

## INVESTIGATION OF SOLUTIONS TO REDUCE FLUORIDE EMISSIONS FROM ANODE BUTTS AND CRUST COVER MATERIAL

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### Abstract

For many aluminium smelters, reducing fluoride emissions is often a condition to increase production. Since they contribute up to 40% of the overall roof vent emissions, anode change operations are often targeted for improvements and specifically the emissions from the anode butts and crust cover. The Rio Tinto Alcan Research Centre, LRF, has been conducting an R&D programme over the past few years aimed at improving the understanding of the physical phenomena involved and ultimately minimising this specific contribution. On this basis, different conceptual solutions have been developed and their relative performance evaluated. These tests, associated with past experience of enclosed butt boxes and crust bins, concluded that any container receiving a hot butt and bath crust would require almost complete sealing to be effective. The next stage in this programme is engineering design with the aim of developing smelter technology with the lowest environmental footprint.

### Introduction

As production is increased, many aluminium smelters are faced with the concurrent challenge of reducing, or at least maintaining, specific fluoride emissions in order to meet their regulatory obligations. Tighter environmental regulations will make this even more difficult in the future, and will require operations to consider investment in state-of-the-art pollution control equipment to help achieve this objective.

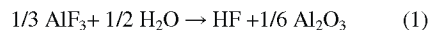
Since anode change operations represent the single largest contributor to overall roof vent emissions, they are often targeted for improvements [1, 2, 3]. A significant contribution to the emission from the anode changing operation occurs when cell hoods are removed, especially during the period when bath is exposed [3]. This contribution can be minimized by reducing the total time that hoods are opened and/or significantly increasing cell exhaust flow during this operation, through the use of a dedicated Boosted Suction System [3].

Two other significant contributions to emissions from the anode change operation are related to the spent anodes and crust cover material after their removal from the cell. These contributions cannot be reduced by better operational practices and therefore require additional equipment to capture the emissions. Some technologies have already been trialed on an industrial scale within Rio Tinto Alcan plants but most have considerable drawbacks which have prevented their widespread deployment. In this context, Rio Tinto Alcan has been conducting an R&D programme over the past few years aimed at improving its understanding of the physical phenomena involved. Different conceptual solutions have subsequently been developed and tested. This paper presents the main conclusions to date from this work.

### Emissions from spent anodes and crust cover material

Hydrogen fluoride (HF) is produced by the chemical reaction between fluoride species and compounds containing hydrogen. In the case of spent anode and crust cover material, ambient moisture is the major source of hydrogen. Fluoride-containing species can be found in the bath crust and in the anode cover mixture on the spent anode as well as impregnated in the surface of the butt itself. Fluoride emissions from these sources are due to two mechanisms.

The first mechanism involves a direct reaction of ambient moisture with bath material. Humidity reacts preferentially with aluminium fluoride (AlF<sub>3</sub>) rather than any other constituent of the bath, because the equilibrium constant is much higher than for the other bath species [4]. The associated chemical reaction is:



This reaction is endothermic, facilitated by an external source of energy, such as the hot anode. The equilibrium constant linking partial pressures (P in atmospheres) and activities (a) of the different molecules in this reaction is as follows:

$$P_{\text{HF}} = \exp\left(-\frac{\Delta G^0}{RT}\right) P_{\text{H}_2\text{O}}^{1/2} a_{\text{AlF}_3}^{1/3} a_{\text{Al}_2\text{O}_3}^{-1/6} \quad (2)$$

In this equation,  $\Delta G^0$  (J) refers to the Gibbs energy of the reaction, R the Gas Constant (8.3144 J/(K.mol)) and T the absolute temperature (K).

The second mechanism involves vaporization of the bath material prior to reaction with moisture. At temperatures above 700 / 800°C, some bath material vaporizes, forming mainly NaAlF<sub>4</sub> [4]. Part of this vapour is hydrolysed by ambient moisture to form HF while another part condenses and forms fluorinated particulates. Because of the relatively high temperature required for such vaporization to occur, this reaction only takes place during the first few minutes following the material removal from the cell. The contribution from this second mechanism is therefore expected to be much lower compared to the first one.

