

**TECHNICAL SUPPORT DOCUMENT FOR
PROCESS EMISSIONS FROM PRIMARY
PRODUCTION OF ALUMINUM:**

**PROPOSED RULE FOR MANDATORY
REPORTING OF GREENHOUSE GASES**

Office of Air and Radiation
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1. Source Description

Aluminum is a light-weight, malleable, and corrosion-resistant metal that is used in many manufactured products, including aircraft, automobiles, bicycles, and kitchen utensils. As of last reporting, the United States was the fourth largest producer of primary aluminum, with approximately eight percent of the world total (USGS 2006). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of carbon dioxide (CO₂) and two perfluorocarbons (PFCs): perfluoromethane (CF₄) and perfluoroethane (C₂F₆). Only these process-related emissions are considered here.

CO₂ is emitted during the aluminum smelting process when alumina (aluminum oxide, Al₂O₃) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na₃AlF₆). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, most of the carbon in the anode is oxidized and released to the atmosphere as CO₂.

In addition to CO₂ emissions, the aluminum production industry is also a source of PFC emissions. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, which are termed “anode effects.” These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF₄ and C₂F₆. For any one smelter, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. As the frequency and duration of the anode effects increase, emissions increase. In addition, even at constant levels of production and anode effect minutes, emissions vary among smelter technologies (e.g., Center-Worked Prebake vs. Side-Worked Prebake) and among individual smelters using the same smelter technology due to differing operational practices.

a. Total U.S. Emissions

Process emissions of CO₂ from the 14 aluminum smelters in the United States were estimated to be 3.9 million metric tons of CO₂ equivalent (MMTCO₂e) in 2006. Process emissions of CF₄ and C₂F₆ from aluminum smelters were estimated to be 2.5 MMTCO₂e in 2006. Total greenhouse gas (GHG) emissions from primary aluminum production in the United States are estimated to be 6.4 MMTCO₂e in 2006 (EPA 2008). In 2006, 13 of the 14 aluminum smelters in the United States accounted for the majority of process emissions. The remaining smelter was shut down for most of 2006, restarting only at the end of that year.

b. Emissions to be Reported

On-site combustion emissions from aluminum production facilities are not addressed within this document; see the background Technical Support Document for Stationary Combustion (EPA-HQ-OAR-2008-0508-004). This document addresses process emissions of PFCs and CO₂. Process CO₂ emissions can come from the following processes during primary aluminum production:

- Consumption of the anode during electrolysis (for both Prebake and Söderberg cells);
- Anode baking process (for Prebake cells only); and
- Calcining emissions (from coke calcining).

EPA’s current understanding is that all prebake smelters in the United States operate their own anode baking furnaces on site. EPA does not believe that any U.S. smelters operate calcining furnaces on site.

2. Options for Reporting Threshold

EPA evaluated a range of threshold options for primary aluminum production facilities. These included emission-based thresholds of 1,000, 10,000, 25,000 and 100,000 mtCO₂e and capacity-based thresholds equivalent to these. EPA also evaluated a requirement that all primary aluminum production facilities be required to report.

The capacity thresholds were developed based on IPCC default emission factors and 100 percent capacity utilization. These are somewhat conservative assumptions, since capacity utilization is often below 100 percent and

emission rates (particularly PFC emission rates) are generally lower than the IPCC defaults. However, both production and emission rates fluctuate; aluminum smelters sometimes shut down for long periods and then begin production again. The conservative assumptions would ensure that plants that have a reasonable chance of emitting more than the threshold quantity were covered.

Table 2-1 illustrates the emissions and facilities that would be covered under these various thresholds.

Table 2-1: Threshold Analysis for Primary Aluminum Production Based on 2006 Emissions and Facility Production Capacity

Emission Threshold Level mtCO ₂ e/yr	Total National Emissions	Total Number of Facilities	Emissions Covered		Facilities Covered	
			mtCO ₂ e/yr	Percent	Facilities	Percent
1,000	6,403,000	14	6,403,000	100	14	100
10,000	6,403,000	14	6,398,000	99	13	93
25,000	6,403,000	14	6,398,000	99	13	93
100,000	6,403,000	14	6,398,000	99	13	93
Production Capacity Threshold mt Al/year						
64	6,403,000	14	6,403,000	100	14	100
640	6,403,000	14	6,403,000	100	14	100
1,594	6,403,000	14	6,403,000	100	14	100
6,378	6,403,000	14	6,403,000	100	14	100

All smelters that operated throughout 2006 would be covered at all capacity and emissions-based thresholds considered in this analysis. This consideration supports either a capacity-based threshold or a requirement that all plants report. A requirement that all plants report would have the additional advantage of simplicity.

