Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

Solution to Reduce Fluoride Emissions from Anode Butts

Guillaume Girault[1], Bruno Petitjean[2], Gaston Riverin[2]
[1]Rio Tinto Alcan L.R.F.; Rue Ste Claire Deville, CS40114; Saint Jean de Maurienne, 73302, France
[2]Rio Tinto Alcan Smelter Technology and R&D; Centr'Alp, BP7; Voreppe Cedex, 38341, France

Keywords: Spent Anodes, Butt box, Fluoride Emissions

Abstract

Reliably achieving target fluoride roof vent emissions remains a challenge for many smelters. Since they contribute up to 40% of the overall roof vent emissions, anode change operations are often targeted for improvements and more specifically the contribution from the spent anode butts. Over the last few years, Rio Tinto Alcan has therefore pursued an ambitious R&D program to understand the physical phenomena involved. Several conceptual solutions were consecutively designed and tested, including different types of enclosed butt boxes.

These initial tests concluded that the efficiency of such solutions is very sensitive to the design of the seals, and this has therefore been the focus of the most recent work. This paper provides an update on the latest development of a new covered pallet device, including the latest measurement campaign, prototyping and industrialization steps for it to be efficiently applied in smelters.

Introduction

Many aluminum smelters are under pressure to further reduce fluoride emissions, as a result of tightening environmental regulations or as part of projects to increase production. The first step typically consists in implementing “Best Operating Practices” as it does not require much capital investment. These relatively well-known standards [1] aim at maintaining good pot sealing conditions and efficient operation of the Gas Treatment Centre, amongst other things.

Once these practices are implemented, and assuming that they are not sufficient to reduce emissions below the required limit, plants will then have to consider investing in some form of technological solution. Because anode change operations are the primary single source of emissions, contributing up to 40% or more to the total, they - and more specifically the contribution from the spent anodes - are often targeted for improvement [2]. Anode butts are also one of the primary sources of potline operators' exposure to hazardous gaseous pollutants [3], which reinforces the need of any solution aimed at reducing them.

In this context, Rio Tinto Alcan initiated an R&D program several years ago, aimed first at gaining a better understanding of the physical phenomenon involved and consequently investigating potential solutions. Preliminary activities led to the selection of two concepts which appeared to be the most promising.

The first one consists in enclosing the spent anode in a sealed box, a solution which has also been investigated by others [4]. An alternative option, which involves covering the spent anode with powdery material, is also currently being considered [3]. Since then, industrialization activities have been conducted on both options. This paper will present an update on the enclosed butt box, as its development has been taken further and is now close to completion.

Description of concept

Lessons from the conceptual work investigation

Introducing the spent anode into a perfectly sealed, enclosed box is expected to limit the contact between the hot fluoride components from the anode cover and ambient humidity, consequently minimizing gaseous fluoride emissions.

To confirm this assumption, proof of concept tests were organized in 2010 at Rio Tinto Alcan's R&D Centre in France (LRF), where tests were conducted under controlled conditions. A prototype box was built with the objective of virtually being 100% closed. Gaps between the cover and the tray, as well as around the anode stem were manually sealed using rock wool. Measurements were conducted to assess its efficiency and a significant reduction was achieved, from an initial 0.16 kgHF/tAl for reference spent anodes down to less than 0.04 kgHF/tAl [1]. Following these encouraging preliminary results, it was decided to test an industrial box based on the same principle, which is represented on the following schematic.

