

PFC AND CARBON DIOXIDE EMISSIONS FROM AN AUSTRALIAN ALUMINIUM SMELTER USING TIME-INTEGRATED STACK SAMPLING AND GC-MS, GC-FID ANALYSIS

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ABSTRACT

PFC (CF₄, C₂F₆, C₃F₈), HFC (CHF₃) and CO₂ emissions were estimated from two potlines of the Hydro Australia Kurri Kurri aluminium smelter in the Hunter Valley, NSW, in 2009. Emissions were estimated using integrated sampling over a two week period followed by laboratory analysis for PFCs, HFCs and CO₂. The PFC emission factors were similar to, but significantly more accurate than, annual PFC emission factors found for other Australian aluminium smelters (Bell Bay, Tasmania; Portland and Pt Henry, Victoria) in 2009, based on *in situ* PFC data measurements at Cape Grim, Tasmania. The CF₄ and CO₂ emission factors at Kurri Kurri are significantly larger than the Australian average CF₄ and CO₂ emission factors reported to the UNFCCC for 2009. C₃F₈ and CHF₃ emissions at Kurri Kurri are low and do not significantly add to GHG emissions from an aluminium smelter.

INTRODUCTION

Perfluorocarbons (PFCs: CF₄, C₂F₆, C₃F₈) are powerful greenhouse gases (GHGs), up to 12,000 times more potent than carbon dioxide (CO₂) on a mass emitted basis, released to the atmosphere during the production of aluminium and by the electronics and refrigeration industries [1-4]. PFCs are formed in the production of aluminium during anode effects (AEs), usually when the alumina (Al₂O₃) feed to the reduction cell is restricted or interrupted. PFCs remain in the atmosphere for thousands of years and are targeted for controls in global and Australian strategies to reduce GHG emissions, in accordance with the requirements of the UN Framework Convention on Climate Change (UNFCCC) and its associated Kyoto Protocol.

PFC emissions from aluminium production, and their C₂F₆/CF₄ ratios, are smelter-technology dependent. Technology changes over the past two decades have resulted in significantly reduced global and Australian PFC emissions. The lowest level PFC emissions are from smelters employing pre-bake (PB) technology with alumina point feeding [5-9]. PFC emission factors have been derived to account for PFC production during AEs, but may not account for the enhanced PFC production during cell start-up procedures, during anode change, or during non-AE periods. If PFC accounting only deals with PFC production during AEs under so-called 'normal operation', then the PFC emissions from aluminium production estimated by this method may be a significant underestimate (20-30%) of the total PFC emissions from aluminium smelting [8,10,11].

The Intergovernmental Panel on Climate Change (IPCC) has recommended indirect (Tier 2) and direct (Tier 3) methodologies to estimate PFC emissions from aluminium smelters for subsequent reporting to national governments and the UNFCCC. The Tier 2 method uses average smelter-technology specific emission factors for calculating CF₄ emissions and average smelter (all technologies) emission factors for calculating C₂F₆ emissions. Because of the inherent uncertainty in Tier 2 methods (±100%), it is *highly* recommended that individual smelters also adopt a Tier 3 approach to estimate PFC emissions, involving direct

measurement of PFCs at individual smelters, with an inherent accuracy of PFC emission estimates of about ±15% [7,12,13].

The IAI (International Aluminium Institute) recommended technologies for the direct measurement of PFC emissions at aluminium smelters involve continuous measurements by FTIR (Fourier Transform Infrared) or TDL (Tunable Diode Laser) absorption spectrometry [4,6,12,14]. These technologies are expensive to purchase and operate, involving skilled technicians at the smelter. Another approach to the measurement of PFC emissions at aluminium smelters involves the collection of exhaust gas samples in sample containers (sampling flasks, bags or absorption tubes) followed by subsequent analysis in a laboratory, usually by gas chromatography (GC) with mass spectrometric (MS) detection [10,12,15]. The advantages of this technique are the low cost and the sampling integration period, which, if chosen appropriately, will sample many AEs, as well as the non-AE periods, including cell start-up and anode change procedures, leading to a more representative estimate of total PFC emissions. Its major disadvantage is that it cannot be used as a diagnostic tool for investigating details of individual AEs, non-AE periods, cell start-up and anode change procedures.

CSIRO has developed a technology for estimating PFC and carbon dioxide (CO₂) emissions, based on *in situ* integrated exhaust gas sampling and subsequent laboratory analysis on a state-of-the-art gas chromatograph (GC) with mass spectrometric (MS) and flame ionization (FI) detection [16,17]. The technology promises to deliver a less expensive, more accurate and more comprehensive methodology to estimate GHG emissions from aluminium smelters.

ANODE AND EXHAUST GAS COMPOSITION

The composition of the bubbles of anode gas of a normal operating cell is predominantly CO₂ and, during an AE, which can last several minutes, the composition is approximately 60-70% CO, 10-15% CO₂, 15-20% CF₄ and 1-3% C₂F₆ [18]. Significant amounts of CO are oxidised to CO₂ before being swept away with ambient air from the cells in the exhaust gas extraction system. PFCs - CF₄, C₂F₆, C₃F₈ - and a CFC (chlorofluorocarbon: CClF₃) have been identified in the exhaust gas of an aluminium smelter [1]. The typical GHG composition of smelter exhaust gas is shown in Table 1.

