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HF Emission Reduction from Anode Butts Using Covered Trays

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Abstract

During the production of aluminum in conventional prebake Hall-Héroult electrolysis, anodes have to be replaced on a regular basis. The anode butts are usually placed on uncovered trays for transportation, a practice that contributes to overall hydrogen fluoride (HF) emission. Anode tray covers developed by Alcoa were implemented at the Deschambault smelter to significantly reduce these fluoride emissions and an Alcoa-STAS R&D team developed a modified version of anode tray covers for the greenfield Alcoa Fjardaál plant.

In 2009, the Alcoa-STAS R&D team designed and fabricated an experimental test garage to allow the accurate full-scale in-plant measurement of temporal HF emissions from cooling anode butt trays.

Over the last two years, comparative measurements were performed on covered and uncovered anode trays in a manner to allow estimation of the overall impact of covered trays back to zero time, or initial butt removal from the pot. This paper presents results from these studies.

Introduction

Located in the heart of an agricultural region, Alcoa Deschambault (ADQ) has always worked at reducing its emissions levels. Since 1998, many improvements and refinements have been performed on the equipment and the operational techniques.

The Deschambault plant was the first aluminum smelter to develop and implement covered anode trays and crust bins, which facilitated a 69% reduction in HF emissions from the anode cooling area. In addition, a dual-draft system, that increased the air flow from the pots on demand during active pot work, was installed to further reduce HF emissions from the potroom roof vents. Over the years, emphasis was shifted to refining and improving the methods and equipment used at the plant: improving dry scrubber efficiency and working in strict compliance with best practices, to name a few. All these efforts contributed to achieving annual total fluoride emissions of 0.24 kg TF/T Al.

A series of tests were carried out to measure the effect of different design parameters on anode tray covers in order to further refine the cover design for the new Alcoa Fjardaál plant. During this period, however, sub-optimal test conditions and limited availability of the test equipment made it difficult to gather large controlled test populations of data. Even so, the new design proved to be an improvement over the previous configuration [1].

In 2009, the Alcoa-STAS R&D team developed a custom designed experimental setup to study HF emissions from covered anode trays and crust bins. The primary goal was to measure the temporal fluoride emission performance of anode tray and crust bin covers as accurately and reproducibly as possible. This data has played a key role in helping to design the next generation of confinement devices [2].

Over the past two and a half years, more than a hundred tests have been conducted in many different configurations to measure emissions from various anode trays and crust bins whether covered or not.

In our previous publications [1-2], we used the actual plant operational methods as our test basis. The anode trays were evaluated after loading with 3 pairs of anode butts. However, waiting for 3 pairs to be placed into the anode trays made it impossible to directly record the emissions for the first 25 to 30 minutes from the removal of the first anode pair from the pot.

To account for fluoride lost while the anode tray sits in the electrolysis hall and during the transit to the test garage, the anode tray emission profiles were extrapolated back to the time of extraction of the first pair of anodes. The exponentially decreasing emission profile made it necessary, in the case of covered trays, to extrapolate approximately 50% of the total HF mass emitted.

In this research effort, we sought to reduce the extrapolation uncertainty of HF emissions as much as possible by using improved test methods to bring the initial extrapolation time to a minimum, that is, on the order of 2-3 minutes instead of 25-30 minutes.

To measure emissions closer to the anode butts extraction time, we performed a series of emission performance tests with only one pair of anode butts placed in the center of a tray. Using this emission profile, we could construct full anode tray emission profiles by superimposing 3 curves (2 butts each) and by shifting the second and third curves by 10 and 20 minutes, respectively, to simulate the time gaps between 3 consecutive anode butt pair extractions. We were thus able to get the anode tray into the test garage usually in less than 3 minutes after anode butt extraction from the pot.

To calculate the overall HF emission profile even more representatively, we incorporated the temporal emissions performance of bare anode butts with those of the covered anode butts. In this manner, we were able to more accurately model the real emission pattern of a covered tray, including the emission component that is lost while the anode butts are carried from the pot to the covered tray. This approach also allowed us to comparatively evaluate the impact of short (30 second) and long (60 second) anode butt transit times, such as expected when using automated rod height gauging compared to manual gauging. Automated rod height gauging is a commercially available option for reducing the period of time the anode butts are exposed to air between removal from the electrolysis cell and insertion into the covered tray. Summer conditions prevailed during all data shown in this report to allow us to measure the fluoride emission occurring during higher ambient air temperature and humidity ranges typical in Quebec (16-25°C, ~ 40-70% RH).