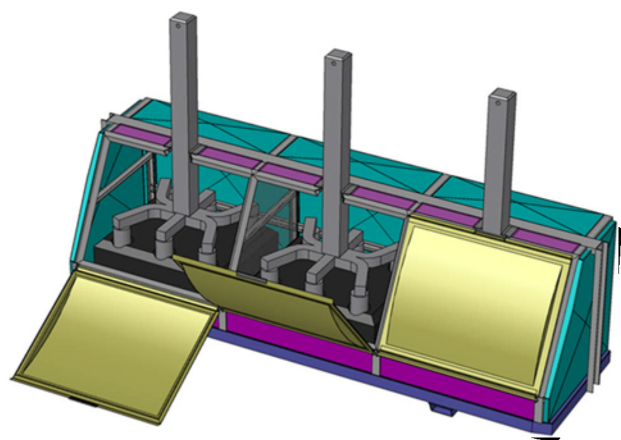


Figure 1 – Initial design of spent anode enclosed box

Surprisingly, the performance of this first industrial design in terms of emission reduction was minimal. The corresponding average emissions and variability were very close to the baseline spent anode measurements. Following that, different modifications were made to the box; however, only resulting in marginal improvements in its efficiency. The conclusion from this initial work was that the efficiency of any enclosed box would be very sensitive to the design of its seals. It was initially thought that an efficient and robust seal compatible with the extreme conditions in which the tray would be operated might lead to unacceptably high costs with no guarantee of long-term performance, which prompted an investigation of the alternative option based on covering the anode with powdery material. However, investigations in different sealing designs for an enclosed box continued considering the high potential of this concept.

New spent anode cover design

Following the disappointing results obtained on the first prototype, a review of the existing sealing concept highlighted several flaws that could explain the ineffectiveness. First, the door closing the box is not on a horizontal plane, which means air leaks out from top to bottom. Ambient air is therefore being sucked in at the bottom of the box through natural convection (stack effect), which is counter-productive when seeking to isolate the spent anode from ambient humidity as much as possible. Secondly, box tightness was provided by a flexible seal located all around the hinged door, which itself leaned against the box structure. Its efficiency therefore depends to great extent on the seal and door conditions and any bend results in significant leakages. Finally, it could be seen that significant emissions occurred around the stem. The initial prototype was equipped with a sealing jaw identical to the one installed on AP pots, which was clearly insufficient for this application.

A new concept for a fully enclosed anode butt box addressing all the listed drawbacks emerged as a result of this review. It consists of a cover that includes the anode stem, so that no sealing is therefore needed around it. The cover rests on the anode tray through a horizontal interface. Careful attention was paid to the design of the seal between the tray and the cover so that it is intrinsically tight even when the flexible seal installed is damaged. An in-built guiding system ensures that the cover is correctly positioned. This overall configuration is expected to provide a very robust design.

A prototype, pictured below, was therefore built for testing at the LRF, and the results of these tests will be discussed.

Figure 2 – Prototype of new anode cover concept

Experimental set-up

The test consisted in inserting spent anodes from one of the LRF AP60 prototype pots (with and without the cover) into a measurement enclosure, pictured below. Each test lasted for approximately 24 hours and different operating parameters were monitored during this period. The time between removing the anode from the pot and introducing it into the enclosure was minimized (<10 min).

Figure 3 – Covered spent anode being introduced into the measurement enclosure

The enclosure stack was equipped with a continuous HF analyzer (Neo Monitor Laser Gas II) as well as temperature and velocity measurement devices to compute gaseous fluoride mass flows. The carbon monoxide (CO) concentration inside the spent anode cover was continuously monitored (Siemens Ultramat 23) to assess the corresponding safety risk. Ambient concentrations of a few selected pollutants (CO, HF and SO_2) were measured in the vicinity of reference spent anodes (Dräger x-am 5600 and Neomonitors LaserGas). Additional measurements included the internal pressure inside the cover (Kimo CP200) as well as the temperatures of the air inside the cover and of the spent anode itself. All measurement devices had been calibrated prior to the test.

A total of 4 reference spent anodes and 14 covered anodes were measured. In order to test the robustness of the seal design, 4 tests out of the 14 corresponded to a configuration in which the mounted flexible seal which improves the tightness between the cover and the tray was removed. This was assumed to be representative of an extreme case in which the seal was severely damaged. In this case, tightness was only ensured by the specific design of the interface between cover and tray.

HF emissions

The following graph shows the emission rate (in mg/s of HF) measured for the 14 anode assemblies as a function of the time after they were individually introduced into the measurement enclosure. The 4 reference spent anodes are noted “REF”; “T1” to “T10” correspond to the 10 tests with the seal in place whereas “T11-WS” to “T14-WS” correspond to the 4 tests with the seal dismantled.

