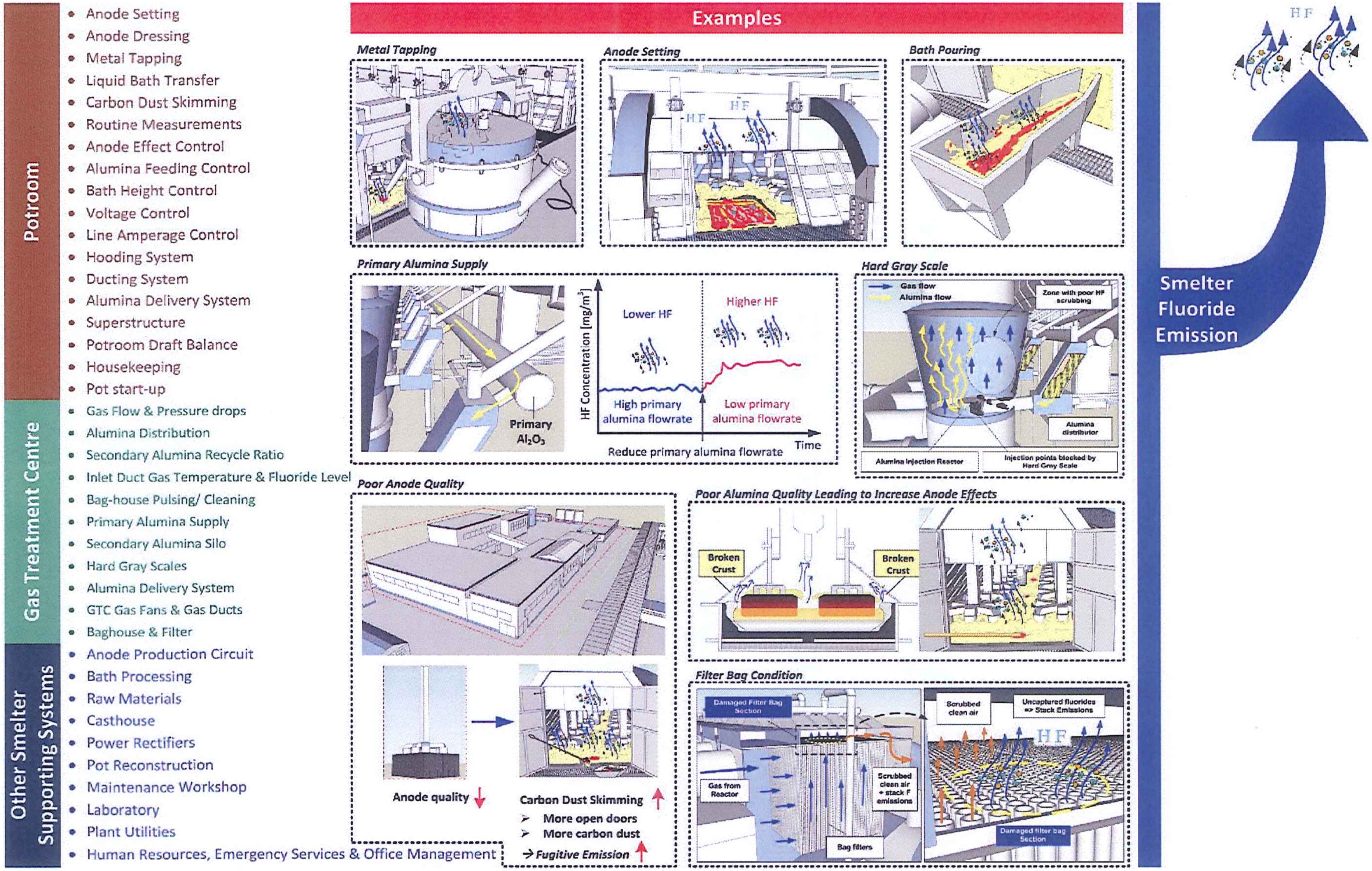


Figure 2.2: Smelter work practices impact on fluoride emission.

