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GHG Measurement and Inventory for Aluminum Production

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Abstract

The primary aluminum industry has achieved good progress over the past decade in reducing GHG emissions associated with metal production. The reductions have been tracked through well documented protocols for the measurement of GHGs associated with production processes as well as established inventory accounting methodologies, vetted by stakeholders from within and outside the industry. These protocols and inventory methodologies are currently in the process of being updated to reflect new findings and changes in the industry over the past decade, to further enhance the accuracy and robustness of GHG accounting for the aluminum industry. This paper discusses the revisions being considered and the factors driving the changes.

Introduction

The primary aluminum industry has worked to build a foundation of standards and measurement protocols from which accurate inventories of GHG emissions can be compiled [1-3]. The standards apply to all scope 1 emissions from primary aluminum production: process CO₂ emissions from bauxite refining and alumina reduction, including fuel combustion, as well as perfluorocarbon (PFC) emissions from the reduction of alumina in electrolytic cells operating with carbon anodes. Figure 1 shows that the industry has made great progress in reducing PFC emissions over the past two decades, primarily due to improved management of existing facilities in the 1990s and capital investments since 2000 in new facilities that operate more efficiently and with higher levels of control than prior technology genres.

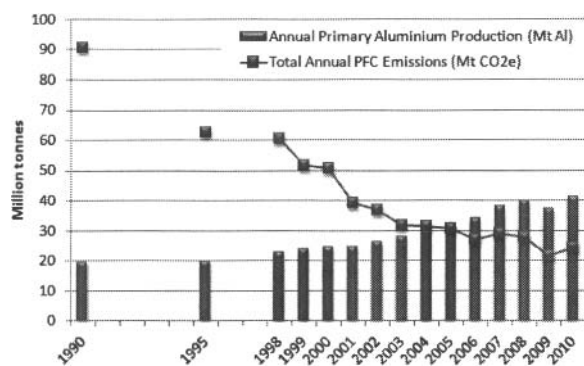


Figure 1. Global Primary Industry PFC Emissions Reduction Performance

Figure 2 shows that PFC emissions per ton aluminum vary markedly among production technologies, the older technologies emitting higher levels of PFCs per ton aluminum produced than the newer point feed prebake (PFPB) technology. The best of

these PFPB facilities, operating with high performing feed control systems, almost eliminate anode effects which are primarily responsible for PFC emissions.

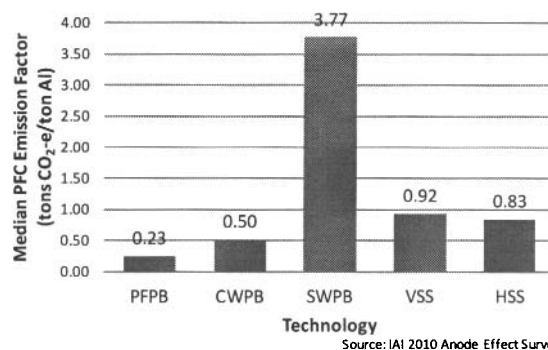


Figure 2. Median PFC Emission Factors by Production Technology

While the median PFPB performance was 0.23 tons CO₂-e/ton Al, the top ten percent of PFPB facilities reporting in the IAI 2010 anode effect survey performed at an average anode effect frequency of 0.061 or better and a PFC emission factor better than 0.06 tons CO₂-e/ton Al. The global average PFC emission factor across all technologies, estimating emissions from facilities not participating in the survey, primarily Chinese production, is 0.59 tons CO₂-e/ton Al.

Accounting for carbon dioxide emissions from the smelting process is rather straight forward and in 2010 represents a global average of under 2 tons CO₂/ton Al. The basic anode production and electrolytic processes result in little uncertainty in accounting for these emissions. PFC emissions, while accounting for the minority of GHG emissions at most modern facilities, remain the most difficult to measure and account for in the total smelter GHG profile. Fortunately for the new, high performing PFPB facilities the amount of PFCs produced in relation to total GHG emissions, CO₂ plus PFCs, reduces the materiality of the uncertainty of PFC emissions assessment.