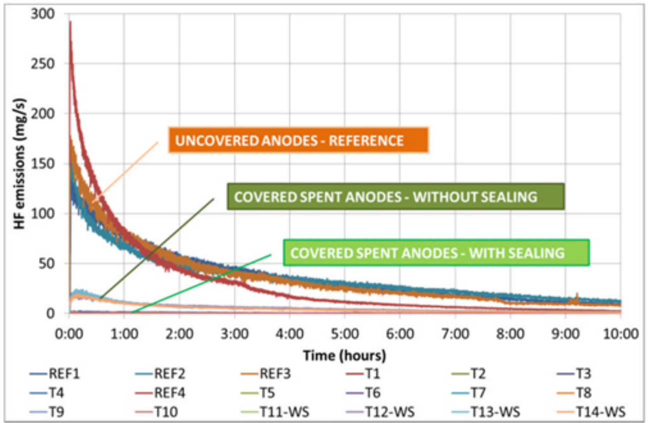


Figure 4 – HF mass flow rate (t_0=time when spent anode introduced into the enclosure)

The baseline measurements from the 4 reference uncovered spent anodes fell within the range measured in 2010 with an identical set-up and in similar conditions [5]. They display the typical rapid decay in emission rate as the spent anode cools down.

The graph clearly shows the benefit from covering the anode, namely a sharp reduction in the emission rate. Removing the flexible seal only results in a relatively minor but still measurable increase in emissions. All the results are well reproduced for the 2 configurations with the cover on.

In order to accurately quantify the overall benefit in terms of cumulative emissions, the correlation between emission rate and time determined during the preliminary investigation [2] was used to estimate and then include the unmeasured contribution from the first 5 to 10 minutes before the spent anode is introduced into the enclosure. The resulting values, averaged for each configuration and integrated over 10 hours, are provided in the following graph (100% = average of the 4 reference measurements).

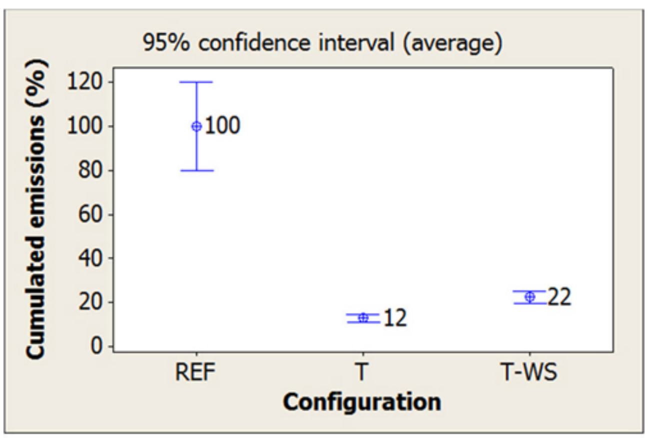


Figure 5 – Cumulative emissions over the 10-hour period (95% confidence interval around the average)

The data shows that covering the spent anode with the new cover allows emissions to be reduced by 88% to approximately 12% of their original contribution when the anode is uncovered. Most of these emissions occur before the spent anode is covered (first 5 to 10min.). Removing the seal only increases emissions by about +10%, a relatively low value that confirms the robustness of the solution.

Spent anode temperature

One of the main process risks associated with the concept is the potential increase in the spent anode cooling time, as a result of less convective exchange. This is turn would impact the spent anode storage building, leading to additional costs and/or logistical challenges.

Preliminary estimates based on Computational Fluid Dynamics (CFD) concluded that covering the spent anode should not result in any significant change in its cooling rate. Indeed, most heat is exchanged through radiation, and is not influenced by the cover.