Experimental Method

The same test garage setup described in 2010 [2], was used to perform all the temporal fluoride emission measurements shown in this report. The same purpose built 24' x 16' portable garage (Figure 1) covered with fireproof fabric was used as a fume collector. The bottom edge of the fabric walls and doors were three feet above the ground to allow free entrance of convective cooling air, as representative of most smelter buildings. The top of the garage roof was equipped with a 16-inch wide vent extending the entire length of the structure. This opening allowed heated air to escape without restriction. In order to accurately measure the mass flow and the HF gas level exiting the vent, an optical flow sensor (OFS2000, Optical Scientific, Inc.), a gas HF detector (GasFinder FC, Boreal Laser, Inc.) and four thermocouples were installed in the roof opening. Other instruments employed in the test garage sensor array included an ambient air thermometer, a hygrometer, one thermocouple to measure the temperature of the anode butt pair, and one additional thermocouple to measure the gas temperature in the center compartment of the anode tray cover. All data were recorded on an SM2000 ABB 12 channel data logger equipped with a graphic interface allowing visual inspection of the sampled data during the test periods.

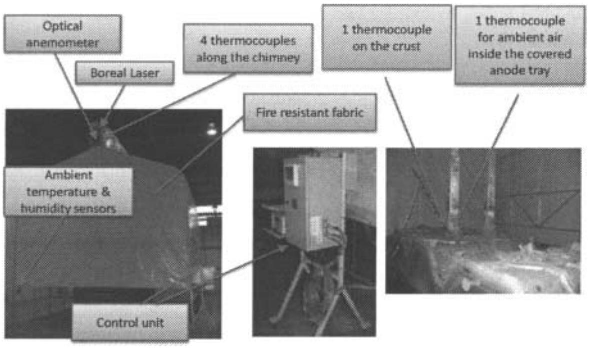

Figure 1: Test setup

We performed two series of tests. The first series had only one pair of anode butts placed in the center of a covered anode tray. For the second, we used the same anode placement on an uncovered anode tray. The pots used for these experiments were selected to be as close to the test garage as possible to reduce the vehicle transit times to a minimum. Also, the vehicle used for the anode butts tray transportation was waiting for the anode butts pair and provided immediate transportation to the test garage. By doing so, we were able to reduce the extrapolated emission time to approximately 2.5 minutes.

The average total test duration was 20 hours to assure that the anode butts were no longer evolving HF prior to their removal from the test area.

The measured HF evolution profiles observed for given test configurations were repeatable, exhibiting a relative standard deviation of total evolved mass HF (kg F) of 4.52%. The average emission performance of individual test conditions was comparatively evaluated with respect to tray loading and environmental factors to identify additional levers impacting HF emissions.

As discussed in prior research [2], a strong correlation ($R^2=0.90$) was observed between the carbon weight and the total quantity of HF released by anode butts during cooling. In order to compensate for variations in the weight of the anode butts, emission results were normalized using the residual carbon weight for each anode tray.

The humidity level of ambient air was expected to play a role in the HF generation process, however the measurement data acquired during summer months did not evidence a significant correlation between evolved HF and ambient humidity. The independence of the total amount of generated HF with respect ambient humidity levels can be attributed, perhaps, to the large excess (>300x) of available water vapor in ambient air compared to the HF concentrations measured during these tests. In a similar manner no significant correlation between HF emissions and air temperature was observed from the cooling tray study, however the limitation of all tests to warm months restricted the temperature range evaluated in this study.

To extend the investigative potential of these results, the recorded observations consisted of the following data: the time at which each pair of anode butts was extracted from the pot, the weight of carbon and the weight of bath in each tray. We also recorded comments regarding the anode butt tray cover condition. The complete data set was recorded on one single sheet. Pictures of the anode tray covers being evaluated in the test garage were taken in order to keep a visual record that could help explain any anomalies observed during subsequent data analysis.

The accuracy of all instruments was verified before testing. The GasFinder unit was calibrated using an HF permeation oven procedure. The OFS output was checked against a well calibrated vane anemometer. The ambient thermometer and hygrometer outputs were also compared to referenced instruments. Finally, all the inputs in the data recorder were calibrated using a Fluke 787 process meter. Baseline/background noise measurements were performed over a period of 3 days with no anode butts in the test garage and showed no reading drift on any instrument or instabilities.

Results

Extrapolation of Emission Profiles
To build the results presented here, we used data produced with one pair of anode butts placed in the center of a tray, regardless of whether the tray is uncovered or covered. The raw temporal emission data was first extrapolated, assuming an exponential decay profile, to the time (T=0) when the anodes were pulled out of the electrolysis cell. For both cases, uncovered and covered anode butts, all extrapolations were performed assuming there was no change in confinement conditions, from the initial extraction time to the end of emission recording. Figure 2 shows such an extrapolation of HF concentration, normalized to the open tray case maximum recorded values.