Pathways for Fluoride Emission

for each smelter work practice

How does anode setting impact on fluoride emission?

Pathway 1: Opening hoods

- Pot suction is reduced when the hoods are open during anode setting, due to the loss of static pressure in the pot.
- When pot suction is reduced, the pot capture efficiency decreases and fluoride emission increases. This relationship has been extensively documented (illustrated in Figure 3.6).
- When the hoods are open for anode setting, particulate and gaseous fluorides escape from the anode cover material which is exposed to the air (illustrated in Figure 3.7).

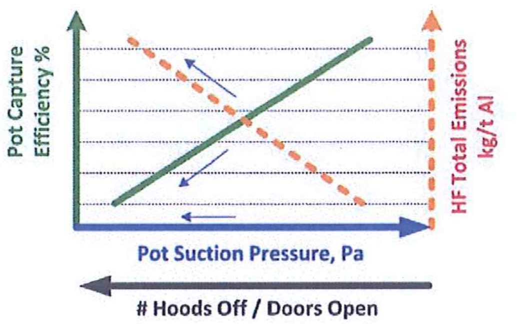


Figure 3.6 – Illustration of the relationship of pot suction, pot capture efficiency and HF total emissions in response to hoods opened and pot end doors removed (not to scale).

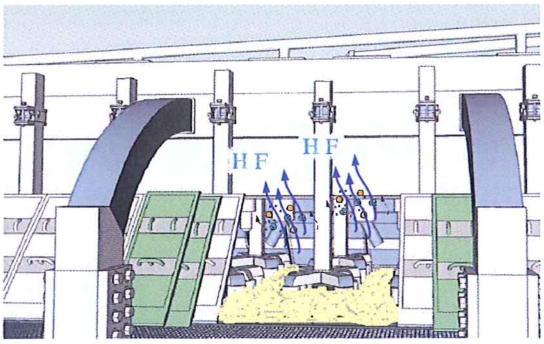


Figure 3.7 – Schematic drawing showing fluoride evolution and emission during anode setting when the hoods are opened.

Pathway 2: Broken crust and opening cavity

- During crust breaking, particulate and gaseous fluorides escape from the holes in the anode crust which is exposed to the air (illustrated in Figure 3.8).
- Fluorides are evolved and emitted from the open cavity after the anode butts are removed and molten bath is exposed to the air (illustrated in Figure 3.9)

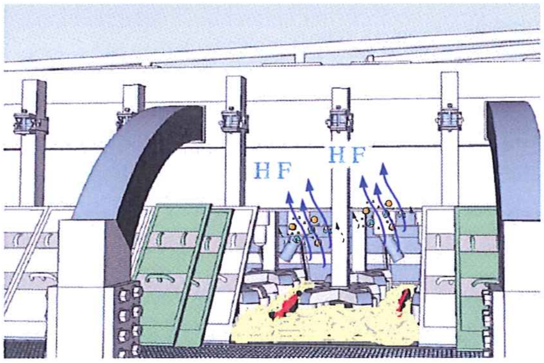


Figure 3.8 – Schematic drawing showing HF evolution and emission from holes in the crust after crust breaking.