3. Options for Monitoring Methods

EPA reviewed a range of protocols for estimating PFC and CO₂ process emissions from primary aluminum production. These protocols include the *2006 IPCC Guidelines*, EPA's Voluntary Aluminum Industrial Partnership (VAIP), the *Inventory of U.S. Greenhouse Gas Emissions and Sinks*, the International Aluminum Institute's (IAI) *Aluminum Sector Greenhouse Gas Protocol*, the Technical Guidelines for the Voluntary Reporting of Greenhouse Gases (1605(b)) Program, EPA's Climate Leaders Program, and The Climate Registry.

The methods described in these protocols and guidance coalesce around the methods described by the IAI's *Aluminum Sector Greenhouse Gas Protocol* and the IPCC guidelines. These methods range from Tier 1 approaches based on aluminum production to Tier 3 approaches based primarily on smelter-specific data. The IPCC Tier 3 and IAI methods are essentially the same. For PFCs, they both require smelter-specific data on anode effect frequency and duration, smelter-specific slope factors, and aluminum production. For CO₂, they require smelter-specific data on anode consumption and anode characteristics (chemical contents)¹.

¹ The IAI protocol includes an alternate approach for calculating CO₂ emissions. However, although this equation does not refer to impurities, it is assumed that these are already factored in and thus not included in the calculation.

a. *Monitoring Methods for PFCs*

1. Option 1: Default Emission Factor

Option 1, which is the same as the IPCC Tier 1 approach, uses the product of aluminum production and a technology-specific default emission factor to estimate PFC emissions from primary aluminum production. Though this methodology is simple, the default emission factors for PFCs have large uncertainties due to the variability in anode effect frequency and duration. Based on 1990 data, the IPCC Guidelines give an uncertainty range of -99 percent to +380 percent for the default factor for the Center-Work Prebake technology, the most common smelter technology in the United States. Moreover, since 1990, all U.S. smelters have sharply reduced their anode effect frequency and duration; through 2006, average AE minutes per cell day have declined by approximately 85%, lowering U.S. smelter emission rates well below those of the IPCC Tier 1 defaults.

2. Option 2: Smelter-Specific Anode-Effect Minutes

Option 2, which is the same as the IPCC Tier 2 approach, uses smelter-specific data on anode effect frequency and duration. Option 2 also uses data on aluminum production and technology-specific slope coefficients.

The slope coefficient represents kilograms of CF₄/metric ton of aluminum produced divided by anode effect minutes per cell-day. The cell-day is the number of cells operating multiplied by the number of days of operation (IPCC 2006). The following equations describe how to calculate CF₄ and C₂F₆ emissions based on the slope method.

$$E_{CF_4} = S_{CF_4} \times AEM \times MP$$

$$E_{C_2F_6} = E_{CF_4} \times F_{C_2F_6/CF_4}$$

where,

E_{CF_4} is emissions of CF₄ from aluminum production (kg CF₄)

$E_{C_2F_6}$ is emissions of C₂F₆ from aluminum production (kg C₂F₆)

S_{CF_4} is the slope coefficient ([kg CF₄/metric ton Al]/[AE-Mins/cell-day])

AEM is anode effect minutes per cell-day (AE-Mins/cell-day)

MP is metal production (metric tons Al)

$F_{C_2F_6/CF_4}$ is the weight fraction of C₂F₆/CF₄ (kg C₂F₆/kg CF₄)

Although Option 2 results in estimates that are considerably more accurate than those based on Option 1, Option 2 is significantly less precise than Option 3, as discussed below.

3. Option 3: Smelter-Specific Anode-Effect Minutes and Slope Coefficients

Option 3 uses the same set of equations and parameters as Option 2. The critical distinction between the two methods is that Option 3 requires recent smelter-specific slope coefficients while Option 2 relies on default, technology-specific slope coefficients. Of the currently operating U.S. smelters, all but one has measured a smelter-specific coefficient at least once. However, to use Option 3, some smelters would need to update these measurements if they occurred more than 3 years ago.

