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FLUORIDE EMISSIONS MANAGEMENT GUIDE (FEMG) FOR ALUMINIUM SMELTERS

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Abstract

All smelters worldwide operate under strict fluoride emission limits and the reduction of fluoride emissions is further driven by health and environmental considerations. A Fluoride Emissions Management Guide (FEMG) has been written by the Light Metals Research Centre (LMRC) on the invitation of Australian Aluminium Council (AAC), under the Asia-Pacific Partnership (APP) on Clean Development and Climate. The aim of the FEMG is to provide a better understanding of the factors affecting and ways of reducing fluoride evolution and emissions in smelters, and further, to provide smelters with an operational guide for reducing and managing fluoride emissions.

Reduction in fluoride emission can be achieved by improvement of operational standards in the smelter. This includes operational, control and maintenance practices in the potroom, GTC, and other areas in the smelter that generate fluoride. Along with incorporated audit guidelines and training package, implementation of this guide can, in a short time, lead to significant reduction in fluoride emissions in aluminium smelters.

Introduction

Generation of fluorides from the aluminium smelting process is unavoidable with the current technology. Hence, all smelters worldwide operate under strict limits of fluoride emissions and these limits are expected to become tighter with time. Table I provides a comparison of production-based regulatory limits for total airborne fluoride emission in primary pre-bake aluminium smelters for different regions of the world, including the current best practice.

The majority of larger capacity modern smelters today limit their fluoride emissions to 0.5-0.6 kg F/t Al [1]. These limits are practically achievable, as demonstrated by the performance of Aldel and Tomago smelters (0.46 kg F/t Al in 2005 [2] and 0.56 kg F/t Al in 2007 [3], respectively). Some of the better performing smelters in the world have reported emissions as low as 0.29 kg F/t Al (Portland in 2008) [4] and 0.25 kg F/t Al (Karmoy in 2006) [5].

Table I. Comparison of production based regulatory limits and the current best practice for total airborne fluoride emissions in the pre-bake aluminium smelting industry.

Region	Regulated Airborne Emissions Limits for Total Fluoride (kg F/t Al)
World Benchmark	0.2 [6, 7]
Europe – Iceland	0.35 [1]
Europe / OSPAR	0.6 [8]
USA – EPA	0.6 – 1.5* [9]

* The limit of 1.5 kg F/t Al is only applicable to older potlines as specified in the National Emission Standards for Hazardous Air Pollutants for Primary Aluminium Reduction Plants.

These legislative limits, the health and safety of the employees and the wellbeing of the environment are major drivers for the smelters to reduce their fluoride emissions.

Mechanisms of Fluoride Generation and Escape Pathways

The majority of gaseous and particulate fluorides emitted from an aluminium smelter are originally generated in a pot. The amount will depend on cell technology, raw materials, process control, and ambient conditions (temperature and humidity) where the smelter is situated [10]. A typical pre-bake, point-fed pot generates about 15-30 kg total F/t Al, with >99% of these fluorides typically captured in the scrubbing system [10, 11].

Gaseous fluoride (HF) is produced when AlF_3 in the bath or as bath vapour ($NaAlF_4$) reacts with a hydrogen source in one or two reactions:

$$2AlF_{3\,(g\ or\ diss)} + 3H_2O_{(g)} \Rightarrow 6HF_{(g)} + Al_2O_{3\,(s\ or\ diss)} \quad (1)$$

$$3NaAlF_{4\,(g)} + 3H_2O_{(g)} \Rightarrow 6HF_{(g)} + Al_2O_{3\,(s)} + Na_3AlF_{6\,(s)} \quad (2)$$

Particulate fluorides, on the other hand, are generated when bath vapour condenses to form droplets or fine bath particles are picked up and entrained in the pot gases.