Opportunities for PFC Measurement and Accounting Improvement

Many primary aluminum smelters have had PFC measurements made in their facilities using the USEPA/IAI Measurement Protocol [2]. A number of findings have resulted from these measurements that point to ways to improve the accuracy and robustness of PFC GHG measurements and inventory.

The Slope and Overvoltage PFC Prediction Models

Historically two different models have been used to relate smelter anode effect performance data to PFC emissions, the “slope” method and the “overvoltage” method. The slope method was the result of early measurement work by Hydro and Alcoa that showed that CF_4 and C_2F_6 emissions per ton aluminum produced were linearly related to the anode effect minutes per cell day over the period that the measurement [4]. Similarly, early work by Pechiney workers who correlated a number of different anode effect parameters showed that the best correlation was between the anode effect overvoltage, the extra voltage due to anode effects above target voltage and thus proposed a linear equation relating the overvoltage parameter to CF_4 and C_2F_6 emission rates per ton aluminum.

As measurement technology has improved and more measurements have been made in which emissions were measured from individual anode effects it has become clear that PFC emissions are not a linear function of time, or overvoltage for individual anode effects. The data show that, while there is a lot of scatter, that the maximum rate of emission comes from the initial seconds of anode effect and that the emission rate decreases with added time on anode effect.

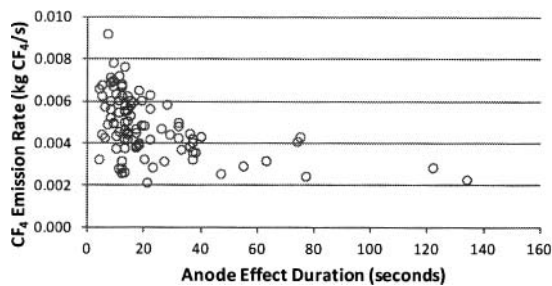


Figure 3. Change in Average CF_4 Emission Rate with Anode Effect Duration

For each anode effect a corresponding “slope” factor can be calculated.

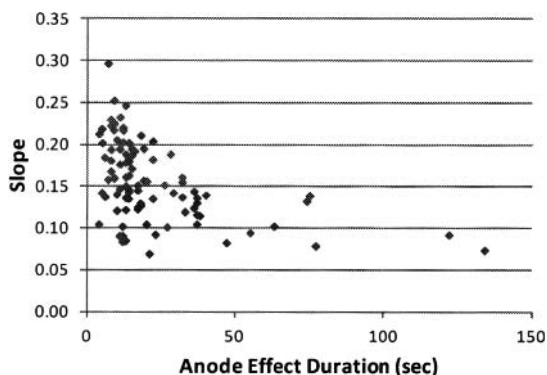


Figure 4. Variation in Apparent CF_4 Slope Factor with Change in Anode Effect Duration

Figures 3 and 4 shows that a changing emission rate, with longer anode effect duration, results in a range of apparent slope values from as high as 0.29 to about 0.07. The average overall slope calculated from the measurement data in the figures 3 and 4 was 0.139, while the average slope factor for anode effects less than 45 seconds duration was 0.151 as compared to the average slope for anode effects lasting more than 45 seconds of 0.091. The robustness of the current overall average slope and overvoltage methods in predicting PFC emissions day in and day out depends on how well the distribution of anode effect durations match that of the measurements. Experience shows that changes in the mix of short and long duration anode effects can introduce uncertainty into the inventory of PFC emissions. We are currently looking into testing a “bin” model that would put anode effects into different time bins, each with its own slope. This would produce a more robust and potentially more accurate result helping to offset the impact of changes in anode effect duration distribution. Alternatively, a best fit equation could be developed from the measurement data and the PFC emissions inventory could be built from calculations of emissions from each anode effect. We hope to be able to test the benefit of these approaches in coming months.