The PFCs originate from carbonyl fluoride (COF₂), which is formed at the anode surface before the formation of PFCs [8]. C₂F₆ may be formed early in an AE, CF₄ throughout the duration of the AE, although this may simply reflect the higher overall levels of PFC emissions early in an AE and the difficulty in detecting low levels of C₂F₆ later [7,18]. It is likely that dry anode gas contains the very reactive COF₂. Once COF₂ is mixed with moist air, it is rapidly converted to HF.

Other gases that have been identified in the smelter exhaust gas are (Table 1) sulphur dioxide (SO₂), carbonyl sulphide (COS), hydrogen sulphide (H₂S), carbon disulfide (CS₂) and methane (CH₄) [12,24]. HFCs (hydrofluorocarbons), also potent greenhouse gases, specifically CHF₃, or other chlorofluorocarbons (CFCs), apart from CClF₃, have not been

identified in the exhaust gases of an aluminium smelter [1]. Smelter gases are removed from the potrooms actively via the exhaust system and passively through the roof vents. The hooding efficiencies of PFC removal via the exhaust systems can be better than 95% for PB technology smelters [12].

Table 1. GHGs and other trace gases found in scrubbed aluminium smelter exhaust gas [1,12,19]

GHG	formula	concentration	GWP ^a	GWP ^b
carbon dioxide	CO ₂	0.5-1%	1	1
PFC-14	CF ₄	300-1000 ppb	7400	6500
PFC-116	C ₂ F ₆	20-90 ppb	12200	9200
PFC-218	C ₃ F ₈	1-3 ppb	8300	7000
CFC-13	CClF ₃	3-10 ppb	14400	14000
hydrogen fluoride	HF	400 ppm		
carbon monoxide	CO	400-1000 ppm	2	
sulphur dioxide	SO ₂	35-70 ppm		
carbonyl sulfide	COS	5 ppm		

a GWP = Global Warming Potential, the integrated (100 year, post emission) impact on radiative forcing of a unit mass of GHG relative the same unit mass of CO₂ [20].

b GWP = GWP in Australia's National Inventory Report 2007 [21].

KURRI KURRI 2008

In April 2008, a feasibility study was conducted at the Hydro Kurri Kurri aluminium smelter (32°S, 151°E) in the Hunter Valley, near Newcastle, NSW, Australia. The experiment was based on instantaneous sampling of ambient air and exhaust gas (after the dry scrubber, described below) into previously evacuated 3 litre stainless steel canisters. The data showed the expected, but highly variable, elevated levels of the major greenhouse gases emitted during aluminium production (CF₄, C₂F₆, C₃F₈ and CO₂), as well as the sulfur species COS. The data showed that >90% of PFC emissions were via the exhaust stacks, <10% via the roof vents. The data showed clearly the need for a time-integrated sampling approach in order to reduce the inherent variability expected and observed using an instantaneous sampling technique.

The instantaneous concentrations of CF₄ measured in the exhaust of potlines #2 and #3 at Kurri Kurri were 20-40 ppb and 0.3-0.5 ppb respectively, the latter being significantly (>2 orders of magnitude) lower than the so-called baseline (100-200 ppb) of a PB smelter, as determined by FTIR techniques, over a period of 60 hours [12]. It is clear that the CSIRO GC-MS based technique can detect lower baselines in and around aluminium smelters than the techniques currently employed by aluminium smelters. The CSIRO GC-MS technique has no difficulty measuring the very low levels of C₂F₆ and C₃F₈ seen in and around aluminium smelters. Every time measurements are made at aluminium smelters using the CSIRO technology an estimate of C₂F₆ and C₃F₈ emissions and emission factors can be made. This contrasts with the low level of information in the literature on C₂F₆ and C₃F₈ emissions and emission factors.

INTEGRATED SAMPLING

Because of the stochastic nature of AEs, it was recognised that, in order to make an accurate estimate of PFC emissions by stack sampling, exhaust gas samples would have to be collected over an extended time period in order to guarantee sampling from a representative number of AEs. Assuming an approximate AE frequency at Kurri Kurri of 0.1-0.2 AEs/cell.day and that, at any of the stack sampling points, the exhaust from about 60 cells could be sampled, a sampling period of two weeks was decided, which would mean that the PFC emissions from 100-200 AEs would be sub-sampled in each sample collected.

During 2007-2009, CSIRO developed a technology to measure PFC emissions from aluminium smelters, utilising high-precision PFC measurements by GC-MS, on large volume air

samples collected over periods up to 1-2 weeks in stainless steel containers, at key locations in an aluminium smelter [16,17]. The advantages are that it is relatively inexpensive compared to FTIR and TDL methods, the GC-MS instrument does not have to be located at the smelter and the integrated air sampling equipment does not require attention by skilled technicians. Similar technology has been developed by Alcan Inc., Canada, using GC-MS analysis, external absorption/desorption carboxen traps, peristaltic pumps and Tedlar sampling bags, which has been used to study PFC emissions during aluminium cell start-up procedures [10,15,23].

The CSIRO technology has a PFC detection limit (DL<1 ppt, parts per 10¹² molar), several orders of magnitude lower than the Alcan DL (9 ppb, parts per 10⁹ molar), and thus the CSIRO technology has no difficulties in measuring C₂F₆ or C₃F₈ emissions, which are typically below the DL of the Alcan technology. Because of its high DL, the Alcan technology cannot adjust emission estimates for variations in smelter background PFC levels. The higher DL in the Alcan technology is due to the PFC desorption step (with N₂), performed external to the GC-MS, whereas in the CSIRO approach, the PFCs are desorbed directly onto the GC-MS column at concentrations orders of magnitude higher than in the Alcan technology.