Potrooms and Gas Treatment Centres (GTCs) are often seen as the main sources of fluoride emissions. While it is important that the different factors related to fluoride emissions from these two key areas are addressed and controlled, it is equally important to realise that a fluoride emissions problem may also be related to other plant areas. Examples are the fluorides released from transport/delivery of spent anode butts and the bath processing plant. The mission to reduce and control smelter fluoride emissions spans across all plants within the smelter and is a responsibility of every individual in the smelter.

Through careful management and control of both operation and maintenance practices around the plant, further reductions in fluoride emissions can be achieved. However, the factors which affect and the ways of reducing fluoride emissions are sometimes not clearly understood, hence there is a need for a management guide to address fluoride emissions in the smelter as a whole.

This paper describes the Fluoride Emissions Management Guide (FEMG) which 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. The paper will focus on the content of the guide and the importance of managing fluoride emissions in the smelters.

What is the FEMG?

The FEMG is a comprehensive guide to managing fluoride emissions in primary aluminium smelters, with a focus on improvements to operational, control and maintenance practices to allow smelters to maximise their environmental performance with their current technologies. It aims to increase understanding of factors controlling fluoride evolution and emission, as well as providing an operational guide to smelters for reducing and managing fluoride emissions. The FEMG covers fluoride emissions from the potroom, GTC and other smelter systems that contribute to emissions, along with incorporated audit guidelines for each area. The guide is specifically prepared for pre-bake, point-fed pot technologies with dry scrubbing technologies.

The FEMG is broken down into 6 main chapters, which are:

- **Introduction & Theory** – covers the background of fluoride generation and drivers to reduce fluoride emissions.
- **Overall Fluoride Emission Management System** – covers the overall concept and approach for managing smelter fluoride emissions.
- **Potroom Systems for Reducing Fluoride** – specifies the Key Performance Indicators (KPIs) and control points for work practices in the potroom.
- **Gas Treatment Centre (GTC) Systems for Reducing Fluoride** – addresses KPIs and control points for work practices in the GTC.
- **Smelter Systems Outside the Potroom and GTC** – details KPIs and control points for other areas in the smelter that affect fluoride emissions.
- **Fluoride Emission Measurement** – lists standard and recommended smelter fluoride measurement methods.

Pictures are extensively used to illustrate issues and potential improvements to lower fluoride emission through daily operations. The recommendations contained in the guide have been proven by world-class smelters and are based upon current best practices, whereby if adopted, significant improvement in fluoride emission can be achieved.

<u>Overall Fluoride Emission Management System</u>

As previously mentioned, reducing fluoride emissions in the smelter should be the responsibility of all smelter personnel and not be focused only at the potroom and GTC areas. The overall concept of the fluoride emission management system applied in the FEMG is a systematic-interconnected network consisting of four main themes, as illustrated in Figure 1. They are:

- Control of work practices within specifications
- Monitoring systems
- Response systems
- Audit systems.

Each of these themes has a very important, specific role in reducing fluoride emissions and requires the involvement of all smelter employees.

<u>Control of Work Practices</u>

When the smelter work practices are not within process and work specification, they can result in a direct or indirect negative impact on the smelter's fluoride emissions. Exposed bath during anode setting and bath pouring operations are examples of work practices that have a direct effect on fluoride emissions. These operations are generally simpler to target compared to those with an indirect impact, such as the influence of poor anode quality on carbon dust generation in pots, which in turn increases fluoride emissions from more frequent dust skimming and open pot doors.

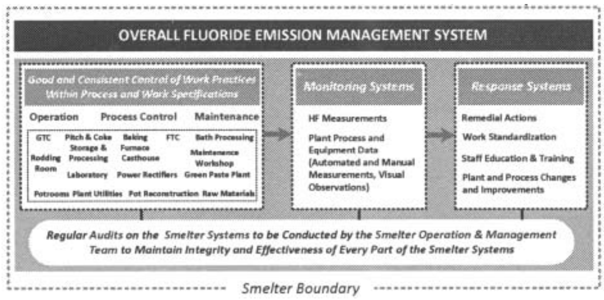


Figure 1.Overall concept behind the fluoride emission management system.

