

CHAPTER 4

METAL INDUSTRY EMISSIONS

Authors

Section 4.2

Laura E. Dawidowski (Argentina), Oleksandra Kolmogortseva (Ukraine), Ingrid Person Rocha e Pinho (Brazil) and Teruo Okazaki (Japan)

Section 4.4

Lukas Dion (Canada), Pernelle Nunez (IAI/UK), Alexey V. Spirin (Russian Federation) and David Sydney Wong (New Zealand)

Section 4.8

David Sydney Wong (New Zealand), Lukas Dion (Canada), Pernelle Nunez (IAI/UK) and Alexey V. Spirin (Russian Federation).

Contributing Authors

Section 4.2

Jan Hendrik Reimink (WSA/Netherlands)

Section 4.4

Simon Gaboury (Canada), Jerry Y. Marks (USA), Andrey V. Panov (Russian Federation), Xin Bo (China) and Xiping Chen (China).

Section 4.8

Michalopoulou Eleni (UK), Hanno Vogel (Germany), Youming Yang (China), Xin Bo (China) and Xiping Chen (China).

Contents

29	4	Metal Industry Emissions.....	4.8
30	4.1	Introduction	4.8
31	4.2	Iron & Steel and Metallurgical Coke Production	4.9
32	4.2.1	Introduction.....	4.11
33	4.2.2	Methodological issues	4.11
34	4.2.2.1	Choice of method: Metallurgical coke production through carbonisation.....	4.12
35	4.2.2.2	Choice of method: iron and steel production.....	4.18
36	4.2.2.3	Choice of emission factors	4.27
37	4.2.2.4	Choice of activity data.....	4.32
38	4.2.2.5	Completeness.....	4.32
39	4.2.2.6	Developing a consistent time series.....	4.35
40	4.2.3	Uncertainty assessment	4.36
41	4.2.4	Quality Assurance/Quality Control (QA/QC), Reporting and Documentation	4.36
42	4.3	Ferroalloy Production	4.37
43	4.4	Primary Aluminium Production	4.38
44	4.4.1	Introduction to Primary Aluminium.....	4.39
45	4.4.2	Methodological issues for primary aluminium production	4.40
46	4.4.2.1	Choice of Method for CO ₂ emissions from primary aluminium production	4.40
47	4.4.2.2	Choice of emission factors for CO ₂ emissions from primary aluminium production.....	4.40
48	4.4.2.3	Choice of method for PFCs	4.41
49	4.4.2.4	Choice of emission factors for PFCs	4.52
50	4.4.2.5	Choice of activity data.....	4.55
51	4.4.2.6	Completeness.....	4.55
52	4.4.2.7	Developing a consistent time series.....	4.56
53	4.4.3	Uncertainty assessment for primary aluminium production.....	4.57
54	4.4.3.1	Emission factor uncertainties.....	4.58
55	4.4.3.2	Activity data uncertainties	4.59
56	4.4.4	Quality Assurance/Quality Control (QA/QC) Reporting and Documentation for primary aluminium	
57		production	4.59
58	4.4.4.1	Quality Assurance/Quality Control (QA/QC)	4.59
59	4.4.4.2	Reporting and documentation.....	4.60
60	4.4.5	Methodological issues for alumina production	4.62
61	4.4.5.1	Alternative alumina refining processes	4.62
62	4.4.5.2	Choice of method for alumina production.....	4.65
63	4.4.5.3	Choice of emission factors for alumina production.....	4.71
64	4.4.5.4	Choice of activity data.....	4.72
65	4.4.5.5	Completeness.....	4.73
66	4.4.5.6	Developing a consistent time series.....	4.73
67	4.4.6	Uncertainty assessment for alumina production.....	4.74