Elimination of the Overvoltage Method for PFC Accounting

While both the slope and overvoltage models have been endorsed by the IPCC, USEPA and IAI in the past, it has been proposed to drop the overvoltage model from future standards. The overvoltage method was used historically for the Rio Tinto AP smelting technology. For recent AP technology potlines the AP data system also collects anode effect duration data allowing the slope factor calculation. Past measurements made where data could be fit to both the overvoltage and to anode effect duration show that both methods give equivalent predictability of emissions. The elimination of the overvoltage method would streamline and simplify standards. Also, the uncertainty of the PFPB IPCC Tier 2 equation factor is considerably smaller for the slope method, +/- 6%, than that of the overvoltage factor, +/- 24%, due mainly to the larger data set, 71 measurements, from which the average slope factor was calculated compared to the nineteen overvoltage measurements included in the calculation of the average Tier 2 overvoltage factor.

Inclusion of Non-Anode Effect PFC Emissions in the Measurement Protocol

Prior work has been presented showing that PFC emissions can occur during periods during which no anode effect has been declared by the potline data system [5]. These non-anode effect (NAE) related emissions can be a significant portion of the overall PFC emissions at a given facility, particularly for modern facilities operating in good control where the total PFC emissions are low compared to global averages. Data for CF_4 emissions from thirteen Chinese smelters are shown in Figure 5 with contributions assigned from anode effects and from NAE emissions.

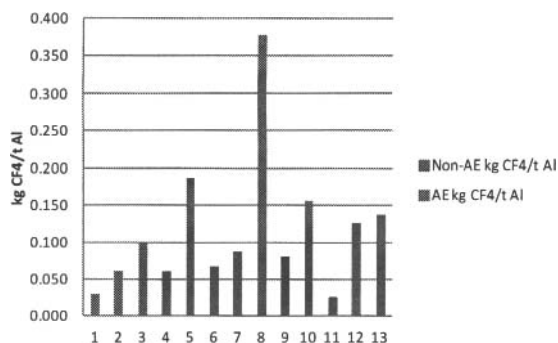


Figure 5. Relative Contributions from Anode Effect Related and Non-Anode Effect CF₄ Emission Rates from 13 Chinese Smelters

There have been a limited number of measurements made outside China where the data have been analyzed for NAE emissions. These results are shown in Figure 6.

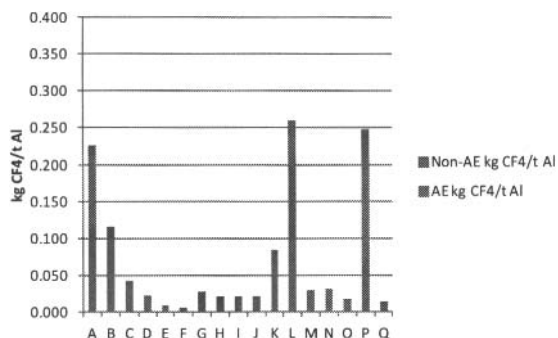


Figure 6. Relative Contributions from Anode Effect Related and Non-Anode Effect CF₄ Emission Rates from 17 Smelters Outside China

Overall, the NAE emissions make up a smaller fraction of the total CF₄ emissions in the limited number of measurements that have been made outside China. The median contribution of NAE emissions measured in Chinese facilities is 70% as compared to a median contribution of 22% for potlines outside China.

The mechanism for the NAE related PFC emissions remain unclear; however, they likely result from polarization of one, or a small number of anodes, to the extent that PFCs are formed while at the same time not exceeding the trigger voltage defined by the site for declaration of an anode effect. Newer control technologies allow operation in lean alumina conditions while avoiding anode effects as typically defined. In particular the Chinese cells also operate at line currents as high as 400KA or more with high energy efficiency, with low anode to cathode separation and operating temperatures less than 950°C. These conditions would favor polarization in parts of the cells potentially exceeding levels that would produce PFCs. Dorreen [6] documented the presence of COF₂ prior to production of CF₄ in laboratory electrolysis cell. This is important because the electrochemical formation of COF₂ occurs at some 680mV lower

potential than that required for direct electrochemical CF₄ formation. COF₂ is thermally unstable at electrolysis cell temperatures and would decompose to CF₄. This mechanism might well account for observations of NAE emissions.