The CSIRO technology uses an all stainless steel sampling system, avoiding the inherent halocarbon contamination often introduced by the use of Tedlar bags and peristaltic pumps. The CSIRO technique is directly linked to absolute, gravimetric PFC calibration scales. The absolute calibration error of these measurements is insignificant (<1%) [3].

KURRI KURRI 2009

In November 2009, a follow-up two week integrated sampling experiment was conducted at the Kurri Kurri smelter, concentrating on the exhaust lines (post dry scrubber), but also directly measuring PFC emissions at the roof vents (previous PFC roof vent emissions at Kurri Kurri in 2008 were estimated from potroom PFC levels). Samples were collected from three exhaust lines (Line 1 North – LINE, Line 2 North – L2NE, Line 2 South – L2SE and one roof vent (Line 2 North, roof vent #10 – L2NR#10). Sampling commenced on November 11 (roof vent) and November 12 (exhaust lines). Sampling at all four locations concluded on November 25. Exhaust gases from the carbon bake furnaces were not analysed and the CO₂ emissions reported here are only for anode consumption (AC), henceforth called CO₂ (AC).

Data on aluminium production, AE frequency, duration and intensity for the cells sampled, and exhaust and roof vent ventilation rates were supplied by Kurri Kurri (E. Dalzell, Hydro Aluminium Kurri Kurri Pty. Ltd., personal communication, 2009). The Time-Integrated Air Sampling (TIAS) unit deployed to each of the four locations consisted of an evacuated stainless steel tank, to which a pressure data logger and a suitable sized section of stainless steel capillary tubing was connected. The TIAS units were stored in a 'spacecase' for convenient and safe shipment and to protect the equipment from the potentially-hazardous environment of an aluminium smelter (Figure 1).

The sampled air or exhaust gas entered the evacuated tank via capillary tubing. The length and internal diameter of the capillary tubing connecting the tank to the sampling point were selected to allow unattended sampling to be conducted over a period of two weeks (November 11-25) at near-constant flow rate. It is important to ensure that the pressure inside the sample collection tank remains suitably sub-ambient, resulting in a linear relationship between tank pressure and time (Figure 2), leading to constant flow, time-averaged sampling [16].

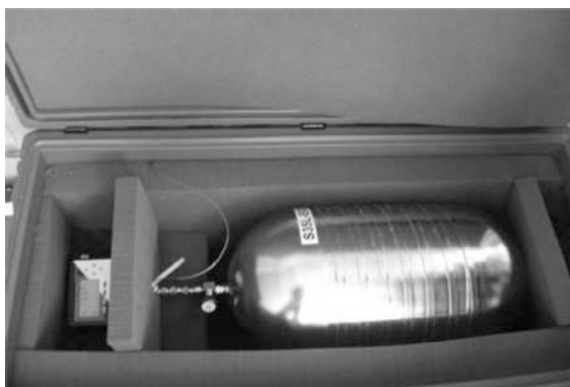


Figure 1. The CSIRO Time Integrated Air Sampling (TIAS) unit contained within a 'spacecase' (1.5m x 0.6m x 0.6m).

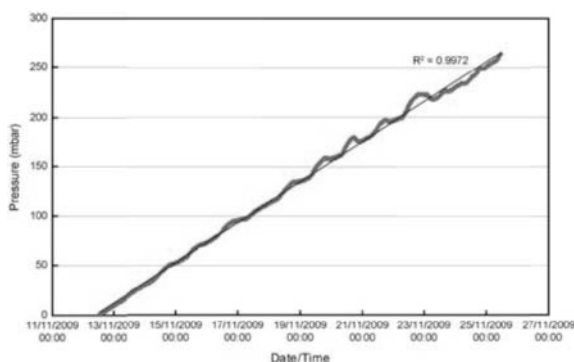


Figure 2. TIAS unit pressure (blue symbols, mbar) as a function of time, sampling from potline 2 north exhaust (L2NE); note linear regression: black line.

To sample from the potlines, the capillary tubing of the TIAS unit was threaded through a sample probe, provided by Hydro Aluminium, which screwed into the side of the potline ducting. The capillary tubing was inserted until it protruded approximately 10 cm beyond the end of the probe, ensuring ~20 cm penetration into the exhaust stream. It was assumed that this, and the long sampling time, ensured representative sampling from the exhaust stream. When sampling from the rooftop exhaust, the capillary tubing was secured directly above the vent fan. An in-line filter containing a small sample of Al_2O_3 was attached to the end of the capillary to remove HF. This compromised COS sampling and the resultant COS data are not reported here.

The pressure in each TIAS unit was recorded throughout the sampling period and plotted as a function of time (Figure 2). Each of the four sampling units exhibited a near-linear relationship between pressure and sampling time, except for deviations recorded due to fluctuations in ambient temperature.