From the above, one would expect fluoride emissions to be influenced by temperature, and the rate at which it decreases, since all the previously described reactions are favoured, both thermodynamically and kinetically, at high temperature. Other parameters include the quantity of bath material exposed to water vapour in the ambient air as well as, to a lesser extent, the bath material composition (higher AlF<sub>3</sub> excess results in higher activity for example).

Experimental set-up

The characteristics of spent anode emissions from older cell technologies and the main drivers influencing these have been previously investigated [5, 6]. It was felt however, that it would be beneficial to update these studies with newer, more accurate, measurement techniques and check whether the conclusions drawn on the basis of older cell technologies are still valid for the latest generation, which are designed in particular with much bigger anode assemblies.

Experimental equipment was installed at the Rio Tinto Alcan Research Centre, LRF, in Saint-Jean-de-Maurienne for this investigation. It consisted of a measurement enclosure in which a single anode assembly or a single crust bin could be placed. The enclosure stack was equipped with a continuous HF analyzer (Neo Monitor), a CO and CO<sub>2</sub> continuous analyzer (Testo). The gas flow rate and temperature were also continuously monitored and there was a facility to conduct manual dust sampling.



**Figure 1 - Measurement enclosure**

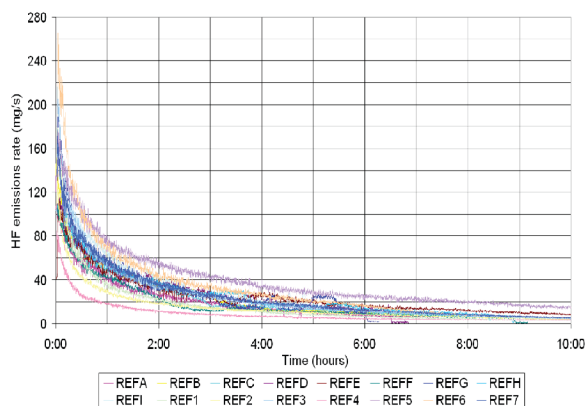
Reference measurements were first carried out to assess the characteristics of the emissions from the spent anodes and crust bins under normal conditions where there was no attempt to minimize or capture the emissions.

Two measurement campaigns were carried out in 2008 (tests numbered A to I) and in 2010 (tests numbered 1 to 7), which consisted in inserting spent anodes from the LRF AP50 prototype cells into the measurement enclosure immediately after their removal from the pots. The time between the anode removal and

its installation in the enclosure was typically 5 to 8 minutes, which is much less than what occurs during published tests carried out in industrial potlines [8]. Additional information, such as the anode location in the cell, age and spent anode mass, as well as ambient meteorological conditions, were also recorded to facilitate data interpretation. The same procedure was applied to crust bins.

Spent Anodes – Baseline measurements

The following graph shows the measured emission rate (in mg/s of HF) of 16 similar anode assemblies as a function of the time after the anode assembly was positioned inside the measurement enclosure.



**Figure 2 - HF emission rate curves for anode assemblies**

The first set of measurements (A to I) showed that the gaseous fluoride emission rate had generally decreased to background level after 10 hours, though a few spent anodes still evolved measurable emissions after this period. For the second measurement campaign (1 to 7), it was therefore decided to leave the anode inside the enclosure for at least 10 hours, and to integrate the emission rate over this period to calculate total specific emission in kgFg/tAl (kilograms of gaseous fluoride emissions per tonne of liquid aluminium produced). The average cumulative emission for the first 10 hours was 0.14kgFg/tAl ± 0.06 (95% confidence interval). Extrapolating these emission rates to account for the initial 5 to 8 minutes where the emissions were not measured adds an extra 0.02kgFg/tAl to the previous contribution.

Figure 3 shows the cumulative emission as a function of time. The results have been normalised on the basis of the cumulative emission after 10 hours and include the contribution from the first 5 to 8 minutes before the spent anodes were placed in the enclosure.

This graph shows that, based on the cumulative emission after 10 hours, approximately 30% is evolved during the first 30 minutes, less than 40% during the first hour and 80% during the first 5 hours.