The green temporal emission profile shown in Figure 2 gives a visual representation of the potential impact of covering anodes from the time of initial removal from the pot. This scenario is unrealistic, however, since there is no presently practical means for covering extracted anodes during transit by the crane. A more practical representation of the butt emission profile would be a composite of both emission profiles, since the butt transit time profile for either condition would be represented by the open tray condition. This condition is the basis of the composite combination profile approach discussed below.

From the data shown in Figure 2 we can construct the temporal HF emission profile observed for the case of 3 anode pairs placed in one single tray. This particular extrapolation and combination gives us an emission performance profile of a full (3-pair) anode tray, that includes (via extrapolation of the T>2.5 minute data) the time while the anode butts are directly exposed to the atmosphere during transit between the electrolysis cell and placement on the tray. Assuming an average cycle time for an anode extraction of 10 minutes, the emission profile of each anode pair was shifted by this amount of time. Figure 3 shows such an extrapolation for an open anode tray condition.

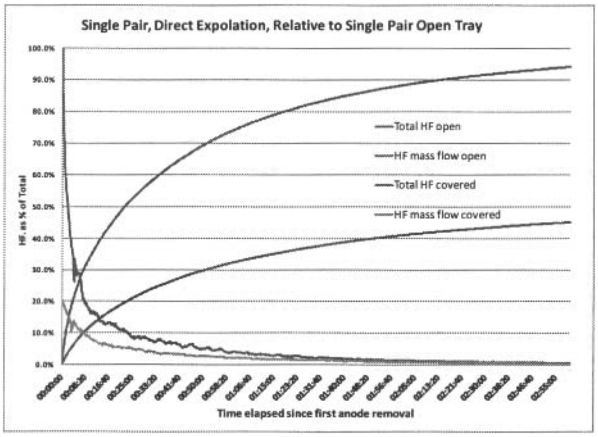

Figure 2: Relative HF concentration and % total mass, for a single anode pair in an open tray and a closed cover. HF percentages are based on the open tray case maximum recorded values.

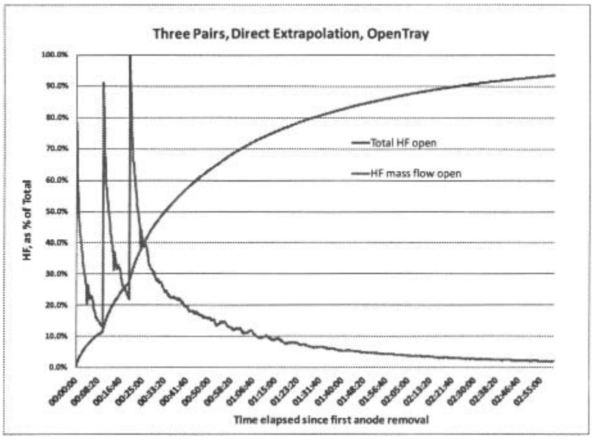

Figure 3: Relative HF concentration and % total mass emission, for 3 anode pairs in an open tray. Data constructed from single anode pair data. HF percentages are based on the open tray case maximum recorded values.

Composite Emission Profiles
To more accurately calculate the overall effective relative reduction in emissions, owing to the use of covered anode trays, we must take into account the fact that part of the emission occurs while the anodes are traveling, openly exposed, from the electrolysis cell to the covered tray. This can be achieved by constructing composite emission profiles using the covered and uncovered anode tray data shown above. An average transit time from the cell to the tray of 60 seconds was used to represent current plant practice. Figure 4 shows a composite emission profile constructed from open tray data for the first 60 seconds and from a covered tray for the remaining time. Given the "front-end loaded" nature of the emission profile shown in Figure 4, reducing the anode butt transit time (open exposure time) to a minimum is a complementary lever for reducing overall fluoride emissions, in conjunction with the use of covered trays.

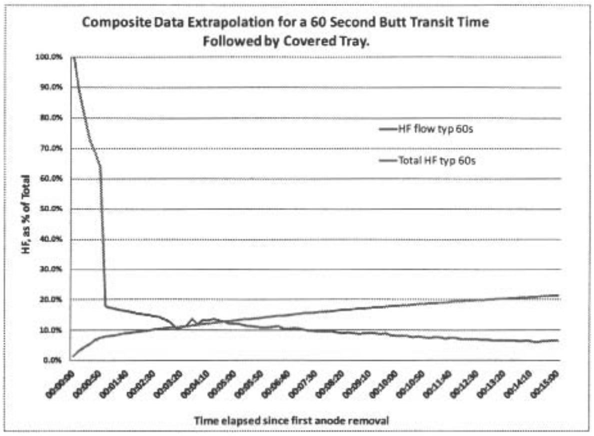

Figure 4: Relative HF concentration and % total mass emission, for 1 anode pair with a 60 second transit time and the remaining time in an covered tray. HF percentages are based on the open tray case maximum recorded values.

