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Latest Progress in IPCC Methodology for Estimating the Extent of PFC Greenhouse Gases Co-evolved in the Aluminium Reduction Cell and Challenges in Reducing these Emissions

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Abstract

In recent years, the primary aluminium industry has increasingly found that perfluorocarbon (PFC) greenhouse gases can be co-evolved in reduction cells during normal operation, i.e. without an anode effect (AE) that is typically defined as when cell voltage exceeds 8 V. Other than during an AE, PFC co-evolution rates are invariably low. However, because of the long duration of these 'low voltage' emissions they can contribute as much than 90 % of a smelter's total PFC output, depending on cell technology, practices and operating conditions. These emissions help explain some of the discrepancy between 'top-down' global atmospheric estimates of PFCs vs. 'bottom-up' industry estimates via the International Aluminium Institute (IAI). To provide a more complete estimate of total greenhouse gas emissions, the Intergovernmental Panel for Climate Change (IPCC) is updating its PFC accounting guidelines for the aluminium industry, covering both anode effect and low voltage emissions – respectively termed 'high voltage anode effect' (HVAE) and 'low voltage anode effect' (LVAE) emissions in the guidelines. The following paper summarises some of the latest progress in this. While the updated 2019 IPCC Refinements provides an important first step in estimating all PFCs co-evolved in the aluminium reduction cell, this paper also explores some of the challenges that remain – firstly in finding a more scientific basis to estimate low voltage PFCs for future IPCC methodologies; and secondly but more importantly, for smelters to determine strategies to detect and mitigate low voltage emissions when they occur.

Keywords: Perfluorocarbons, greenhouse gas emissions, IPCC methodology, anode effect PFCs, low voltage PFCs.

1. Introduction

This article discusses the latest progress and challenges in the global effort to account for PFCs from aluminium smelting, particularly with the inclusion of low voltage PFCs (termed 'low-voltage anode effects' or LVAEs) in updated greenhouse gas (GHG) accounting guidelines from the Intergovernmental Panel for Climate Change (IPCC). It follows on from a detailed investigation of the fundamental mechanisms and underlying causes of all PFC coevolution – from anode effects (AEs) and during 'normal' cell operations (low voltage PFCs) in two ICSOBA articles by Welch et al. ("Part 1" and "Part 2") [1 - 2]. Part 2 in particular describes the impact of changes in cell design that have resulted in low-voltage PFCs becoming more prevalent in modern aluminium reduction cells.

Perfluorocarbons (PFC) – in particular tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) – are potent GHGs with extremely long lifetimes in the atmosphere (50 000 and 10 000 years, respectively) and with high global warming potentials (GWP over a 100-year period) at 6 630 and 11 100 times the equivalent of CO_2, respectively [3]. While very low trace levels of PFC do occur naturally (in the range of ~ 0.1 - 10 t CF_4/y), anthropogenic sources of emissions are 3 to 5 orders of magnitude greater (~ 11 000 t CF_4/y) [4].

The two major anthropogenic sources of PFCs are primary production of aluminium and manufacture of semi-conductors/electronics; other sources include industrial rare-earth metal smelting (with a similar fluoride-salt electrochemical process to aluminium smelting), production of fluorochemicals (e.g., HFC, HCFC), waterproofing of circuit-boards and textiles [5].

1.1. PFCs from Aluminium Smelting

In the aluminium reduction cell, PFCs occur when the electrical potential across the anode E_{anode} exceeds the threshold that enables PFC co-evolution, i.e. the reversible potential $E_{reversible}$ for reactions that generate PFCs. Typical anode reactions are summarised below (gas products in bold) – for more details, refer to [1 - 2]:

- Reactions in normal aluminium reduction (equations 1 and 2) are enabled when E_{anode} exceeds 1.07 - 1.19 V
- Reactions for PFC co-evolution (producing COF_2, or CO and CF_4) enabled once E_{anode} exceeds 1.83 - 1.89 V (equations 3 and 4)
- Reactions for direct or independent PFC co-evolution are enabled at much higher anode potentials, at $E_{anode} > 2.59$ V (equations 5 and 6).

Typical reactions in normal aluminium electrolysis:	$E_{reversible}$(V)	Eqn.
$Al_2O_3(s) + 3C = 3\mathbf{CO}(g) + 2Al(l)$	1.07	(1)
$Al_2O_3(s) + 1.5C = 1.5\mathbf{CO_2}(g) + 2Al(l)$	1.19	(2)
Reactions with PFCs co-evolved:		
$Al_2O_3 + 3C + 2Na_3AlF_6 = 3\mathbf{COF_2}(g) + 4Al(l) + 6NaF(l)$	1.89	(3)
$Al_2O_3 + 4.5C + 2Na_3AlF_6 = 3\mathbf{CO}(g) + 1.5\mathbf{CF_4}(g) + 4Al(l) + 6NaF(l)$	1.83	(4)
Reactions with directly PFCs co-evolved, at higher potentials:		
$3C + 4Na_3AlF_6 = 3\mathbf{CF_4}(g) + 4Al(l) + 12NaF(l)$	2.59	(5)
$2C + 2Na_3AlF_6(l) = \mathbf{C_2F_6}(g) + 2Al(l) + 6NaF(l)$	2.75	(6)

Note that the COF_2 in equation (3) *spontaneously* reacts with anode carbon to form CF_4 gas:

$2COF_2(g) + C = 2CO(g) + CF_4\,(g)$ $G_{1233\,K} = -45.77$ kJ (7)

To enable each reaction, extra entropic energy TΔS is required in addition to the $E_{reversible}$ to *complete* the formation of gas products at the anode – this can be supplied either electrically by anode overpotential or through joule heating. This is discussed in further depth by Welch et al. [1-2].

1.2. PFCs from Anode Effects

Historically the aluminium industry considered that ‘anode effects’ were good for the cells as they helped “clean up the sludge/muck” in the cell, which tended to accumulate through centre- or side-breaking and feeding a mass of alumina in excess of that able to dissolve it. Until approaching the turn of the century, operating control logic scheduled regular anode effects – such as once per week – to bring about this benefit. In the absence of sensitive gas analysis

5. Conclusions

Recent developments in modern aluminium cells means that the past definitions and assumptions of when PFCs are generated in cells have had to be challenged and re-assessed. The knowledge that PFCs can be generated during normal operating voltages (< 8 V) is now being taken into account in the latest 2019 IPCC guidelines for GHG accounting (now accepted by the IPCC, but yet to be adopted by the UNFCCC for implementation by governmental bodies). As anode effect emissions are better addressed, low voltage emissions will pose the next challenge to the smelting industry.

This all points to an industry need for:

- A new approach to signal processing to achieve optimum benefit of modern cell technologies and for better scientific understanding of the process.
- Faster response to indicators of potential approach to PFC coevolution (such as EGA's 'near-AE' logic) in order to prevent, or shorten the duration of the occasional AEs,
- Implementation of advanced control logic that accounts for and minimises the impact of spatial variations in the cell that are inevitable.
- Redesign of equipment and layout used for alumina feeding to increase their reliability and flexibility.

These will all drive reductions in total PFC emissions with further benefits to cell performance and smelter KPIs.

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