Table 2 shows the details of the integrated sampling at Kurri Kurri during November 2009. The three exhaust gas samples were collected over 309-310 hours and the roof vent sample over 332 hours. The combined exhaust samples were sub-sampled from 230 million m^3 of exhaust gas (at STP), from 171 cells (48% of total cells operating at Kurri Kurri during the sampling period) which produced 2883 tonnes of aluminium (47% of total production) and experienced 857 identifiable AEs (53% of total). The average temperature of the exhaust gas during sampling was 81°C. The roof vent sample was collected from 19 million m^3 (at STP) of roof vent gas. The AE frequency for the cells sampled was 0.39 AEs/cell/day,

compared to a total smelter average during this period of 0.35 AEs/cell/day, about 1 AE/cell every 3 days.

Table 2. Integrated sampling at the Hydro Kurri Kurri aluminium smelter over the period 12-25 November 2009: sampling locations, periods, exhaust volumes sampled from, temperature of exhaust gas, number of cells sampled and their associated aluminium production during the sampling period.

location	hrs	exhaust vol. Mm^3	temp. $^{\circ}\text{C}$	no. cells	Al prod ⁿ tonnes	no. AEs	AEs/cell/day
L1N	309	65±2	77±6	55	920	316	0.45
L1S	ns ^a			63	1060	271	0.33
L2N	310	88±5	82±6	59	1022	198	0.26
L2S	310	78±7	83±8	57	941	343	0.47
L3N	ns			60	1094	260	0.34
L3S	ns			60	1073	223	0.29
L1N+L2		231±26		171	2883	857	0.39
total				354	6110	1611	0.35
L2NR#10	332	19±1	25 ^b	~3 ^c	~51		

^a not sampled

^b assumed equal to ambient temperature

^c L2NR has 20 roof fans extracting ambient potline air from 59 cells

ANALYSIS AT CSIRO

Prior to analysis, a sub-sample of each of the TIAS samples was transferred into a stainless steel flask, to which was added a measured amount of air of known chemical composition (PFCs, CO_2 , CO etc.) to create a sample at above atmospheric pressure with known dilution. The resultant samples were transferred using the over-pressure to a cryo-focusing Medusa GC-MSD for PFC, HFC and CFC analyses [17], a GC-FID for CO_2 analysis and a GC-MRD for CO and hydrogen (H_2) analyses. The dilution procedure ensured the levels of the species of interest were close to those of the corresponding calibration standards. The dilutions introduce uncertainties into the PFC and HFC measurements of about 0.5% (CF_4), 2% (C_2F_6), 7% (C_3F_8) and 16% (CHF_3), which are on average, about 4 times larger than the Medusa instrument measurement uncertainties – 0.3% (CF_4), 0.6% (C_2F_6), 3% (C_3F_8) and 2% (CHF_3). The combined dilution and measurement operations introduce maximum uncertainties of about 1% (CF_4), 3% (C_2F_6), 10% (C_3F_8) and 17% (CHF_3). The TIAS samples were diluted originally in January 2010, with repeat dilutions in March 2010. The results obtained in March were within 0.6% of those obtained in January for CF_4 and within 5-10% for C_2F_6 , C_3F_8 and CHF_3 showing the general stability of these trace gases in these stainless steel containers over these time periods.

RESULTS

The exhaust gas air and roof vent samples showed enhanced (above ambient) concentrations for the greenhouse gases – CF_4 , C_2F_6 , C_3F_8 , CHF_3 (HFC-23) and CO_2 , as well as for CO and H_2 ; the latter two gases are not considered to be greenhouse gases. The concentrations measured for these species on all samples are shown in Table 3. The largest enhancements (ratio to baseline air) were seen for PFCs and CO , followed by H_2 , CO_2 and CHF_3 . The roof vent concentrations were much closer to ambient than to the exhaust gas concentrations, indicating that the majority of emissions are captured by the exhaust gas ventilation system.

Table 4 shows the masses emitted for PFCs, HFC-23 and CO_2 during the sampling period. The total emissions were: 105 kg (CF_4), 7.9 kg (C_2F_6), 0.27 kg (C_3F_8), 0.10 kg (CHF_3) and 5380 tonnes (CO_2). The mass ratio of C_2F_6 to CF_4 was 0.08, compared to 0.10 in the *National Inventory Report 2010* for 2009 [21].

Table 3. Concentrations of PFCs, HFC-23 (ppb), CO₂, CO and H₂ (ppm) measured in the exhaust lines of potrooms #1 and #2 and from the roof top of potroom #2 at Kurri Kurri during November 2009^a. The data shown are the measured concentrations minus the background atmospheric values.

species	L1N(E)	L2N(E)	L2S(E)	L2N(R)#10	atmos ^b
CF ₄	112.4±1.3	72.4±0.7	164.9±1.7	0.27±0.03	0.078
C ₂ F ₆	4.7±0.1	3.2±0.1	8.5±0.2	0.013±0.001	0.004
C ₃ F ₈	0.066±0.007	0.13±0.01	0.20±0.02	0.0007±0.0001	0.0005
CHF ₃	0.18±0.02	0.11±0.02	0.19±0.04	0.02±0.003	0.022
CO ₂	15824±13	11882±10	9137±7	436±0.3	385.2
CO	805±8	916±9	799±8	0.658±0.007	0.045
H ₂	319.5±0.6	468.5±0.9	458.9±0.9	0.867±0.002	0.523

^a for the PFCs and HFCs, the combined measurement/dilution uncertainties are shown; for CO₂, CO and H₂ we use five times the measurement precision for repeat analyses on the GC-FID and MRD instruments at Aspendale.