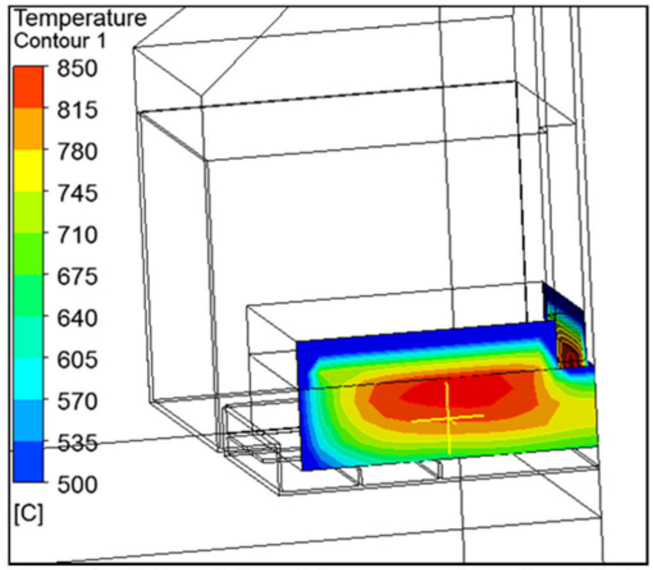


Figure 6 – CFD modeling of the spent anode cooling with the cover on

Measurements confirmed these results, as shown on the following graph. Compared to the reference, cooling was somewhat faster when the cover was on. On the other hand, removing the seal seemed to have the unexplained effect of slightly reducing the cooling rate, though the number of points is insufficient to reach a firm conclusion. At this stage, it is therefore considered that the cover does not impact the cooling rate either positively or negatively.

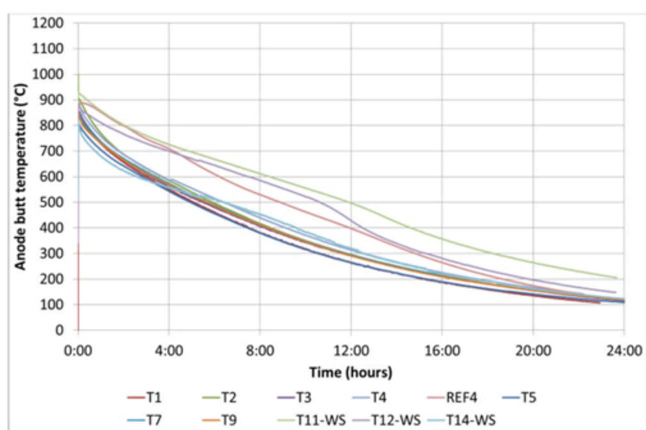


Figure 7 – Spent anode temperature in three different configurations

Carbon monoxide measurements

Carbon monoxide concentration was continuously measured inside the anode cover in order to assess the risk of reaching explosive conditions as a result of incomplete combustion in this confined space. A preliminary study indicated the corresponding safe limit above which this risk could arise. The following graph represents the measured concentrations as a percentage of the safe limit.

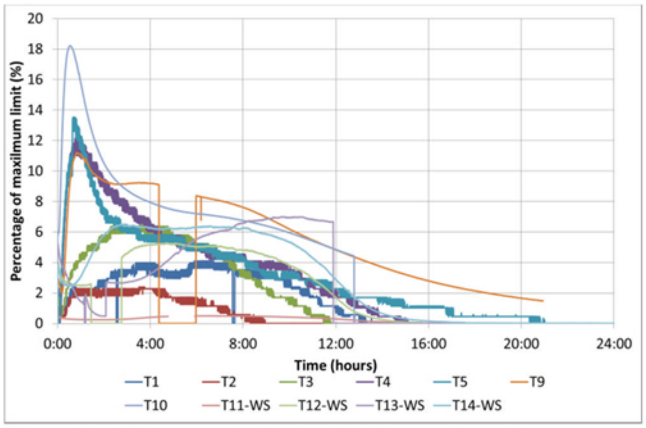


Figure 8 – CO concentration inside the spent anode cover

The maximum concentration recorded was less than 20% of the safe limit, confirming the very low probability of its occurring. It was however confirmed as a point worth considering when designing enclosed butt boxes.

Industrial hygiene measurements

Preliminary measurements were conducted in order to evaluate the order of magnitude of the concentration of HF and SO_2 to which operators are exposed when standing close to a (reference / uncovered) spent anode.