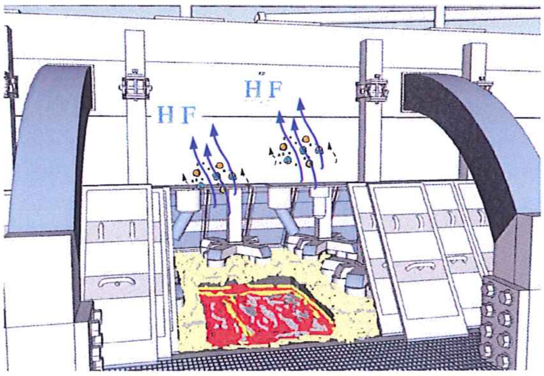


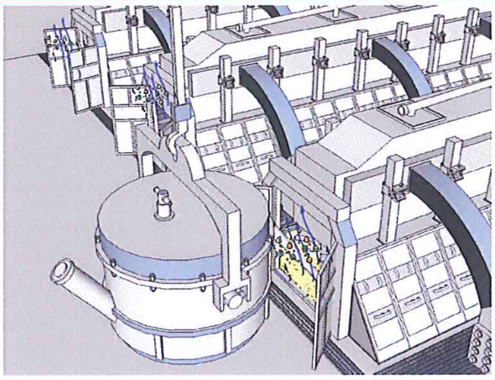
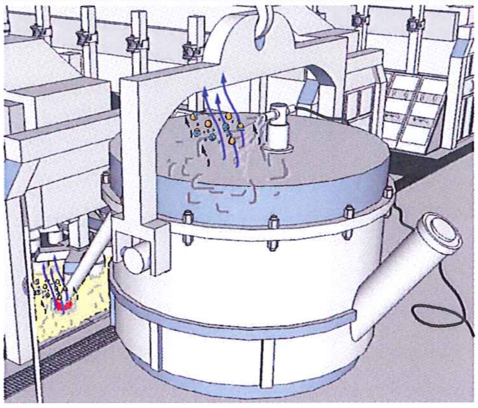
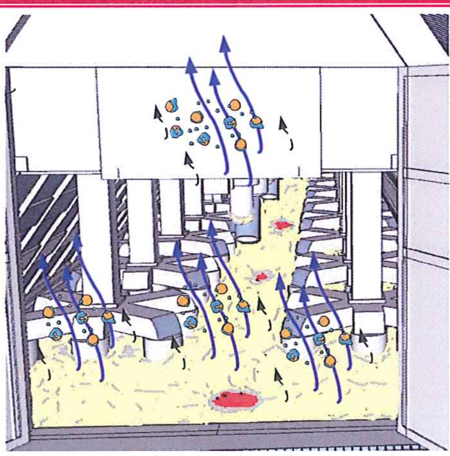
Figure 3.9 – Schematic drawing showing fluoride evolution and emission from the anode cavity after the anode butts are removed.

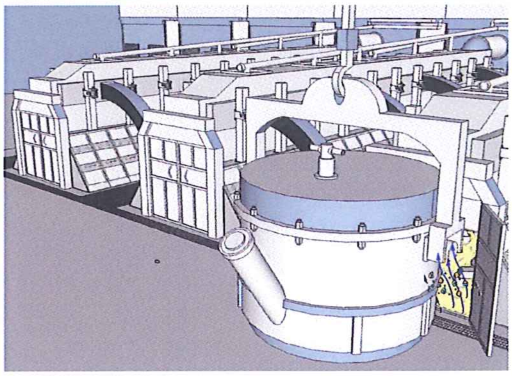
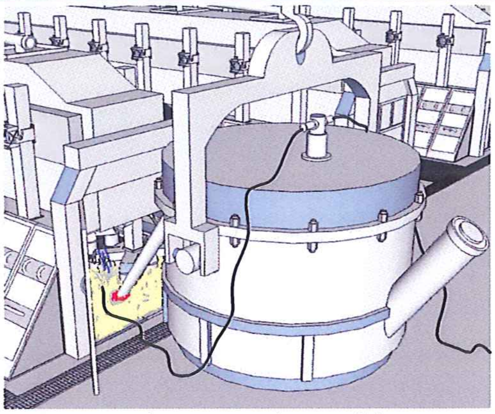
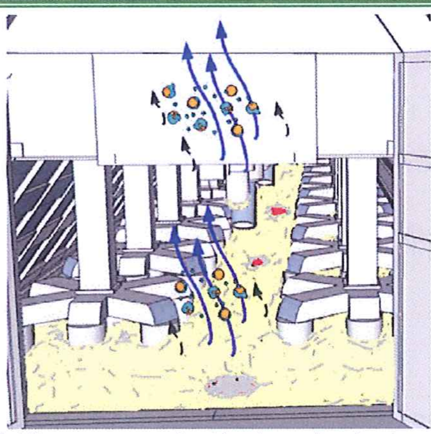
Good / Best Practices

vs. Poor Practices

How to reduce fluoride emission during metal tapping?