^b background atmospheric data at Cape Grim, Tasmania (41°S, Nov 2009)

Table 4. Mass of PFCs, HFC-23 (CHF₃) and CO₂ emitted by the exhaust stacks (E), roof vents (R) and total (E+R) during the sampling periods.

location	CF ₄ kg	C ₂ F ₆ kg	C ₃ F ₈ g	CHF ₃ g	CO ₂ tonne
location	CF ₄ kg	C ₂ F ₆ kg	C ₃ F ₈ g	CHF ₃ g	CO ₂ tonne
L1N(E)	28.6±1.2	1.9±0.1	36±5	32±5	1960±60
L2N(E)	24.9±1.7	1.7±0.1	95±13	25±6	1972±110
L2S(E)	50.7±5.1	4.2±0.6	131±25	42±13	1340±120
L2(E) ^a	75.6±5.4	5.9±0.6	226±28	67±14	3312±160
sub-total ^b	104±6	7.8±0.6	262±29	99±15	5272±170
L2N(R) ^c	0.28	0.04	1.8	0.13	38.7
L2N(E+R)	25.2	1.8	97	25	2011
exhaust eff.	99%	99%	98%	98%	98%
L1N(E+R) ^d	28.9±1.2	1.9±0.1	37±5	33±5	1999±60
L2S(E+R) ^e	51.2	4.2	134	43	1367
L2(E+R)	76.4±5.4	6.0±0.6	231±28	68±14	3378±160
Total ^f	105±6	7.9±0.6	268±30	101±15	5380±170
CO ₂ -e (tonnes)	684	73	1.9	1.4	5380
mass (g)/AE	123	9.6	0.23	0.11	

^c based on (L2N(R)#10)*20 (there are 20 roof fans for L2N(R))

^d assume same exhaust efficiencies per species as in L2N(E+R)

^e sum (L2N(E+R), L2S(E+R))

^f sum (L1N(E+R), L2(E+R))

For the PFCs and CO₂, 98-99% of emissions were via the exhaust lines and 1-2% through the roof vents, consistent with the overall hooding efficiency at Kurri Kurri (95±1%, P. Reny, Hydro Aluminium Kurri Kurri, personal communication 2008).

Table 5 shows the emission factors for PFCs, HFC-23 and CO₂ during the 2-week sampling period. The emission factors (g/tonne Al) were: 35±3 (CF₄), 2.6±0.3 (C₂F₆), 0.08±0.02 (C₃F₈), 0.04±0.02 (CHF₃) and 1.95±0.11 (CO₂ (AC), tonne/tonne Al). The CO₂-e emission factor (= CO₂ (AC) + PFCs + HFC-23) measured at Kurri Kurri was 2.2±0.2 (CO₂, tonne/tonne Al).

Table 5. PFC, HFC (g/tonne Al) and CO₂ (tonne/tonne Al, anode consumption) emission factors for the combined exhaust stack and roof vent emissions at Kurri Kurri.

location	CF ₄	C ₂ F ₆	C ₃ F ₈	CHF ₃	CO ₂	CO ₂ -e
L1N(E+R)	31	2.1	0.04	0.04	2.17	
(1)	(0.1)	(0.01)	(0.01)	(0.01)	(0.07)	
L2(E+R)	39	3.1	0.12	0.03	1.72	
(3)	(0.3)	(0.01)	(0.01)	(0.01)	(0.08)	
mean	35	2.6	0.08	0.04	1.95	
(3)	(0.3)	(0.02)	(0.02)	(0.02)	(0.11)	
CO ₂ -e	0.23	0.024	<0.001	<0.001	1.95	2.2
(0.02)	(0.003)			(0.11)	(0.2)	

Table 6 and Figure 3 show a comparison of emission factors obtained at Kurri Kurri in this experiment to emission factors reported by Hydro Aluminium [24], in the *National Inventory Report 2010* [21], by IAI [25], to 'best practice' factors summarised by Keniry [26] and factors derived by CSIRO from analysis of PFC plumes seen at Cape Grim, Tasmania, from the Portland, Point Henry and Bell Bay smelter plumes [27]. Note the long-term decline in the CF₄ emission factor in the *National Inventory Report*, and as deduced from the Cape Grim data, and the rapid decline in the CF₄ emission factor reported by Hydro Aluminium for Kurri Kurri during 2005-2007 [24], coinciding with the refurbishment of potline #1. Prior to refurbishment, potline #1 was responsible for about half of Australia's CF₄ emissions.

Table 6. Comparison of PFC (g/tonne Al) and CO₂ (tonne/tonne Al) emission factors obtained at Kurri Kurri to emission factors reported by (i) Hydro Aluminium for Kurri Kurri Potline #1 [24], (ii) in the *National Inventory Report 2010* [21], (iii) to IAI reported factors [25], (iv) 'best practice' factors summarised by Keniry [26] and (v) factors derived by CSIRO from analysis of PFC plumes seen at Cape Grim, Tasmania, from the Portland, Point Henry and Bell Bay smelter plumes [27].