68	4.4.6.1	Emission factor uncertainties.....	4.74
69	4.4.6.2	Activity data uncertainties	4.74
70	4.4.7	Quality Assurance/Quality Control (QA/QC), Reporting and Documentation for alumina	
71		production	4.76
72	4.4.7.1	Quality Assurance / Quality Control (QA/QC)	4.76
73	4.4.7.2	Reporting and Documentation	4.77
74	4.5	Magnesium Production	4.78
75	4.6	Lead Production.....	4.78
76	4.7	Zinc Production	4.78
77	4.8	Rare Earths Production	4.79
78	4.8.1	Introduction	4.79
79	4.8.2	Methodological Issues	4.80
80	4.8.2.1	Choice of method for CO ₂ emissions from primary rare earth metal production	4.80
81	4.8.2.2	Choice of emission factors for CO ₂ emissions from primary rare earth metal production ..	4.83
82	4.8.2.3	Choice of method for PFCs	4.84
83	4.8.2.4	Choice of emission factors for PFCs	4.88
84	4.8.2.5	Choice of activity data and emission factors	4.89
85	4.8.2.6	Completeness.....	4.89
86	4.8.2.7	Developing a consistent time series.....	4.90
87	4.8.3	Uncertainty assessment	4.90
88	4.8.3.1	Emission factor uncertainties.....	4.90
89	4.8.3.2	Activity data uncertainties	4.91
90	4.8.4	Quality Assurance/Quality Control (QA/QC), Reporting and Documentation	4.91
91	4.8.4.1	Quality Assurance/Quality Control (QA/QC)	4.91
92	4.8.4.2	Reporting and Documentation	4.92
93		References	4.93
94			

Equations

96	Equation 4.1 (updated)	CO ₂ Emissions from coke production (Tier 1a).....	4.15
97	Equation 4.1a (new)	CH ₄ Emissions from coke production (Tier 1a)	4.15
98	Equation 4.1b (new)	CO ₂ emissions from metallurgical coke production (Tier 1b)	4.15
99	Equation 4.2 (updated)	CO ₂ emissions from metallurgical coke production.....	4.16
100	Equation 4.4 (unchanged)	CO ₂ emissions from iron and steel production (Tier 1)	4.23
101	Equation 4.5 (unchanged)	CO ₂ emissions from production of pig iron not processed into steel (Tier 1)	4.23
102	Equation 4.6 (unchanged)	CO ₂ emissions from production of direct reduced iron (Tier 1)	4.23
103	Equation 4.7 (unchanged)	CO ₂ emissions from sinter production (Tier 1)	4.23
104	Equation 4.8 (unchanged)	CO ₂ emissions from pellet production (Tier 1)	4.23
105	Equation 4.8a (new)	CO ₂ emissions from flaring (Tier 1)	4.23

Final Draft

106	Equation 4.9 (unchanged)	CO ₂ emissions from iron and steel production (Tier 2)	4.24
107	Equation 4.10 (updated)	CO ₂ emissions from sinter production (Tier 2).....	4.24
108	Equation 4.11(unchanged)	CO ₂ emissions from direct reduced iron production (Tier 2).....	4.25
109	Equation 4.12 (unchanged)	CH ₄ emissions from sinter production (Tier 1)	4.26
110	Equation 4.13 (unchanged)	CH ₄ emissions from blast furnace production of pig iron (Tier 1).....	4.26
111	Equation 4.14 (unchanged)	CH ₄ emissions from direct reduced iron production (Tier 1).....	4.26
112	Equation 4.14A (new)	N ₂ O emissions from flaring (Tier 1)	4.27
113	Equation 4.14b (new)	N ₂ O emission factors from flaring of blast furnace gas and converter gas	4.30
114	Equation 4.24a (new)	Total PFC emissions	4.42
115	Equation 4.25 (updated)	HVAE PFC emissions (Tier 1 method)	4.45
116	Equation 4.26 (updated)	HVAE PFC emissions by Slope method (Tier 2a and Tier 3a methods).....	4.45
117	Equation 4.27 (updated)	HVAE PFC emissions by Overvoltage method (Tier 3a method).....	4.46
118	Equation 4.27a (new)	HVAE PFC emissions (Tier 2b and Tier 3b method)	4.47
119	Equation 4.27b (new)	HVAE PFC emissions (Tier 2b and Tier 3b method).....	4.48
120	Equation 4.27c (new)	LVAE PFC emissions (Tier 1 and Tier 3 methods – production-based)	4.49
121	Equation 4.27d (new)	LVAE PFC emissions (Tier 3 method – as ratio of HVAE emissions)	4.49
122	Equation 4.27e (new)	Total PFC emissions for start-up of electrolysis cells (Tier 3 _{csu} method)	4.50
123	Equation 4.27f (new)	Emission rate coefficients for HVAE PFC (Tier 2b method).....	4.54
124	Equation 4.27g (new)	Tier 1: Sintering process emissions based on alumina production data.....	4.66
125	Equation 4.27h (new)	Tier 3: Emissions based on carbonate raw material inputs to the sintering kiln ...	4.68
126	Equation 4.27i (new)	Emissions captured during carbonization process and contained in produced sodium carbonate	4.69
127			
128	Equation 4.27j (new)	Emissions from un-calcined SKD not recycled to the kiln.....	4.69
129	Equation 4.27k (new)	Weighted average content CO ₂ in ‘i’ Bauxites (Nephelines).....	4.70
130	Equation 4.27l (new)	Emissions from Bauxites (Nephelines) residue	4.70
131	Equation 4.27m (new)	Emissions from carbon-bearing non-fuel materials.....	4.70
132	Equation 4.27n (new)	CO ₂ absorption through use of circulating water collected from bauxite/nepheline storage residue area and/or absorption through bauxite residue neutralization	4.71
133			
134	Equation 4.35 (new)	Process CO ₂ Emissions from anode consumption (Tier 1).....	4.82
135	Equation 4.36 (new)	Process CO ₂ Emissions from anode consumption (Tier 3).....	4.82
136	Equation 4.37 (new)	PFC emissions from rare earth metals production (Tier 1 and Tier 3)	4.87
137			