As expected, the measured concentration varied considerably depending on the measurement point, and in particular its distance from the spent anode. Changes in ventilation conditions (outside wind) also affected the results. While the number of measurements was not sufficient to estimate the average exposure accurately, it was clear that relatively high HF and SO_2 concentrations could be measured in the close vicinity of the anode butt (1-2 m).

On the other hand, it was not possible to replicate the measurements on the covered spent anode, since this would have meant entering the measurement enclosure, which was impractical and raised safety issues. But considering the significant drop in the measured HF emissions at the enclosure stack, there is no doubt that any operator standing next to a covered tray would be much less exposed. Additional measurements would however be necessary to quantify the benefit with greater precision.

Furthermore, operators wore personal CO detectors when opening the cover; the results showed that the levels were much lower to the exposure limit of 25 ppm for every single measurement. As a reference, the US ACGIH Threshold Limit Value for CO is 25 ppm.

Industrialization

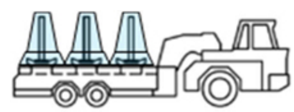
In parallel to designing and testing the anode butt cover, work was done to evaluate full implementation of this technology in an aluminum smelter. The industrialization phase is essential to ensure the successful integration of new equipment in an industrial environment. It covers the main technical and Health, Safety and Environment (HSE) aspects and aims to reduce or eliminate the impact on plant productivity and overall cost. An additional objective is to facilitate implementation in several plants while shortening the learning curve. The base case for our study is an existing smelter using AP3X pot technology.

Part of the industrialization work involves optimizing the following steps: (1) transporting the covers to the pot rooms, (2) handling the anodes, removing the used anode, installing the new anode and handling the cover over the hot butts, (3) removing the cover at the anode pallet storage and (4) storage.

The outcome of this optimization process will be described below. The real value of the technology package is to provide the best design for anode butt covers that ensure complete sealing for potential plant application, plus integration in a plant.

1- Transportation of the covers to the pot room

One option is to transport the covers on the top of the new anodes, after placing them in the anode storage area. Other options investigated involve using additional equipment or require storage space for the covers.

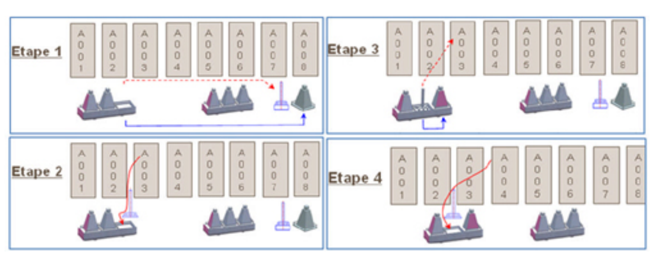


Once they have arrived in the reduction pot rooms, the covers are handled by the Pot Tending Assembly (PTA) using the cover hooking device compatible with the existing PTA. Therefore, the hooking device installed on the cover needs to be simple enough to adapt to most current equipment

2- Handling in the pot rooms

A sequence is defined for cover handling, as follows: (a) remove the first cover and set it on the floor close to the pallet; b) remove the first new anode and set it on the floor; c) position the first hot anode butt in the pallet; d) install the new anode at the same location in the pot; e) cover the hot anode butt with the cover of the adjacent anode on the pallet.

A precise study was performed to evaluate all cover movements carefully from removal from over a new anode to positioning over a hot anode butt, as schematically represented in Figure 9 below.



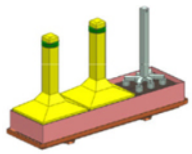


Figure 9 – Example of anode change operation with covers

Handling the covers involves greater use of the PTA. The aim is therefore to identify interactions or interference with all the equipment involved (pallets, PTA tools and cabin, process vehicles, etc.) while minimizing machine utilization rate. The overall impact of the PTA utilization time is expected less than 5%.