		CF ₄	C ₂ F ₆	CO ₂ (AC)	CO ₂ -e (CO ₂ (AC)+PFC)
		g/tonne Al		tonne/tonne Al	
KK ^a L1, L2	2009	35±3	2.6±0.3	1.95±0.11	2.2±0.2
KK L1 [24]	2007	60			
	2006	200			
	2005	2200			
Portland [27]	2009	36±25			
Pt Henry [27]	2009	51±18			
Bell Bay [27]	2009	20±13			
DCCEE [21]	2009	20	2	1.48	1.63
IAI PFPB [25]	2009	34	4.0		
Keniry [26]				1.54±0.15	2.04

^a Kurri Kurri

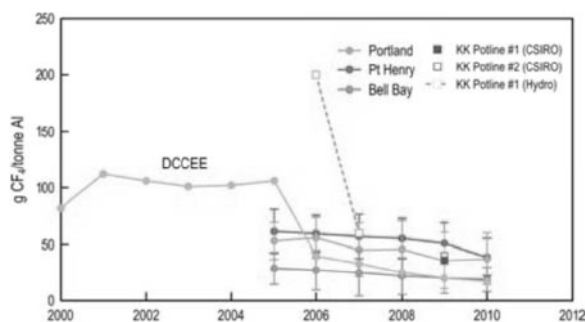


Figure 3. CF₄ emissions factors (g CF₄/tonne Al) for Australian aluminium smelters at Kurri Kurri (KK, Hydro, CSIRO), Portland (CSIRO), Pt Henry (CSIRO), Bell Bay (CSIRO), and the Australian average in the *National Inventory Report 2010* [21].

DISCUSSION

The Kurri Kurri experiments in 2008 and 2009 identified emissions of the expected PFCs: CF₄, C₂F₆ and C₃F₈, as well as CO₂. The PFC concentrations in the exhaust gas at Kurri Kurri were lower than measured by Harnisch [1], but the approximately 20-fold reductions in PFC concentrations from CF₄ to C₂F₆ and again from C₂F₆ to C₃F₈ were seen in both studies. Unlike Harnisch [1], the Kurri Kurri experiments did not identify CClF₃ emissions from aluminium production, but did identify small emissions of CHF₃. The potline exhaust gas extraction system was shown to be 98-99% efficient in

removing PFCs and CO₂ from the potrooms, only 1-2% escaping via the roof vents.

During the two week experiment in 2009 at Kurri Kurri, the total emissions of CO₂ from the 354 reduction cells was approximately 5380 tonnes (Table 4), with 684 tonnes (CO₂-e) of CF₄, 73 tonnes (CO₂-e) C₂F₆, 1.9 tonnes (CO₂-e) of C₃F₈ and 1.4 tonne (CO₂-e) of CHF₃. The PFC emissions at Kurri Kurri contribute about 14% of the total CO₂-e emissions from the reduction cells and likely about 13-14% of the total CO₂-e from the aluminium production at Kurri Kurri (including the anode bake CO₂-e emissions).

Not surprisingly, there is a qualitative relationship between the number of AEs and the resultant PFC production. Potline 2S had the largest PFC emissions during the 2-week period and the largest number of AEs. Each AE at Kurri Kurri produced about 0.1-0.2 kg of CF₄. This relationship may be made more quantitative if the AEs were weighted by duration and intensity. The AE frequency for the cells sampled was 0.39 AEs/cell/day, compared to a total smelter average during this period of 0.35 AEs/cell/day, about 1 AE/cell every 3 days. Keniry [25] suggests that 0.3 AEs per day is typical for an aluminium smelter and best-practice is less than 0.1 per day.

The average CF₄ emission factor derived from the two week experiment at Kurri Kurri was 35±3 g/tonne Al which is 75% higher than the 2009 Australian average emission factor in the *National Inventory Report 2010* [21] (20 g/tonne Al). However the Kurri Kurri emission factor is in good agreement with the range of the annual average emission factors (20-50 g/tonne Al) found for SE Australian smelters during 2009 (Portland, Pt Henry, Bell Bay) by analysis and modelling of PFC data from Cape Grim, Tasmania [27] (Figure 3) and in excellent agreement with the IAI reported global average emission factor for smelters employing PFPB technology in 2009 (34 g/tonne Al) [25].

The Kurri Kurri results include PFC emissions from possible cell start-up and anode change procedures, and during non-AE periods, experienced on potlines 1 and 3 during the two week period. PFC emission factors quoted in the *National Inventory Report 2010* or in the IAI Anode Effect Surveys likely do not include all PFC emissions from start-up or anode change procedures or non-AE periods. A study of 17 smelters (outside China) has shown that total PFC emissions from aluminium smelting could be underestimated by ~20% or more [8], especially if data from smelters inside China are included [14].

The average C₂F₆ emission factor from Kurri Kurri was 2.6±0.3 g/tonne Al, close to the Australian average 2009 factor in the *National Inventory Report 2010* (2 g/tonne Al) [21] and lower than the IAI recorded global average value (4 g/tonne Al) for PFPB technology in 2009 [25]. The literature data on C₂F₆ in exhaust gases suggest that measurements are close to their DLs. The Kurri Kurri C₂F₆ emission factor may be one of the most accurate yet obtained.

The C₃F₈ and CHF₃ emission factors (0.08 and 0.04 g/tonne Al respectively) have not been reported before and are insignificant in calculating the PFC/HFC contribution to CO₂-e emissions from the reduction cells, enhancing GHG emissions expressed as CO₂-e, calculated from CF₄ and C₂F₆ emissions only, by less than 1%.