Fluoride emissions from metal tapping can be minimised through the following best practice.

	BAD Practice ✗
1	 Opening the tap end doors of a group of pots which are to be tapped.
2	 Releasing the extracted fumes to the potroom environment.
3	 Leaving the tap hole open after completion of tapping.

	GOOD Practice ✓
1	 Opening the tap end door of a single pot right before tapping.
2	 Connecting a hose onto the crucible vent and directing the extracted fumes back to the pot.
3	 Sprinkling some crushed bath or alumina into the tap hole to help form a crust which closes the tap hole.

Potential Improvements

for each work practice

Checklists for Auditing

work practices

What are the potential improvements?

Potential improvement to reduce fluoride emission during gas flows & pressure drops over GTC compartments		
No Cost	1	Continuous monitoring of overall GTC gas flowrate & pressure drop, and adopt a pro-active culture to investigate and correct any abnormal deviations in either parameters, before they become major issues.
	2	Regular audit of long term gas flows through each GTC compartment and correct damper positions for each compartment to balance long term pressure drops.
	3	Regular audits of the main GTC fans to check that it is still meeting draft specifications – see Section 4.9 on maintenance.
Low Cost	1	Install system that allows monitoring of pressure drops over individual GTC compartments.
	2	Increase overall gas flow by operating fans at higher draft (if not already at design limit).
	3	Install bag filters with higher cloth area (e.g. star shaped bags) to lower bagfilter pressure drop. This can increase air-to-cloth ratio available, allowing increases in scrubbing capacity and overall gas flowrate.
High Cost	1	Additional scrubbing capacity (more main fans, more GTC reactors and baghouse compartments).
	2	Additional booster draft capacity potroom (separate auxiliary pot ducts or damper valves in pot ducts) to reduce fugitive emissions during anode setting & other pot operations.

✓ Checklist to reduce fluoride emission during control of gas flows & pressure drops over GTC compartments

	Check items				
1	Is overall inlet gas flow to the GTC normal?	YES		NO	
2	Is overall pressure drop across the whole GTC normal?	YES		NO	
3	Is gas flowing to each individual GTC compartment? Has this been checked physically / visually?	YES		NO	
4	Do any of the GTC compartments have low gas flow?	YES		NO	
5	Are the individual GTC compartment pressure drops and gas flowrates within specification and balanced?	YES		NO	

Fluoride Monitoring & Measurements

6.6 Continuous Fluoride Emission Monitoring

What are continuous fluoride measurements and what value can they offer?

In addition to the regulatory or standard fluoride measurement techniques presented in previous sections, continuous/real-time fluoride measurements have also been employed in many modern smelters around the world, particularly to monitor GTC stack fluoride emissions and potroom fugitive fluoride emissions. Although standard or regulatory measurement techniques are much more robust and accurate, they have the disadvantage of being relatively time-consuming, labour-intensive and only provide single emission data points for each measurement site, typically over a 24 hour period.

In contrast, continuous measurements provide smelter management/operations staff the ability to study or monitor fluoride emissions in real-time, i.e. in direct response to operations and process events (e.g. in the GTC or potroom, such as shown in Figure 6.18). As such they can be used to monitor the quality of different operations and work practices, e.g. anode setting, hooding quality on pots, etc.

A number of different technologies and providers exist in the industry for both GTC stack and potroom roof vent measurement. For gaseous HF emission, these include (but are not limited to)[19]:

- Tunable Diode Laser (TDL) Spectroscopy – Boreal Laser, OPSIS, LasIR, NEO
- Fourier Transform Infrared (FTIR) Spectroscopy – MDA FTR, MIDAC, Gasmet
- HeNe laser direct absorption – SBL.