Use of Option 3, which is similar to the IPCC Tier 3 approach, leads to significantly more precise PFC emissions estimates than use of Option 2. For individual facilities using the most common smelter technology in the United States., the uncertainty (95% confidence interval) of estimates developed using the Option 2 approach is ±50 percent,² while the uncertainty of estimates developed using the Tier 3 approach is approximately ±15 percent (Marks 2008). For a typical U.S. smelter emitting 175,000 metric tons of CO₂-eq in PFCs, these errors result in

² The most common smelter technology in the United States is the center-work prebake (CWPB) technology. The 2006 IPCC Guidelines provide a 95% confidence interval of ±6 percent for the CWPB default slope coefficient. However, this range is not the range within which the slope coefficient from a single CWPB has a 95 percent chance of falling. Instead, it is the range within which the true mean of all CWPB slope factors has a 95 percent chance of falling.

absolute uncertainties of $\pm 88,000$ mtCO₂e and $\pm 26,000$ mtCO₂e, respectively. The reduction in uncertainty associated with moving from Option 2 to Option 3, 62,000 mtCO₂e, is as large as the emissions from many of the sources that would be subject to the rule.

Option 3 requires that slope coefficients be measured using a method similar to the *USEPA/IAI Protocol for Measurement of Tetrafluoromethane and Hexafluoroethane from Primary Aluminum Production*. This protocol was first published in 2003 and updated in 2008. The protocol establishes guidelines to ensure that measurements of smelter-specific slope-coefficients are consistent and accurate (e.g., representative of typical smelter operating conditions and emission rates). These guidelines include recommendations for documenting the frequency and duration of anode effects, measuring aluminum production, sampling design, measurement instruments and methods, calculations, quality assurance and quality control, and measurement frequency.

Both the *Protocol* and industry experts currently recommend that smelter operators re-measure their slope coefficients at least every three years, and more frequently if they adopt changes to process control algorithms or observe changes to typical anode effect duration (Marks, 2008a). Specifically, the Protocol recommends that operators repeat measurements of slope coefficients for CF₄ and C₂F₆ if one or more of the following apply:

1. Thirty-six months have passed since the last measurements (i.e. triennial measurements are recommended);
2. A change occurs in the control algorithm that affects the mix of types of anode effects or the nature of the anode effect termination routine;
3. Changes occur in the distribution of duration of anode effects (e.g. when the percentage of manual kills changes or if, over time, the number of anode effects decreases and results in a fewer number of longer anode effects)

Changes to process control algorithms or to the typical duration of anode effects can change the relationship between anode effect minutes, production, and emissions, that is, they can change slope coefficients. In addition, more subtle changes can also change slope coefficients over time. According to industry experts, the rate of these more subtle changes has not been sufficiently studied to specify a frequency for re-measurement of less than once every three years. Thus, Option 3 requires that slope factors be re-measured at least once every three years.

During the past few years, multiple U.S. smelters have adopted changes to their production process which are likely to have changed their slope coefficients (Marks, 2008a). These include the adoption of slotted anodes and improvements to process control algorithms. Although some U.S. smelters, such as those operated by Alcoa, have recently updated their measurements of smelter-specific coefficients, others may not have.

While the cost to implement Option 3 is significantly greater than the cost to implement Option 2, the benefit of reduced uncertainty is considerable, as noted above. The costs that would be incurred by smelters measuring slope factors are discussed in the Regulatory Impact Analysis for this rulemaking (EPA-HQ-OAR-2008-0508-002).

Another Tier 3 method included in the IPCC Guidelines is the Overvoltage Method. This method relates PFC emissions to an overvoltage coefficient, anode effect overvoltage, current efficiency, and aluminum production. The overvoltage method was developed for smelters using the Pechiney technology. It is EPA's understanding that no U.S. smelters have used the Pechiney technology for at least a decade.

b. Monitoring Methods for CO₂

CO₂ emitted during electrolysis

1. Option 1: Default Emission Factor

Option 1, which is the same as the IPCC Tier 1 approach, uses the product of aluminum production and a technology-specific default emission factor to estimate CO₂ emissions during electrolysis. This methodology is simple, and the difference in accuracy between emission estimates developed using Option 1 and Option 2 (five to ten percent) is notably lower for U.S. smelters than the difference for the PFC estimates. (The IPCC Guidelines note, "the reactions leading to carbon dioxide emissions are well understood, and the emissions are very directly connected to the tons of aluminum produced through the fundamental electrochemical equations for alumina reduction.") However, as part of typical operations, facilities regularly monitor inputs to higher Tier methods (e.g.,

consumption of anodes); consequently, the incremental cost to develop an Option 2 or Option 2/3 hybrid estimate will be small.