The CO₂ (AC) emission factor for Kurri Kurri is 1.95±0.11 tonne/tonne Al, more than 30% higher than the Australian national average in the *National Inventory Report 2010* (1.48 = 413 kg C/tonne Al) [21]. The total effective CO₂ emission factor for aluminium production (CO₂ (AC) + CO₂-e (PFCs)) for Kurri Kurri (2.2±0.2 tonne/tonne Al) is about 35% higher than the factor given in the *National Inventory Report 2010* (1.63 tonnes CO₂-e/tonne Al for 2009, not including CO₂-e

emissions from anode production (AP)) [21], but similar to that estimated by Keniry [26] for typical-practice reduction cells (2.04 tonne/tonne Al, not including CO₂-e from AP). Keniry estimates best-practice emission factors to be 1.42 tonnes CO₂-e/tonne Al, not including CO₂-e from AP. It is not obvious why the Kurri Kurri CO₂ (AC) emission factor is higher than the Australian national average.

CONCLUSIONS

PFC (CF₄, C₂F₆, C₃F₈), HFC (CHF₃) and CO₂ emissions were estimated from two potlines of the Hydro Australia Kurri Kurri aluminium smelter in the Hunter Valley, NSW, in 2009. The emission factors (g/tonne Al) were: 35±3 (CF₄), 2.6±0.3 (C₂F₆), 0.08±0.02 (C₃F₈) and 0.04±0.02 (CHF₃).

The Kurri Kurri CF₄ emission factor is similar to, but significantly more accurate than, annual PFC emission factors found for other Australian aluminium smelters (Bell Bay, Tasmania; Portland and Pt Henry, Victoria) in 2009, based on continuous PFC data collected at Cape Grim, Tasmania [27]. These four smelters accounted for about 45% of Australian aluminium production in 2009. The CF₄ emission factors are, on average, significantly larger (~75%) than the Australian average CF₄ emission factor reported to the UNFCCC for 2009, but the uncertainties on these factors are large (50%-60%), except Kurri Kurri (9%). The high CF₄ emission factors may be because (i) measured emission factors include all PFC emissions (from AEs and non-AEs) whereas the factors reported to the UNFCCC are based on PFC emissions from AEs only; (ii) the CF₄ emission factor measured at Kurri Kurri over a two week period may be higher than the annual average CF₄ emission factor at Kurri Kurri; (iii) the PFC emission factors from the Australian aluminium smelters not surveyed by CSIRO to date (Tomago, NSW; Boyne Island, Queensland) could be lower than the national average.

The CO₂ (AC) emission factor at Kurri Kurri is similar to that estimated for typical-practice reduction cells, but is also significantly (~30%) higher than the Australian national average reported to UNFCCC for 2009. PFC-218 (C₃F₈) and HFC-23 (CHF₃) emissions from aluminium smelting are low and do not significantly add to GHG emissions from an aluminium smelter.

CSIRO has developed an inexpensive technology for accurate, direct measurement of total GHG emissions (PFCs, HFCs, CO₂) from aluminium smelting. In order to accurately estimate Australian GHG emissions from aluminium smelting, all Australian smelters need to be surveyed.

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REFERENCES

1. Harnisch, J., Die globalen atmosphärischen Haushalte der spurengase tetrafluormethan (CF₄) und hexafluorethan (C₂F₆), *Dissertation zur Erlangung des Doktorgrades der Mathematisch-Naturwissenschaftlichen, Fakultäten der Georg-August-Universität zu Göttingen*, 1996.
2. Harnisch, J., Reactive Fluorine Compounds, Chap. 3 in: *Handbook of Environmental Chemistry, 4(E), Reactive Halogen Compounds in the Atmosphere*, P. Fabian & O. Singh (eds.), Springer, Berlin-Heidelberg, 81-111, 1999.