Figures

139	Figure 4.1 (unchanged)	Illustration of main processes for integrated iron and steel production	4.10
140	Figure 4.6 (updated)	Estimation of CO ₂ emissions from metallurgical coke production	4.17
141	Figure 4.7 (updated)	Decision tree for estimation of CO ₂ emissions from iron and steel production	4.19
142	Figure 4.8a (new)	Decision tree for estimation of CH ₄ emissions from coke production.....	4.20
143	Figure 4.8b (updated)	Decision tree for estimation of CH ₄ emissions from iron and steel production	4.21

144	Figure 4.8c (new)	Decision tree for estimation of N ₂ O emissions from iron and steel production.....	4.22
145	Figure 4.8d (new)	Energy or IPPU CO ₂ emissions allocation in an integrated iron and steel facility ...	4.33
146	Figure 4.12 (updated)	Decision tree for calculation of total PFC emissions from primary aluminium	
147		production	4.43
148	Figure 4.12a (new)	Alumina production processes	4.63
149	Figure 4.12b (new)	Decision tree for estimation of CO ₂ emissions from alumina production	4.67
150	Figure 4.17 (new)	Decision tree for calculation of CO ₂ emissions from primary rare earth (RE) metal	
151		production	4.81
152	Figure 4.18 (new)	Decision tree for calculation of PFC emissions from primary rare earth (RE) metal	
153		production	4.86
154			

Tables

156	Table 4.1a (new)	Emission allocation from metallurgical coke production	4.12
157	Table 4.1b (new)	Tiers to estimate CO ₂ emissions from metallurgical coke production – carbonisation	
158		process	4.14
159	Table 4.1 (updated)	Tier 1 default CO ₂ emission factors for coke production	4.28
160	Table 4.2 (updated)	Tier 1 default CH ₄ emission factors for coke production (non fugitives), iron and steel	
161		production	4.29
162	Table 4.2b (new)	Tier 1 default N ₂ O emission factors for coke production and iron and steel production	
163		4.30
164	Table 4.3 (updated)	Tier 2 material-specific carbon contents for iron and steel production (tonnes C/tonne)	
165		4.31
166	Table 4.4 (updated)	Uncertainty ranges	4.36
167	Table 4.14a (new)	Summary of accounting methods for PFC emissions	4.44
168	Table 4.15 (updated)	Technology specific default emission factors for the calculation of HVAE and LVAE	
169		emissions from aluminium production (Tier 1 method)	4.52
170	Table 4.16 (updated)	Technology specific coefficients for the calculation of HVAE PFC emissions from	
171		aluminium production using slope methodology (Tier 2a method)	4.53
172	Table 4.16a (new)	Specific HVAE-CF ₄ emission rate coefficients based on the anode effect duration (Tier	
173		2b method)	4.53
174	Table 4.16b (new)	Uncertainty range ^c (%) in estimating PFC emissions from individual HVAEs (Tier 2b	
175		methods)	4.54
176	Table 4.16c (new)	Summary of which guidelines to refer to, for time consistent PFC inventories	4.57
177	Table 4.17 (updated)	<i>Good practice</i> reporting information for calculating CO ₂ and PFC emissions from	
178		aluminium production by tier	4.61
179	Table 4.17a (new)	Technology specific default emission factors for the calculation of CO ₂ emissions from	
180		alternative sintering processes (Tier 1 method)	4.71
181	Table 4.17b (new)	Default uncertainty values for Bauxite/Nepheline sintering processes	4.75
182	Table 4.26 (new)	Tier 1 default emission factors for calculating CO ₂ emissions from anode consumption	
183		4.83
184	Table 4.27 (new)	Data sources and uncertainties for parameters used in Tier 3 method for CO ₂ emissions	
185		from anode consumption	4.84