Construction of Full Anode Tray Composite Emission Profiles

The HF emission behavior expected from full (3-pair) anode trays can be constructed by combining and extrapolating the temporal profiles shown above, as shown in Figure 5. The HF emission profile shown in Figure 5 represents 3 pairs being withdrawn from the electrolysis cell at ten minute intervals and exposed to the atmosphere for 60 seconds before they are inserted into covered anode trays. Three integrating total HF emission profiles are also shown in Figure 5, corresponding to different anode exposure times and cooling configurations. The red line in Figure 5 (Total HF open) is identical to that shown in Figure 3, corresponding to the HF emission profile expected from a 3-pair anode change using an uncovered anode tray. The orange line in Figure 5 (Total HF type 60s) represents the HF emission profile expected for an anode change where the average transit time for each anode pair between the pot and covered anode tray is 60 seconds. The light blue line in Figure 6 (Total HF type 30s) represents a 30 second transit time using a covered tray. As can be seen from inspection of the comparative emission profiles shown in Figure 5, emissions from anode butts after placement in/on the tray account for a major fraction of the overall integrated HF emission of the butts.

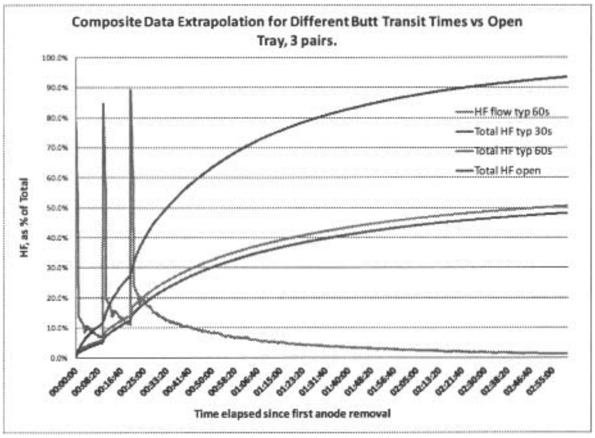

Figure 5: Relative HF concentration and % total mass emission, for 3 anode pairs in various configurations. HF percentages are based on the open tray case maximum recorded values.

Discussion and Conclusion

The anode butt HF emission tests discussed in this paper present a quantitative evaluation of the efficiency of the tray covers currently in use at Alcoa plants. While using well maintained anode tray covers, we have measured a 49% reduction in total anode butt HF emissions using a 60-second butt transit time and a 52% emission reduction when using a 30-second anode butt transit time. These anode butt transit times (60 or 30 seconds), shown in Figure 6, are intended to reflect work practices expected at modern smelters that use manual anode rod gauging or automated anode rod gauging, respectively.

The measurement strategy employed in this study allows for reduction of the extrapolated portion of the temporal HF emission profile to a minimum in order reduce uncertainty in the calculated emission data. Reducing the extrapolation time from 30 minutes to 2.5 minutes raised the proportion of actual measured values from 50% to 83% of the total calculated HF emissions over an anode butt extraction and cooling cycle.

When comparing our 2010 results [2] with current results, the relative HF capture efficiency values for the covered trays are basically the same (0.23% difference). However, the absolute emissions values were overestimated by a large proportion (47%) in the initial work, since extrapolating backwards from the 30th minute severely overestimates the first two peaks in the temporal emission profile of the 3-pair anode tray. The excellent agreement observed between the relative HF emission reduction efficiencies in the earlier and present work, regarding temporal emissions while butt trays were inside the test garage, attests to the reproducibility of the experimental conditions employed in this work.

As evident in the results presented in this study, the highest peak HF emission occurs at the time of initial anode butt extraction from the electrolysis cell. Unfortunately, there is no commercial solution presently available for eliminating this initial anode butt exposure period. As shown in Figure 5, the use of covered anode trays offers a presently available, practically implementable option for significantly reducing HF emissions from extracted anode butts.

The covered anode tray performance observed in this study (49% reduction in total HF) agrees well with our plant observation of a 69% reduction in butt cooling room emissions and corroborates the representative nature of the experimental design. This performance data contrasts what has been observed by others [3] and may reflect substantial differences in test garage or anode tray design.

The hydrogen fluoride generated during the anode butt cooling process accounts for an appreciable portion of the total HF emissions from an aluminum smelter. At Alcoa Deschambault, work practices and equipment have been improved and implemented over the years to systematically reduce the plant's annual fluoride emission levels. The anode tray cover is one of the engineering improvements contributing to this effort. Since 2000, this technology has proven effective in reducing both the total mass and concentration level of HF in the potrooms.

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