<u>Monitoring Systems</u>

Successful management of any process requires good measurements. Measurement systems are important to determine whether the operations are performing within the required specifications, otherwise actions can be taken to rectify the problem. The most effective monitoring system designs include a combination of numbers, charts, colour and alarms, which provide meaningful and relevant information to the users.

For monitoring of fluoride emissions, specific equipment and methods, such as US EPA Methods 13A and 14, have been developed to measure the level of fluoride emissions as required by law.

<u>Response Systems</u>

Once information from the monitoring systems has been received and analysed, response systems can be developed. They include:

- Remedial actions
- Work standardisation
- Staff education and training
- Plant and process changes and improvement

The response systems can range from an immediate to long term response. They are important for keeping practices within specifications, as well as for operational and financial optimisation. Furthermore, the response systems are utilised to prevent and reduce undesirable process conditions from occurring.

<u>Smelter Audit Systems</u>

An audit is an on-site review conducted to determine the existing status of a process and whether a certain quality condition has been achieved, ensuring that issues, problematic areas and improvement opportunities are identified and addressed. The level of audits in the smelter can vary from simple (i.e. hooding tightness) to comprehensive assessment (GTC operation). It should be conducted on a regular basis by the smelter operations and management team, and cover the entire systems in the smelter to maintain the integrity and effectiveness of every part of the smelter systems.

Why is Fluoride Emission Management Important?

All smelters worldwide are driven by the same factors to control and reduce their fluoride emissions. Some of the problem areas that smelters face are explored below.

<u>High Total Fluoride Emissions</u>

Some smelters face difficulties in keeping their fluoride emissions well below the legal limits, which may result in the possibility of heavy fines or even plant closure, should the situation continue to occur. High levels of fluoride emission will also affect the health of employees, particularly those working in areas where fluorides are generated. Skin/respiratory irritation, dental/skeletal fluorosis, and liver, kidney, or heart damage are some of the risks employees face with prolonged high exposure to fluorides [12]. A change in the operational standards is one way of making a difference in the level of fluoride emission in the smelter.

By going through each step in every work practice, potential pathways of fluoride evolution can be easily identified. In metal tapping, for example, the fluoride is generated during the opening of tap end doors, as shown in Figure 2. Pot suction is lowered when there are gaps in the cell (including opening of doors and hoods) due to the loss of static pressure in the pot. The reduction of pot suction will lower the pot capture efficiency and hence, results in higher fluoride emission. Furthermore, fumes released from the crucible vent during the metal siphoning process are a major source of fluoride emission during metal tapping.

When the pathways of fluoride generation have been identified, potential improvements can be recognised and change in work practices can be made. As shown in Figure 3, by comparing the smelter's current work practices against the world's best practices, poor work practices can be easily targeted and operational standards can be systematically improved. Audit checklists, like that shown in Table II, are a good tool for smelter managers or superintendents to use for conducting regular audits, ensuring that work practices are maintained within specified standards.

<u>Increase in Amperage</u>

The aluminium industry continues to shift towards higher amperage cells to obtain higher levels of productivity and greater economic returns. This shift requires better control and management of fluoride emissions before it can proceed. Increases in line amperage will inevitably lead to higher heat generation from the pots. Poor management of pot heat balance can lead to direct increases in fluoride emissions, for example from more frequent unscheduled anode changes and carbon dusting. Furthermore, if pot heat balance is not managed properly, gas duct temperatures in the GTC can rise excessively, decreasing the efficiency of the gas scrubbing system. Greater heat generation in the pot can also cause increased rates of crust collapse, resulting in more open holes in the crust, which again increases duct temperatures in the GTC.