Final Draft

186	Table 4.28 (new)	Tier 1 default emission factors and uncertainty ranges for the calculation of PFC	
187		emissions from rare earth production	4.88
188	Table 4.29 (new)	Data sources and uncertainties for parameters used in Tier 3 method for PFC emissions	
189		4.89
190	Table 4.30 (new)	<i>Good practice</i> reporting information for calculating CO ₂ and PFC emissions from rare	
191		earth metal production by Tier.....	4.92

192 **Boxes**

193	Box 4.0 (new)	Flaring activities in metallurgical coke and iron and steel productions.....	4.13
194	Box 4.1a (new)	Fully automated anode effect intervention strategies for PFC emissions	4.40
195	Box 4.2 (updated)	High and low voltage anode effect description	4.41
196	Box 4.3 (new)	PFC emissions during start-up of electrolysis cells.....	4.50
197	Box 4.4 (new)	Anode effect description (for rare earth metal production by fluoride electrolysis).....	4.85
198			

4 METAL INDUSTRY EMISSIONS

Users are expected to go to Mapping Tables in Annex 5, before reading this chapter. This is required to correctly understand both the refinements made and how the elements in this chapter relate to the corresponding chapter in the *2006 IPCC Guidelines*.

4.1 INTRODUCTION

No Refinement

Final Draft

4.2 IRON & STEEL AND METALLURGICAL COKE PRODUCTION

The production of iron and steel leads to emissions of carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). This chapter provides guidance for estimating emissions of CO₂ and CH₄.¹

The iron and steel industry broadly consists of:

- Primary facilities that produce both iron and steel;
- Secondary steelmaking facilities;
- Iron production facilities; and
- Offsite production of metallurgical coke.

Figure 4.1 illustrates the main processes for iron and steel production: metallurgical coke production, sinter production, pellet production, iron ore processing, iron making, steelmaking, steel casting and very often combustion of blast furnace and coke oven gases for other purposes. The main processes may occur under what is referred to as an 'integrated' facility and typically include blast furnaces, and basic oxygen steelmaking furnaces (BOFs), or in some cases open hearth furnaces (OHFs). It is also common for parts of the production to be offsite under the responsibility of another operator such as an offsite coke production facility.

In some countries, there will be coke production facilities that are not integrated with iron and steel production (i.e., 'offsite'). This chapter provides guidance for estimating emissions of CO₂ and CH₄ from all coke production to ensure consistency and completeness. Countries should estimate emissions from onsite and offsite coke production separately under higher tiers as the by-products of onsite coke production (e.g., coke oven gas, coke breeze, etc.) are often used during the production of iron and steel.

Primary and secondary steel-making:

Steel production can occur at integrated facilities from iron ore, or at secondary facilities, which produce steel mainly from recycled steel scrap. Integrated facilities typically include coke production, blast furnaces, and basic oxygen steelmaking furnaces (BOFs), or in some cases open hearth furnaces (OHFs). Raw steel is produced using a basic oxygen furnace from pig iron produced by the blast furnace and then processed into finished steel products. Pig iron may also be processed directly into iron products. Secondary steelmaking most often occurs in electric arc furnaces (EAFs). In 2003, BOFs accounted for approximately 63 percent of world steel production and EAFs approximately accounted for 33 percent; OHF production accounted for the remaining 4 percent but is today declining.