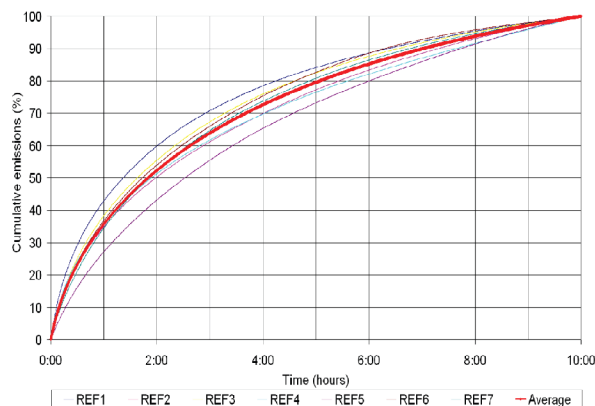


Figure 3 - Cumulative emissions for experiments 1 to 7

Manual dust sampling was also carried out. This sampling showed that the cumulative particulate fluoride emission was less than 0.01kgFp/tAl during this period and thus makes only a minor contribution to the total fluoride emission. Total dust emissions represent approximately 0.02kgPt/tAl. Chemical analysis of the dust showed that approximately 50% of the bath vapours evolved is hydrolysed to HF, the rest condensing as fluorinated particulates.

Spent anodes – Discussion

The overall average cumulative emission is consistent with previously published information, though it is on the high side [1, 2, 3, 5, 6]. When compared to existing information, the curve of cumulative emission versus time also has a slightly different shape, as represented below [5, 6].

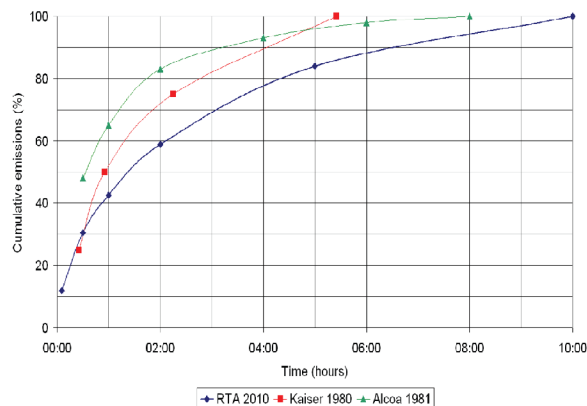


Figure 4 - Comparison of experimental results with published information [5, 6]

Compared with the published information, in our experiments a greater part of the total emission occurred at a later stage. We believe that this is due to the much bigger anode assemblies that have been used for these tests. The higher thermal inertia of the larger spent anodes results in a slower cooling rate, contributing to maintaining emission rates for a longer duration.

The data analysis then focused on investigating the drivers for the large variability. Plotting 1/(emission rate) versus time results in a

linear relationship. Consequently, emission rates can be described by the following equation:

$$Emission\ rate\ (mg\ /\ s) = \frac{1}{At + B} \quad (3)$$

The mathematical function  $At+B$  represents the number of seconds required to emit 1 mg of HF at the time  $t$ ;  $B$  corresponds to this duration at  $t_0$  ( $1/B$  is the emission rate in mg/s at  $t_0$ ) and  $A$  relates to how quickly the rate of emission decays with time. Equation (3) can be integrated to obtain the cumulative emission for a given time  $t$ .

$$Cumulative\ emission\ (mg) = \frac{1}{A} (\ln(At + B) - \ln(B)) \quad (4)$$

Each experimental curve, representing the emission from a single spent anode, could therefore be characterized by these two parameters. The following graph provides examples of actual and corresponding modelled curves to illustrate the good fit between the two.