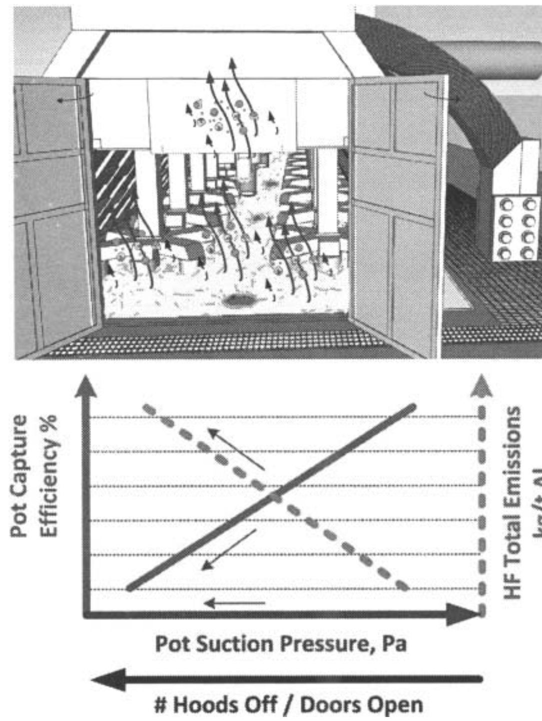


Figure 2. Schematic diagram showing how fluoride evolution and emission occur when the tap end door is opened during metal tapping procedure [Top], and how pot suction affects the pot capture efficiency and HF total emissions (not to scale) [Bottom].

Inlet duct gas temperature is an important operational parameter. Above certain temperatures, the scrubbing efficiency is lowered as particulate fluorides captured on the surface of the bagfilters begin to react, forming HF which is released as a gaseous stack emission. The bagfilters in the GTC also have critical temperature limits, above which they are irreversibly damaged – in some smelters, the gas would then be bypassed from the GTC, sending all pot gases to be released into the environment without scrubbing. Both of these aspects will lead to higher total fluoride emissions and reduction in the operating safety margin of a smelter.

Table II. Checklist of key areas to reduce fluoride emissions during metal tapping.

	Check items				
1	Only open the tap end door before metal tapping	YES		NO	
2	Use a hose to direct the extracted fumes back to pot	YES		NO	
3	Cover the tap hole by sprinkling some crushed bath or alumina into the tap hole	YES		NO	
4	Close the tap end door when metal tapping is finished.	YES		NO	

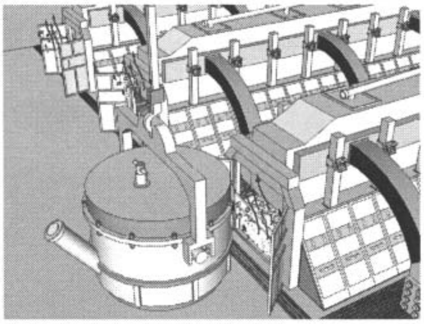
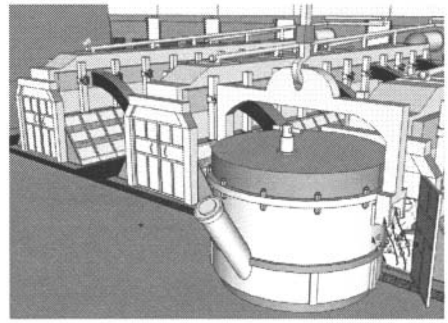
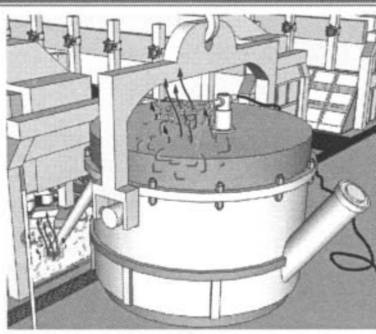
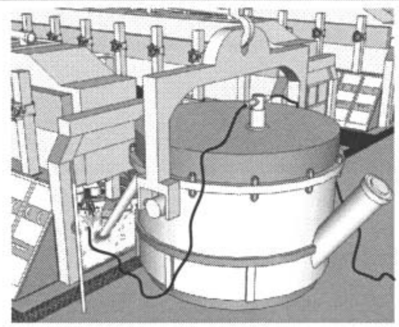
	BAD Practice ✗		GOOD Practice ✓
1	 Opening the tap end doors of a group of pots which are to be tapped.	1	 Opening the tap end door of a single pot right before tapping.
2	 Releasing the extracted fumes to the potroom environment.	2	 Connecting a hose onto the crucible vent and directing the extracted fumes back to the pot.