Iron production:

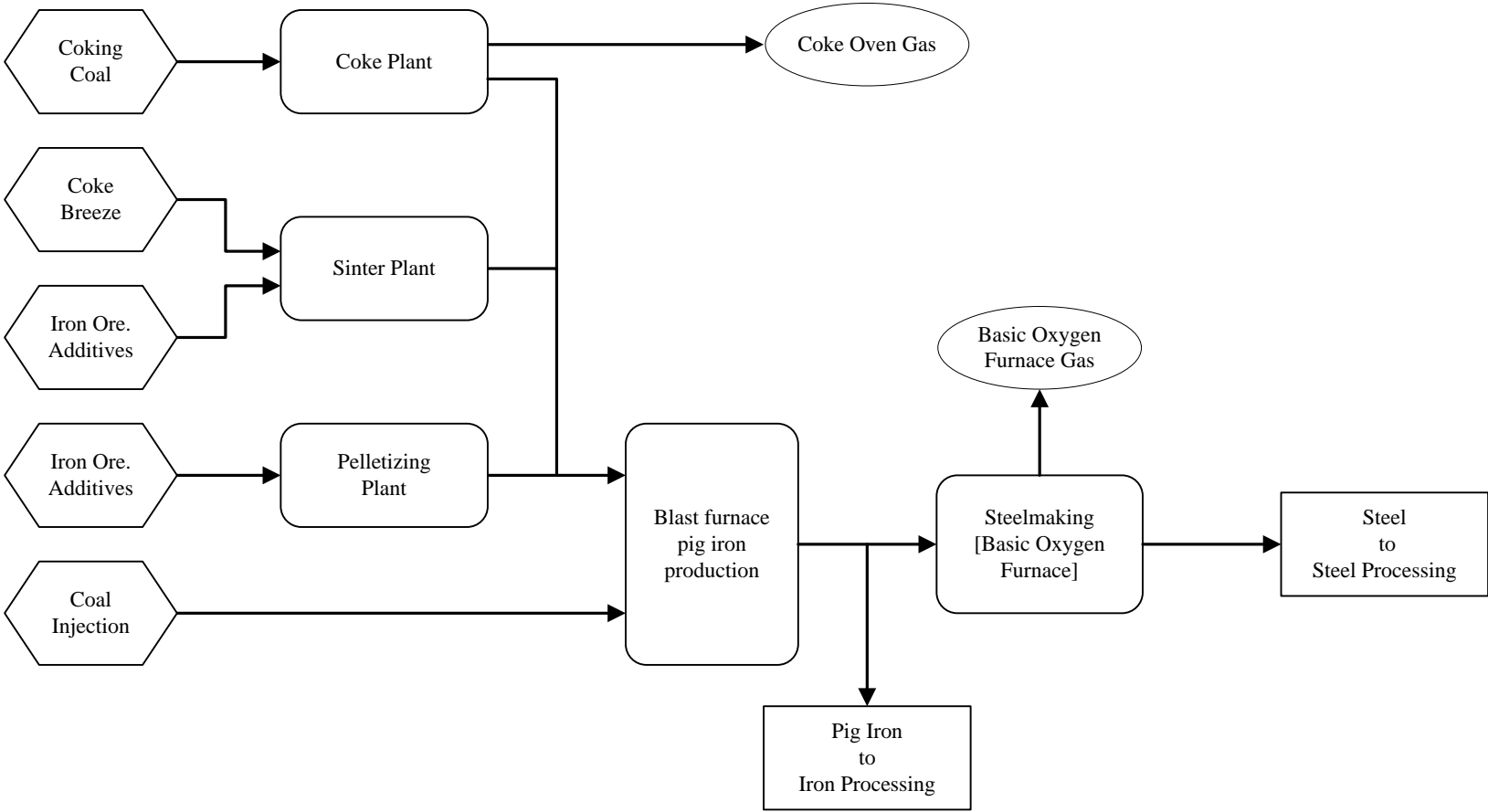
Iron production can occur onsite at integrated facilities or at separate offsite facilities containing blast furnaces and BOFs. In addition to iron production via blast furnace, iron can be produced through a direct reduction process. Direct reduction involves the reduction of iron ore to metallic iron in the solid state at process temperatures less than 1000°C.

Metallurgical coke production:

Metallurgical coke production is considered to be an energy use of fossil fuel, and as a result emissions should be reported in Category 1A of the Energy Sector. The methodologies are presented here in Volume 3, however, because the activity data used to estimate emissions from energy and non-energy in integrated iron and steel production have significant overlap. All fuel consumed in this source category not allocated as inputs to the sinter plants, pelletisation plants and blast furnace should be regarded as fuel combustion, which is dealt with and reported in the Energy Sector (see Volume 2: Energy).