It has been suggested [7] that industry standard definitions of “anode effect” should be reevaluated in light of observations of CF₄ emissions at average cell voltages well below those typically used to trigger anode effect termination control routines. This proposal may well have some merit. There is currently no accepted standard for voltage criteria for the declaration of a cell being on anode effect. Voltage trigger criteria ranging from as low as 6.5V to as high as 10V have been observed in my prior measurements at different facilities. As cells grow larger, with more anodes and greater anode surface area, the detection of local polarization events sufficient to produce PFC emissions will become more difficult, perhaps impossible, by the traditional means of measuring average cell voltage.

Additional measurements of PFC emissions, carefully correlated with instrumented production cells, are needed to understand better the NAE emissions. In addition to providing improved voltage criteria with which to calculate PFC emissions such measurements may prove to be important to operation of large, high amperage cells at maximum efficiency. In any case a revised PFC measurement standard should include guidance for measurement of the emissions of significant PFC emissions that occur outside the bounds of what is considered time on anode effect. Recent measurement data show that while the concentrations of these emissions might be very low compared to emission rates when the cell is on declared anode effect, the fact that the NAE emissions occur almost continuously can make their contribution to total PFC emissions from given facilities substantial.

PFC Emissions From New Cell Starts

PFC emissions from cells that are being started are referred to in the IAI Greenhouse Gas Protocol as “Non Steady State Emissions” and while it is noted that PFC emissions result from the special condition of extended voltage operation, it is also noted that this non steady state condition is not counted as an anode effect. This statement has been erroneously interpreted by some as an indication that emissions during the high voltage period of cell start up should not be included in site GHG inventories. The IPCC Good Practice Guidance for inventory of GHGs from aluminum production notes that sampling for PFCs during measurements should include the entire range of normal smelter operation including cell startup or restart. Companies reporting anode effect data as part of the IAI anode effect survey have a mixed response to reporting high voltage cell start up time as part of their anode effect reporting with some reporting all high voltage cell start time as anode effect minutes and others excluding this time.

Many companies have adopted cell start practices that minimize or totally eliminate a period of high voltage for starting new cells. Measurements made during a limited number of starts of new cells using this procedure confirm that no PFCs are emitted. The most comprehensive study to date looked at the emissions from the start up of ten cells during a new potline start and concluded that the slope for the high voltage period of new cells was similar to that for mature cells that experienced anode effects [8]. Other

reports [9] indicate that the slope for the high voltage period for cell start ups is lower than the slope for typical anode effects. The measurement data reported here for the change in apparent slope values with added time on anode effect tends to support that view. Given that the average cell life is of the order of 2000 days the overall impact of cell starts on GHG inventory of ongoing smelter operations would be very low and not material to the overall GHG emissions from the operation. However, for a comprehensive accounting of PFC emissions, particularly for start up of new smelter lines, development of better guidelines for how to account for PFC emissions for new cell starts is needed. To develop better guidelines additional measurements of PFC emissions during cell start ups are needed.

Summary

Arguably the global aluminum sector has one of the best systems of any global industrial sector for reporting annual, global GHG emissions. The GHG reporting infrastructure is built on a base of international survey data and a solid foundation of measurement and reporting protocols and standards that have been developed and tested by industry, government and non-governmental stakeholders. Excellent progress has been made over the past two decades in reducing the PFC emissions component of primary aluminum's GHG signature. The industry continues to explore ways to further improve the robustness, the accuracy and the completeness of its reporting.

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