Figure 3. Examples of recommended best practice to minimise fluoride emissions during initial steps of metal tapping, presented as comparison of existing work practices and best practice (bad vs. good practice).

By installing an online measurement and monitoring of inlet duct gas temperatures, a pre-warning system for high temperatures, as illustrated in Figure 4, can be adopted. Such a system will allow for investigation or action before a bypass from the GTC is activated. Furthermore, regular measurement of inlet duct gas fluoride level allows for detection of long term shifts/fluctuations in fluoride generation from the potroom. This will enable adjustments in scrubbing efficiency, for example, by increasing secondary alumina recycle rate to respond to higher levels of fluoride in the incoming gas to the GTC.

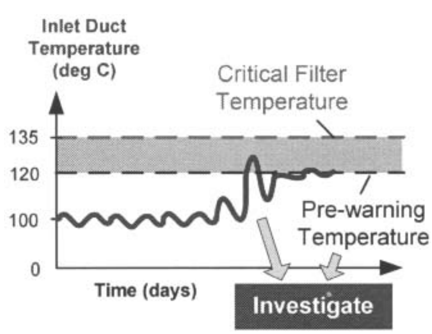


Figure 4. Schematic of continuous temperature measurement of GTC duct gas inlet temperature to detect and treat issue before critical temperature is reached.

With continual increases in amperage, however, existing GTCs can only cope to certain extent before some capital investment is required to accommodate the increase in the level of fluoride generation. Some potential improvements are shown in Table III.

Table III. Potential improvements that can be done to reduce fluoride emission due to shift in inlet duct gas temperature.

Potential improvement to reduce fluoride emission due to increase in inlet duct gas temperature and fluoride level.		
Low Cost	1	Use higher temperature bagfilter materials to sustain higher temperature operation and minimise GTC bypass on hot days.
	2	Measure and monitor inlet duct gas fluoride level using stack-type testing methods, over regular intervals (e.g. once per fortnight).
	3	If at risk of exceeding temperature limits of bagfilters, implementing a heat exchanger system to cool inlet gas ducts before the gas reaches the bagfilters at the GTC.
High Cost	1	Continuous monitoring (laser) of inlet duct gas fluoride level.
	2	Install higher scrubbing capacity (more gas flow) for higher amperage or higher line capacity.

Customisation and Implementation of FEMG

As potroom and GTC technologies vary from smelter to smelter, it is important for the management guide to be adaptable to any variation in technologies and work practices. The FEMG is customisable to meet the need of any specific smelter.

Ultimately, the guide achieves its purpose when the content is being implemented in the smelter. The development of an implementation plan is important to allow the smelter to distribute the relevant information to all its personnel that play a role in fluoride emissions. It will also ensure that maximum gains can be achieved by the smelter in reducing fluoride emissions.

An example of the customisation and implementation process for the FEMG is summarised in Figure 5 and consists of several steps.

Figure 5. Customisation and implementation process of FEMG.

External Audit and Customisation Visit

The purpose of an initial audit and customisation visit is to obtain relevant information and data on smelter technology, as well as smelter's operation, control and maintenance practices to customise the FEMG. The information obtained will ideally include photos of bad/good work practices, operational schedules, smelter layout, and other relevant smelter information.

Concurrently, operational, control and maintenance practices in the smelter will be reviewed to assess the current practices. The audit will be based on the audit guidelines/checklists and recommended best practices specified in the FEMG.