3. Mühle, J., A. Ganesan, B. Miller, P. Salameh C. Harth, B. Grealley, M. Rigby, L. Porter, P. Steele, C. Trudinger, P. Krummel, S. O'Doherty, P. Fraser P. Simmonds, R. Prinn & R. Weiss, Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane & octofluoropropane, *Atmos. Chem. Phys.*, 10, 5145-5164, 2010.
4. Li, W., X. Chen, J. Yang, C. Hu, Y. Liu, D. Li & H. Guo, Latest results from PFC investigations in China, *Light Metals 2012*, C. Suarez (ed.), TMS (The Minerals, Metals and Materials Society), 619-622, 2012.
5. Gamble, H., G. Mackay, D. Karecki, J. Pisano & H. Schiff, The measurement of fluorocarbon emissions from Canadian alumina reduction plants, *Light Metals 2000*, J. Kazadi & J. Masounave (eds.), TMS (The Minerals, Metals and Materials Society), 339-352, 2000.
6. Gamble, H., D. Karecki, G. Mackay & H. Schiff, A streamlined, portable mid-IR TDL based system for on-site monitoring of PFCs from potroom exhaust ducts, *Light Metals 2003*, P. Crepeau (ed.), TMS (The Minerals, Metals and Materials Society), 215-219, 2003.
7. Marks, J., R. Kantamaneni, D. Pape & S. Rand, Protocol for measurement of tetrafluoromethane and hexafluoroethane from primary aluminium production, *Light Metals 2003*, P. Crepeau (ed.), TMS (The Minerals, Metals and Materials Society), 221-225, 2003.
8. Marks, J. & C. Bayliss, GHG measurement and inventory for aluminium production, *Light Metals 2012*, C. Suarez (ed.), TMS (The Minerals, Metals and Materials Society), 805-808, 2012.
9. Dando, N., L. Sylvain, J. Fleckenstein, C. Kato, V. Van Son & L. Coleman, Sustainable anode effect based perfluorocarbon emission reduction, *Light Metals 2011*, S. Lindsay (ed.), TMS (The Minerals, Metals and Materials Society), 325-328, 2011.
10. Maltais, J.-N., J. Ross, A. Marcoux & G. Gaudreault, Application of a method for the determination of PFC emissions during aluminium pot start-up, *Light Metals 2010*, J. Johnson (ed.), TMS (The Minerals, Metals and Materials Society), 271-276, 2010.
11. Li, W., Q. Zhao, J. Yang, S. Qiu, X. Chen, J. Marks & C. Bayliss, On continuous PFC emission unrelated to anode events, *Light Metals 2011*, S. Lindsay (ed.), TMS (The Minerals, Metals and Materials Society), 309-314, 2011.
12. Dando, N., In-plant PFC monitoring: technology options and performance concerns, *Light Metals 2003*, P. Crepeau (ed.), TMS (The Minerals, Metals and Materials Society), 205-210, 2003.
13. Marks, J., PFC emissions from global primary aluminium production, *Proceedings of the 9th Australasian Aluminium Smelting Technology Conference and Workshops*, Skyllas-Kazacos, M. & B. Welch (eds.), Terrigal, NSW, Australia, 4-9 November 2007, 53-60.
14. Li, W., Q. Zhao, S. Qui, S. Zhang & X. Chen, PFC survey in some smelters of China, *Light Metals 2011*, S. Lindsay (ed.), TMS (The Minerals, Metals and Materials Society), 357-360, 2011.
15. Bouchard, V., J.-N. Maltais, J. Ross & M. Gargon, An innovative method for sampling and analysis of tetrafluoromethane and hexafluoroethane emitted from aluminium smelters using sorbent tubes, *Light Metals 2009*, G. Bearne (ed.), TMS (The Minerals, Metals and Materials Society), 255-258, 2009.
16. Leist, M., P. Steele, Z. Loh, P. Krummel & P. Fraser, Time-integrated atmospheric sampling and analysis, Abstracts: *Cape Grim Baseline Air Pollution Station Annual Science Meeting 2008*, P. Krummel & N. Derek (eds.), Centre for Australian Weather and Climate Research, CSIRO Marine and Atmospheric Research, 27-28 November 2008, 22.
17. Miller, B., R. Weiss, P. Salameh, T. Tanhua, B. Grealley, J. Mühle & P. Simmonds, Medusa: a sample pre-concentration and GC-MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulphur compounds, *Anal. Chem.*, 80, 1536-1545, 2008.
18. Tabereaux, A., N. Richards & C. Satchel, Composition of reduction cell anode gas during normal conditions and anode events, *Light Metals 1995*, TMS (The Minerals, Metals and Materials Society), 325-333, 1995.
19. Harnisch, J., R. Borchers & P. Fabian, COS, CS₂ and SO₂ in aluminium smelter exhaust, *Environ. Sci. & Pollut. Res.*, 2 (4), 229-232, 1995.
20. Forster, P. And V. Ramaswamy, Coordinating Lead Authors, Changes in Atmospheric Constituents and in Radiative Forcing, Chapter 2 in: *Climate Change 2007: The Physical Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Solomon, S. et al. (eds.), Cambridge University Press, Cambridge, UK & New York, NY, USA, 129-234, April 2007.
21. DCCEE, *Australian National Greenhouse Accounts, National Inventory Report 2010*, Volume 1, Australian Government, Department of Climate Change and Energy Efficiency, 292 pp, 2012.
22. Holliday, R. & J. Henry, Anode polarization and fluorocarbon formation in aluminium reduction cells, *Industry and Eng. Chem.*, 51 (10), 1289-1292, Oct 1959.
23. Maltais, J.-N., A. Marcoux, C. Manard, J. Ross, Y. Lavoie & C. Munger, A method for the determination of CF₄ and C₂F₆ emitted from smelters, *Proceedings of the 9th Australasian Aluminium Smelting Technology Conference and Workshops*, Skyllas-Kazacos, M. & B. Welch (eds.), Terrigal, NSW, Australia, 4-9 November 2007, 443-451.
24. Hydro Aluminium, Going Green, in *Inside Hydro Aluminium Kurri Kurri*, No. 2, September 2007, p. 11.
25. IAI, *Results of the 2009 Anode Effect Survey*, International Aluminium Institute, Report on the Aluminium Industry's Global Perfluorocarbon Gases Emissions Reduction Programme, 56 pp., 5 July 2010.
26. Keniry, J., Changing CO₂ emission patterns, *Proceedings of the 9th Australasian Aluminium Smelting Technology Conference and Workshops*, Skyllas-Kazacos, M. & B. Welch (eds.), Terrigal, NSW, Australia, 4-9 November 2007, 513-525.
27. Fraser, P., B. Dunse, P. Steele, P. Krummel & N. Derek, Perfluorocarbon (PFC) emissions from Australian aluminium smelters, 2005-2009, *Proceedings of the 10th Australasian Aluminium Smelting Technology Conference*, Launceston, Australia, 9-14 October, 2011, Welch, B., G. Stephens, J. Metson & M. Skyllas-Kazacos (eds.), Copyright School of Chemical Engineering, University of New South Wales, ISBN: 978-0-7334-3054-1, 14 pp.