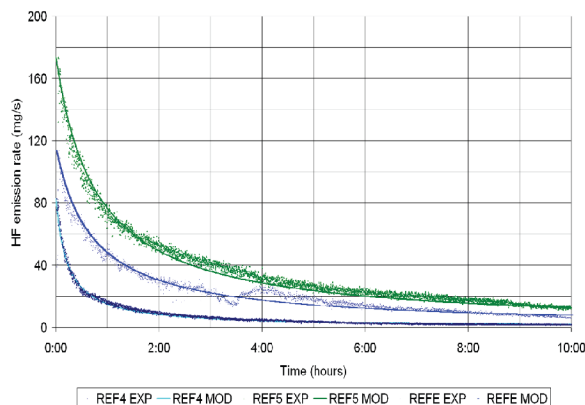


Figure 5 - Comparison of actual and modelled curves

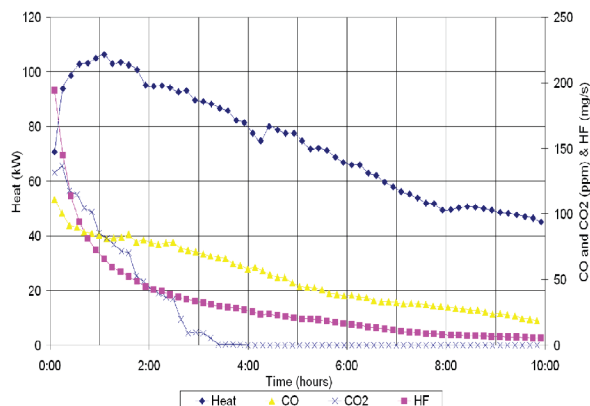
On this basis, it is then possible to investigate what influences the two parameters  $A$  and  $B$ . Interestingly, the parameters were found to be uncorrelated. Both parameters exhibited high variability, with the standard deviation representing approximately 40% (for  $1/A$ ) and 30% (for  $1/B$ ) of their corresponding averages.

A statistical analysis was conducted in order to determine the correlations between these parameters and potential influences such as the spent anode carbon mass, the mass of cover material, ambient absolute humidity, and the anode location in the cell prior to removal. Overall, only a weak correlation between ambient absolute humidity and the parameter  $B$  was found.

The following graph represents HF emissions, CO and CO<sub>2</sub> emissions as well as the heat exhausted at the stack from a typical example (trial number 6). Three phases can be identified:

- A first phase, lasting for approximately 30 minutes, during which HF emissions decrease very rapidly and the exhaust heat increases (probably as the measurement enclosure heats up).

- A second phase of approximately 1 to 2 hours, when the exhaust heat and CO emissions remain constant. During this period, HF emissions reduce at a slower rate compared to the first phase.
- A third and final phase, characterised by a slow decrease in the HF and CO emissions as well as the heat dissipation.



**Figure 6 - HF, CO, CO<sub>2</sub> emissions and exhaust heat**

As expected, the emission rate decay (A) appears to be related to the kinetics of the spent anode cooling. A longer cooling time results in a slower decrease in the emission rate. It is thought that the carbon oxidation participates in maintaining the spent anode surface temperature at a high level, slowing down the emission decreasing rate.

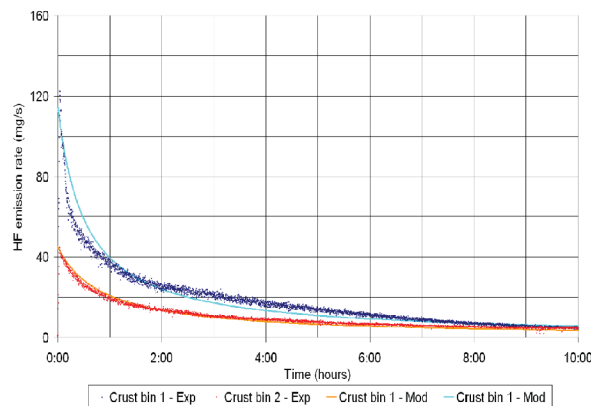
Crust cover material – Baseline measurements

While the R&D programme primarily focused on the contribution of the spent anodes, a few tests were carried out to estimate the emissions from the crust cover material, using the same procedure. Bins containing crust cover material (typically around 700kg), corresponding in size to the skimming from a single anode cavity, were inserted inside the measurement enclosure within minutes of the material being extracted from the cell.

Two typical examples of the emission curves obtained are shown in Figure 7, as well as their corresponding modelled curve built on the same principle as the one used for the spent anodes. Similar to the spent anodes, there is a good fit between the experimental and modelled curves. The emissions from the crust bins exhibit lower initial rates and decrease more rapidly than for the spent anodes. This results in lower emissions for the crust bins. Total emissions, integrated over a period of 10 hours, are estimated to be slightly less than 0.10kgFg/tAl.