Customisation of FEMG & Identification of Improvements

Using the customisation material and photos, a tailored FEMG for specific smelter's technology and operational, control and maintenance practices can be developed. From the audit review, KPIs and improvement opportunities to reduce fluoride emissions across all areas of the smelter can be identified. This will ensure the content of a customised FEMG and any improvement to work practices is specific and relevant to all the personnel in the smelter.

Strategic Planning and Implementation of FEMG

It is important to develop a strategic plan to address areas of improvement. The implementation process may include:

- **Smelter personnel training** – training of smelter staff in the identified areas of improvement based on the customised FEMG and training workshops.
- **Implementation of changes in practices** – smelter personnel to apply the necessary changes as per the guidelines in FEMG.
- **Regular audits** – smelter managers to monitor the changes in practices by conducting regular audits.
- **Fluoride monitoring equipment** – fluoride emission monitoring equipment could be used to monitor the changes in the smelter's fluoride emission as improvements to practices are implemented. This can be done by comparing baseline measurements (1-3 months prior to changes) against measurements 1-3 months after implementation of FEMG practices.

If adopted, smelters stand to achieve significant improvement in environmental performance and operational standards for fluoride emissions reduction.

Case Study

A smelter case study with the FEMG was carried out by the LMRC. An audit was conducted in two sections of a potroom and in a GTC area in a smelter, using the checklists provided in the FEMG. During the auditing process, some good practices and improvement opportunities were recognised. One example was the use of anode rod seals to minimise emissions from the pathway shown in Figure 6.

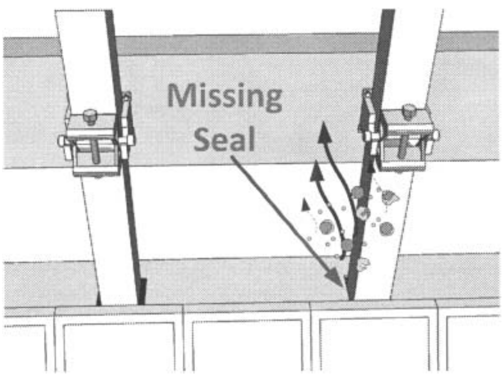


Figure 6. Schematic diagram of fluoride emission from the gap left between the anode rod and the skirt due to damage or missing seal.

The openings in the cell superstructure around the anode rods are designed to accommodate anode change process. Prior to the audit and training sessions, most of the operators did not understand the role of anode rod seals. Hence, no routine check on the condition of the anode rod seals was done. On average per pot, five seals were missing and seven seals were damaged.

Through the training sessions, the importance of anode rod seals on maintaining pot suction and therefore, keeping the fluoride in the pot becomes clear to the operators. These anode rod seals can reduce fluoride emissions by as much as 20% [7]. After the training sessions, regular checks were scheduled on anode rod seals whereby, damaged seals were repaired and missing seals were replaced immediately.

Feedback obtained from the operators was generally positive. Operators found the guide to be very practical, particularly the pictures or schematic drawings used to illustrate the problems and the recommendations. The theory and background information contained in the FEMG for each practice provides a better understanding of the importance of each operation – through this understanding, it is easier for operators to implement the FEMG's best practice recommendations.

Implementation of the FEMG was also a good opportunity to test the robustness and practicality of the guide. Feedback from the operators and smelter personnel was integrated into the guide, improving the quality and usefulness of the guide.

Conclusions

The mission to manage and reduce fluoride emissions extends across all areas of the smelter. Every individual in the smelter is responsible and plays a vital role in achieving this goal. Although the potroom and the GTC are likely to be the main areas contributing to fluoride emissions, it is important to realise that other plant areas, such as the bath plant, may also contribute to fluoride emissions.

The FEMG provides a structured approach to a better understanding of the factors affecting and the ways of reducing fluoride generation and emissions. The ultimate aim of this customisable guide is to provide practical and technical information to help smelters achieve significant improvements in their environmental performance with their current technologies. Through careful management of operation, process control and maintenance practices across the plant, significant reduction in fluoride emissions and improvement of operational standards can be achieved in the smelters.

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