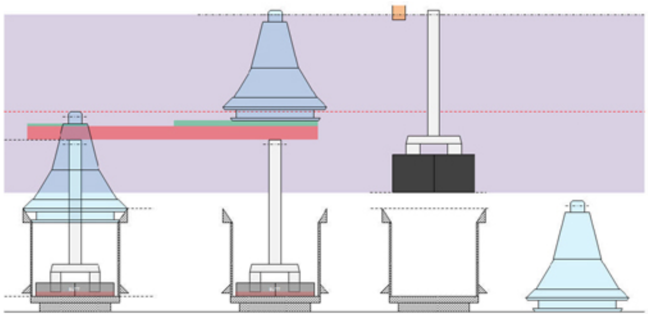


Figure 10 – Sequence of anode change operation with covers

It should be noted that the covers are designed to make sure that the anode butts will be completely covered, taking into account the real plant conditions, such as:

- the height of the anode butt
- the inclination of the anode butt including the rod.
- the condition of the pallets, to ensure good sealing with the covers.

3- Removal of the cover in the anode pallet storage

In the anode pallet storage area, the covers stay on the anode butts set on the pallet to cool. When the anode butts are cold, the covers are removed from the pallet and installed on another pallet with new anodes. It should be noted that fluoride and particulate emissions will be significantly reduced in the storage area. As previously discussed, anode butt cooling time is not negatively affected.

4- Transportation of anodes butts and handling in the pallet storage area

The pallets loaded with their anode butts are then transported to the anode cleaning station where no changes to existing equipment are needed, where the butts are removed and the pallet is cleaned by tilting.

Figure 11 – Handling of covers in storage area

Additional advantages:

Several options, solutions and / or technologies exist to reduce fluoride emissions with different degrees of effectiveness with or without capital investment.. Depending on the situation at the plant, a single solution or a combination of technologies can be selected.

One advantage of the anode butt cover solution is that it can be implemented on both brownfield or greenfield sites. The anode covers can also be adapted to any electrolysis technologies.

Furthermore, the solution does not require equipment downtime, and thus has a minimum impact on pot room operations.

On the operational side, covering the butts limits their chemical reactivity with bath and the anode itself. This leads to a secondary benefit, which is expressed in less carbon consumption. This effect was not measured during our testing campaign. On the other hand, based on our modeling calculations, this benefit can be estimated at around 5 to 7 kg of C per tonne of aluminum. This benefit in terms of carbon consumption needs to be validated in a larger campaign.

Cost and economic aspects

A cost estimate was performed for complete implementation in an aluminum smelter (AP3x – 250 kt/y). The main cost items are: (1) fabrication of the covers, (2) modification of the bins to ensure good sealing with the covers and (3) modification of handling equipment.

It always difficult to evaluate a particular technology for fluoride reduction knowing that it depends on numerous parameters including a particular plant operation. For our case, we propose a rating based on effectiveness (cost in $ per kg of fluoride reduced) and on overall benefit (specific fluoride reduction in kg F per t of aluminum produced). For these two criteria, we estimate a benefit of 0,12 kg F / t Al. and an effectiveness of $19 / kg F collected. From experience, these results compare very favorably to other technologies for fluoride reduction.

Conclusions

The new covered pallet device proposed has shown impressive performance in terms of reducing fluoride emissions; the benefit is estimated at 0.10 kg F / t Al according to our measurement campaign. This underlines the importance of carefully designing the seal between the covers and the pallets. The concept will also significantly reduce the exposure of potline operators to HF.

The proposed design is simple, flexible and easy to adapt. Development of the anode butt covers is now complete and RTA has developed a specific methodology that would allow for rapid, easy and cost-effective implementation of this technology, applicable to both greenfield or brownfield sites.

References

[1] Jean-Pierre Gagné et al., New Design of Cover for Anode Trays, Light Metals 2006, TMS, 213-217.

[2] Jean-Pierre Gagné et al., Update on the evaluation of the HF emission reduction using covered anode trays, Light Metals 2010, TMS, 291-294.

[3] Guillaume Girault et al., Investigation of solutions to reduce fluoride emissions form anode butts and crust cover material, Light Metals 2011, TMS, 351-356.

[4] Nursiani Tjahyono et al., Fluoride Emissions Management Guide (FEMG) for aluminum smelters, Light Metals 2011, TMS, 301-306.

[5] Jean-Pierre Gagné et al., HF emission reduction from anode butts using covered trays, Light Metals 2012, TMS, 557-560.