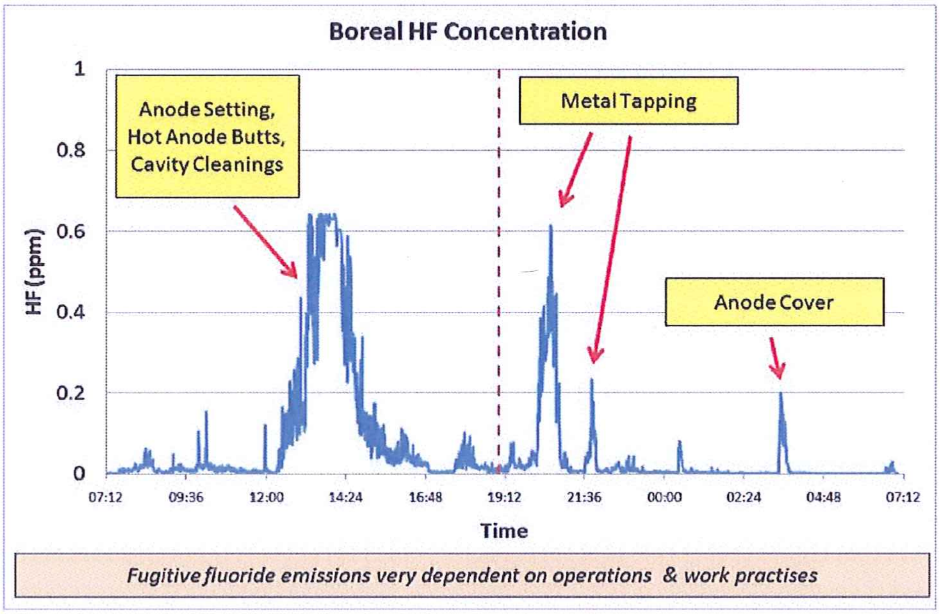


Figure 6.18: Example of continuous HF emissions from a potroom roof, measured using Boreal laser over 24 hours.

[19] Whiteley, K. (1998) Continuous Long Path Gaseous HF Monitoring in a Potroom Roof Vent. *Proc. 6th Australian Aluminium Smelting Workshop*

Audit Survey Worksheets

for Potroom & GTC

FLUORIDE EMISSIONS MANAGEMENT GUIDE (FEMG)

GAS TREATMENT CENTRE (GTC) AUDIT SURVEY

Version 06.11.2010

Smelter		**Area**		**Date & Time**	

Surveyor Name(s)		**Host Name(s) & Position**	

GTC GENERAL INFORMATION

GTC Type		*E.g. single stage injector, two stage, etc.*
Year Installed		
No. of GTC Units		*Each GTC unit: A baghouse filter, reactor, flow damper*
No. of Pots Serviced		

GAS FLOW & PRESSURE DROPS OVER GTC UNITS

	Check items				
1	Is overall inlet gas flow to the GTC normal?	**YES**		**NO**	
2	Is overall pressure drop across the whole GTC normal?	**YES**		**NO**	
3	Is gas flowing to each individual GTC compartment? Has this been checked physically / visually?	**YES**		**NO**	
4	Do any of the GTC compartments have low gas flow?	**YES**		**NO**	
5	Are the individual GTC compartment pressure drops and gas flowrates within specification and balanced?	**YES**		**NO**	

The following are questions to ask or tasks to do in order to complete the above checklist.

1) How is the gas flow to each GTC compartment unit monitored?

____

____

2) Ask the operator to indicate on the SCADA system the gas flow and pressure drop for the following GTC parts. What are the process specification limits for the gas flow and pressure drop parameters and verify whether they are within the specified limits.
   - Individual GTC unit (distribution across the units)
   - Individual baghouse (distribution across the baghouses)
   - Overall GTC

____

____

3) Are there any systems (e.g. alarms, manual observation, logging, automatic response, manual response) in placed to address imbalances of gas flow or pressure drops?

____

____