2. Options 2 and 3: Smelter-specific anode consumption

Options 2 and 3, which are the same as the IPCC Tier 2 and 3 approaches, respectively, estimate CO₂ emissions from electrolysis based on metal production and net anode consumption. Options 2 and 3 are mass balance approaches that assume that all carbon from net anode consumption is ultimately emitted as CO₂. Both anode consumption and aluminum production are collected as part of typical facility operating processes. Other terms in the Option 2/3 equation make minor adjustments for non-carbon components of the anodes (e.g., sulfur and ash). The distinction between Option 2 and Option 3 is that Option 2 uses default values for these minor components while Option 3 uses specific facility operating data for these components. Since the concentrations of these components are small (typically less than one percent to five percent), facility-specific data on them is not as critical to the precision of emission estimates as is facility-specific data on net anode consumption. Option 3 improves the accuracy of the results but the improvement in accuracy is not expected to exceed 5 percent (IPCC 2006).

The following equation describes how to calculate emissions based on these parameters for each technology type.

For Prebake cells:

$$E_{CO_2} = NAC \times MP \times ([100 - S_a - Ash]_a / 100) \times (44/12)$$

where,

E_{CO_2} is CO₂ emissions from prebaked anode consumption (metric tons CO₂)

MP is total metal production (metric tons Al)

NAC is net prebaked anode consumption per metric ton Al (metric tons C/metric tons Al)

S_a is sulfur content in baked anodes (percent weight)

Ash_a is ash content in baked anodes (percent weight)

44/12 is CO₂ molecular mass: carbon atomic weight ratio (dimensionless)

For Söderberg cells:

$$E_{CO_2} = (PC \times MP - [CSM \times MP]/1000 - BC/100 \times PC \times MP \times [S_p + Ash_p + H_p] / 100 - [100-BC]/100 \times PC \times MP \times [S_c + Ash_c] / 100 - MP \times CD) \times (44/12)$$

where,

E_{CO_2} is CO₂ emissions from paste consumption (metric ton CO₂)

MP is total metal production (metric ton Al)

PC is paste consumption (metric ton/metric ton Al)

CSM is emissions of cyclohexane soluble matter (kg/metric ton Al)

BC is binder content in paste (percent weight)

S_p is sulfur content in pitch (percent weight)

Ash_p is ash content in pitch (percent weight)

H_p is hydrogen content in pitch (percent weight)

S_c is sulfur content in calcined coke (percent weight)

Ash_c is ash content in calcined coke (percent weight)

CD = carbon in skimmed dust from Söderberg cells (metric ton C/metric ton Al)

44/12 is CO₂ molecular mass: carbon atomic weight ratio (dimensionless)

The data reported by companies participating in EPA's Voluntary Aluminum Industrial Partnership (VAIP) has generally not included smelter-specific values for each of these variables. However, most participants in VAIP have

used either data on paste consumption (for Söderberg cells) or on net anode consumption (for Prebake cells), along with some smelter-specific data on impurities, to develop a hybrid Option 2/3 estimate (i.e., combination of smelter-specific and default factors).