First lessons from the baseline measurements

Emissions from spent anodes and crust cover material have been estimated to be around 0.16kgFg/tAl and 0.10kgFg/tAl respectively. For both, the contribution of particulate fluoride is minimal, estimated to be less than 0.01kgFg/tAl. It is to be noted that, under normal operating conditions, a portion of these emissions escapes from the potline roof vent whilst they are cooling on-line, with the rest being emitted from the anode cooling building.



**Figure 7 - Crust cover material typical HF emissions**

A high variability in emissions from spent anodes has been observed. Both the initial emission rate as well as the rate at which the emissions decrease are very variable. A statistical analysis has concluded that the different carbon and cover masses do not explain the variability of these two parameters. This is thought to be due to the relatively small range of masses explored (similar anode sizes; the standard deviation of the carbon and cover masses represented 11% and 14% of their respective averages). Comparing the emission rate curves from smaller anode assemblies does indeed suggest that bigger sizes result in an extended period of emissions. Ambient humidity does not seem to influence emissions, probably because water vapour is already in large excess even in the driest conditions (range explored: from 4.1 to 6.8 g/kg averaged over the 10 hours period). This high variability implies that it is necessary to conduct a high number of experiments when measuring these emissions.

The factor A, representing the rate at which emissions reduce with time, has a stronger impact on the overall variability than B (75% of the variability is explained by A). This factor is related to the thermal behaviour of the spent anode and how quickly it cools down, which is thought to be itself, to a degree, influenced by the anode combustion. For a given anode size, qualitative parameters, such as the spent anode shape and cover integrity, are suspected to be the most important factors.

**Solutions for reducing fluoride emissions from spent anodes and crust cover material**

Once this preliminary analysis of reference spent anodes and crust cover material had been completed, the experimental set-up was used to test different conceptual solutions.

Enclosed spent anode boxes

This concept aims at minimizing the spent anode exposure to both ambient moisture and oxygen from the air. It was assumed that the efficiency of this type of equipment depends on its sealing level. Such a concept is not new and has already been tested and implemented by Rio Tinto Alcan and others [7, 8].

In order to prove the concept, a prototype box was built, with the objective of being close to 100% tight. Gaps between the cover and the tray, as well as around the anode stem were manually sealed using rock wool. This prototype is shown in Figure 8.



The same protocol as the one used for the baseline measurements was applied; spent anodes were placed in the prototype box immediately after their removal from the cell, and the box was itself placed in the measurement enclosure shortly after.



**Figure 8 - Sealed anode box used for the proof of concept test**

Six trials were conducted with this prototype, and the results were very repeatable. Emissions were very low, averaging  $0.04\text{kgFg/tAl}$  ( $\pm 0.005$ ), excluding the contribution from the first minutes. Although the tightness was considered as being close to 100% tight, it was not sufficient to fully counteract the internal pressure building related to the gas generation and heat. Following these encouraging preliminary trials, it was decided to test an industrial box based on the same principle.

A new concept was designed, based on Rio Tinto Alcan's past experience in the Alma smelter where several concepts had been tested in the past. Particular attention was paid to the sealing system around the anode stem.

Another measurement campaign of six tests was then organised, based on this prototype. The corresponding average emissions and variability were very close to the spent anodes baseline measurements. Different modifications of the box were made, providing only marginal improvement to its efficiency. It could be seen that the buoyancy driving force of the hot spent anode was so strong that emissions would escape from any small gaps in the box.

These tests concluded that a container receiving a hot spent anode would require almost complete sealing to be effective. This was deemed to be impractical in industrial conditions, as it would be difficult to maintain good sealing in the long term.

#### Covering the anode with a granular material

An alternative concept to the enclosed anode box was therefore considered, which consisted in burying the spent anode in a granular material available in the smelter, such as crushed bath, cover mix or alumina.