CO₂ emitted during anode baking

1. Options 2 and 3: Smelter-specific anode consumption

Options 2 and 3, which are the same as the IPCC Tier 2 and 3 approaches, respectively, estimate CO₂ emissions from combustion of materials during anode baking. (There is no Tier 1 approach for estimating these emissions.) The Option 2/3 equations rely on a mass balance approach involving the chemical contents of the anodes and packing materials. No anode baking emissions occur when using Söderberg cells, since these cells are not baked before aluminum smelting, but rather, bake in the electrolysis cell during smelting. The following equations describe how to calculate emissions from anode baking of Prebake cells.

$$E_{CO_2PV} = (GA - H_w - BA - WT) \times (44/12)$$

$$E_{CO_2PC} = PCC \times BA \times ([100 - S_{pc} - Ash_{pc}] / 100) \times (44/12)$$

where,

E_{CO_2PV} is CO₂ emissions from pitch volatiles combustion (metric tons CO₂)

E_{CO_2PC} is CO₂ emissions from bake furnace packing material (metric tons CO₂)

GA is initial weight of green anodes (metric tons)

H_w is hydrogen content in green anodes (metric tons)

BA is baked anode production (metric tons)

WT is waste tar collected (metric tons)

PCC is packing coke consumption (metric tons/metric ton BA)

S_{pc} is sulfur content in packing coke (percent weight)

Ash_{pc} is ash content in packing coke (percent weight)

As is the case for CO₂ emitted during electrolysis, the Option 2 approach relies on industry-wide defaults for minor anode components, requiring smelter-specific data only for the initial weight of green anodes (GA) and for baked anode production (BA), while Option 3 requires smelter-specific values for all parameters. Again, the concentrations of minor components are small, limiting their impact on the estimate of CO₂ emissions from anode baking. In addition, anode baking emissions account for approximately 10 percent of total CO₂ process emissions, so reducing the uncertainty in this estimate will have only a minor impact on the overall CO₂ process estimate. For EPA's VAIP program, many smelters report only some smelter-specific values for the concentrations of minor anode components.

4. Procedures for Estimating Missing Data

Where anode effect minutes per cell day data points are missing, the average anode effect minutes per cell day of the remaining measurements within the same reporting period may be applied. However, these parameters are typically logged by the process control system as part of the operations of nearly all aluminium production facilities and the uncertainties in these data are low.

It is assumed that aluminum production levels will be known, since businesses rely on accurate monitoring and reporting of production levels. Consequently, there is less than 1 percent uncertainty in the data for the annual production of aluminum. The likelihood for missing data is low.

For CO₂ emissions, the uncertainty in recording anode consumption as baked anode consumption or coke consumption is estimated to be only slightly higher than for aluminium production, less than 2 percent (IPCC, 2006). This is also an important parameter in smelter operations and is routinely/continuously monitored. The likelihood for missing data is low.

5. QA/QC Requirements

As noted above, Option 3 for estimating PFC emissions would require that smelter-specific slope coefficients be measured at least every thirty-six months in accordance with the 2003 (for measurements through 2008) or 2008 (for measurements after 2008) *EPA/IAI Protocol for Measurement of Tetrafluoromethane and Hexafluoroethane Emissions from Primary Aluminum Production*. As noted in the Protocol, key monitoring issues that should be addressed before undertaking a study include the following.

- Measurement conditions should reflect typical operations at the smelter.
- Measurements should be conducted at locations that capture cells where anode effect data is being collected and where there is good flow homogeneity in the gas being sampled.
- Measurements should account for background PFC concentrations, and assess the need to quantify fugitive losses (specifically if collection system efficiencies are less than 90 percent).
- The sampling time should be at least 72 hours; however, a “rule of thumb” should be that the slope coefficient running average does not change by more than 10 percent from the previous average value.

6. Reporting Procedures

Reporting of the following data would be useful for confirming emissions calculations and/or calculating emission rates that could be compared across facilities and over time for data quality control purposes:

- Aluminum production amount in metric tons aluminum
- Smelter technology used
- PFC-specific information:
 - Anode effect minutes per cell-day
 - Smelter-specific slope coefficient
 - Last date when smelter-specific slope coefficient was measured
 - Certification by owner/operator that measurements of slope coefficients were conducted in accordance with the 2003 (for measurements through 2008) or 2008 (for measurements after 2008) *EPA/IAI Protocol for Measurement of Tetrafluoromethane and Hexafluoroethane Emissions from Primary Aluminum Production*.
 - Criteria used by the smelter to measure the frequency and duration of anode effects
- CO₂-specific information:
 - Anode consumption.
 - Smelter-specific inputs to the CO₂ process equations (e.g., levels of impurities) that were used in the calculation. Exact data elements required will vary depending on smelter technology.

7. References

EPA (2008) Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006. U.S. Environmental Protection Agency, Washington, DC.

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