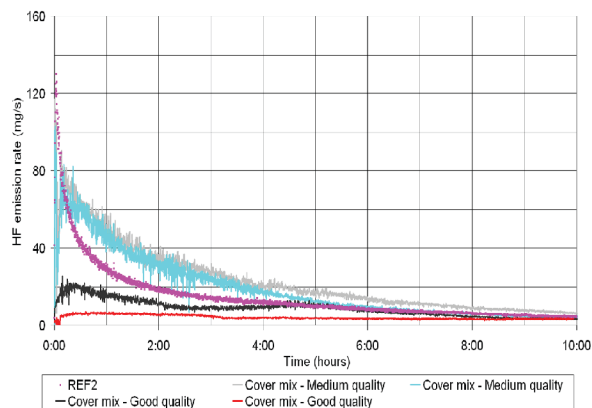
Proof-of-principle trials confirmed the potential of this solution. Spent anodes were placed in a tray and completely covered with approximately one tonne of crushed bath material before being inserted into the measurement enclosure as in Figure 9. The tests were repeated five times and the emissions were very low and repeatable, averaging  $0.05\text{kgFg/tAl}$  ( $\pm 0.01$ ), excluding the contribution from the first minutes, a performance similar to that obtained with the first prototype "fully" sealed anode box.



**Figure 9 - Spent anode covered with cover mix**

Following these initial successes, tests using cover mix and alumina were conducted. While they confirmed that using cover mix was also very efficient in reducing emissions (nine tests averaging  $0.06\text{kgFg/tAl}$ ), they indicated that alumina cannot be used. Covering the hot butt with alumina resulted in geysers being formed because of this material's fluidizable nature. This in turn generated high levels of dust emissions and poor efficiency in reducing HF emissions.

Additional tests were organized to estimate the sensitivity of the cover quality on emissions. The quality of the cover was visually evaluated as being either "good" (the spent anode was completely recovered) or "medium" (there were still a few visible parts). The following graph represents typical emission curves for one reference / uncovered spent anodes, spent anodes with "good" and "medium" cover.



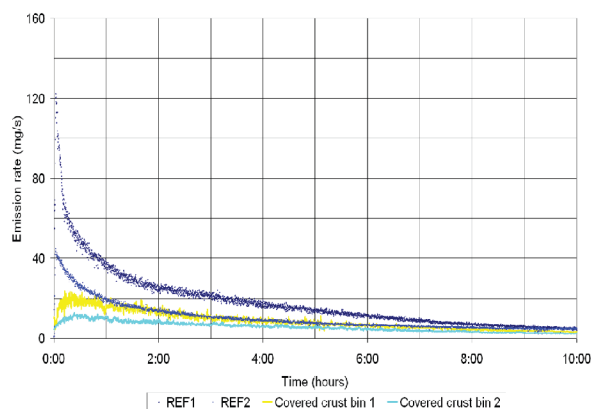
**Figure 10 - HF emission rate of spent anodes with different cover qualities**

The conclusion is similar to that drawn from the anode box test. For the concept to be efficient the spent anode needs to be completely covered. Spent anodes that are incompletely covered exhibit similar emissions to the baseline values.

In practice, the spent anode could be recovered with granular material by using, for example, autonomous pallets, equipped with reservoirs containing the appropriate material, or alternatively using the pot tending crane.

Enclosed crust bin

Installing a simple cover on the crust bin significantly reduces its emissions. A few tests conducted with such covers in place concluded that emissions below 0.04kgFg/tAl can be achieved (compared with a reference value of 0.10kgFg/tAl, refer to Figure 11). Whereas it was necessary to have complete seal on the spent anode box to achieve good performance, the crust bin cover efficiency is less sensitive to sealing.



**Figure 11 - HF emission rates of covered crust bins**

**Conclusions**

The results of these tests have improved our understanding of the behaviour of spent anodes and crust cover material emissions. Spent anode and crust bin emissions have been estimated to be around 0.16kgFg/tAl and 0.10kgFg/tAl respectively. It is thought that this contribution could theoretically be reduced to less than 0.05kgFg/tAl through the implementation of an efficient fume capture. On this basis, different conceptual solutions aimed at reducing this contribution have been tested.

The sealed box concept provided good results. However, a container receiving a hot spent anode requires almost complete sealing to be effective. This was deemed difficult to achieve and maintain in industrial conditions, and it was therefore decided to investigate alternative solutions. On the other hand, a simple cover on the crust bin is sufficient to be effective.

Testing the covering of the spent anode with a granular material has been successful, but similarly to the sealed anode box, it requires very good coverage to reduce emissions significantly.

The next stage in this programme is engineering design, with the objective of developing a viable industrial solution based on these concepts.

**Acknowledgments**

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