¹ No methodologies are provided for N₂O emissions. These emissions are likely to be small, but countries can calculate estimates provided they develop country-specific methods based on researched data.

Figure 4.1 (unchanged) Illustration of main processes for integrated iron and steel production*



*Modified from: European conference on “The Sevilla Process: A Driver for Environmental Performance in Industry” Stuttgart, 6 and 7 April 2000, BREF on the Production of Iron and Steel – conclusion on BAT, Dr.Harald Schoenberger, Regional State Governmental Office Freiburg, April 2000. (Schoenberger, 2000)

4.2.1 Introduction

No Refinement

4.2.2 Methodological issues

The coke-making process comprises: (1) coal handling and preparation, including transportation, discharge, storage, crushing, bed blending, that in all cases cause dust emissions, but not GHG emissions, and (2) coke oven battery operations, including coal charging, chamber heating and firing, coking, coke pushing and quenching and coke handling (i.e. storing, transporting, crushing and screening), where GHGs do occur. The term ‘coking’ refers to the carbonization process that takes place in the ovens which is a thermal distillation process that removes volatile matter from the coking coal, in the form of gases or liquids, to produce coke. There are two technological options for coke-making which differ primarily in the treatment of coke-making by-products:

- Coke production *with* by-product recovery where organic liquids, including coal tar and light oil, are recovered.
- Coke production *without* by-product recovery, where all ovens operate under negative pressure and, consequently, there are no leakages under normal operating conditions. All the by-products are retained and burned, instead of recovered. This process is usually accompanied by heat recovery and, in many cases, also the cogeneration of electricity.

GHG emission sources from metallurgical coke production include:

- Stack emissions which comprise GHG emissions from both the carbonisation (fuel transformation) of the coal, and from fuel combustion. These emissions should all be reported in the Energy Sector, in Manufacture of Solid Fuels in IPCC category 1.A.1.c. The emission estimation methodology from the carbonisation of coal is presented here as there is a significant overlap with the activity data used for iron and steel production. The estimation methodology for combustion emissions is described in Chapter 2 Volume 2 of *2006 IPCC Guidelines*.
- Fugitive emissions, which comprise:
 - Diffuse emissions (i.e. not emitted via stacks or vents) that occur during regular or irregular operations, originating from the transportation of coke, the use of ascension pipes, coke pushing, quenching and leakages in the battery. These diffuse emission sources are inherently difficult to monitor and therefore to quantify. CH₄ is the only GHG with significant diffuse emissions. These emissions should be reported under the Energy Sector, in the Fugitive emissions subsection (IPCC category 1.B.1c), and the methodology to estimate them is presented in Chapter 4 Volume 2 of the *2019 Refinement*.
 - Flaring emissions of, inter alia, CO₂, CH₄ and N₂O which occur primarily during emergencies and coke oven gas (COG) consumer maintenance. Where coke production is integrated with iron and steel manufacturing facilities, COG is usually burned as part of a gas mixture that contains blast furnace gas (BFG) and other gases produced, such as converter gas. Where these gases are used for the coke production, these emissions should be reported under the Energy Sector: (1) CH₄ and N₂O in IPCC category 1.B.1c, and the methodology to estimate them is presented Section 4.3.2.2 Chapter 4 Volume 2 of the *2019 Refinement*, and (2) CO₂ should also be reported under IPCC 1.B.1c category, except for when the simplified mass-balance approach is applied (Tier 1.b) and in that instance the CO₂ emissions should be reported together with direct emissions under the category 1.A.1.c. (Refer to Box 4.0)
 - Venting emissions of un-burned COG rarely occur and are considered negligible.

Table 4.1.a presents a summary of the allocation of emissions from metallurgical coke production.

TABLE 4.1A (NEW) EMISSION ALLOCATION FROM METALLURGICAL COKE PRODUCTION					
Processes and gases		Carbonisation emissions	Combustion emissions	Fugitive emissions	
				Diffuse emissions	Flaring emissions
Coal charging	CO ₂	NO	NO	NO	NO
	CH ₄	NO	NO	1.B.1c ⁽³⁾	NO
	N ₂ O	NO	NO	NO	NO
Chamber heating and firing	CO ₂	NO	1.A.1.c ⁽²⁾	NS	NO
	CH ₄	NO		1.B.1c ⁽³⁾	NO
	N ₂ O	NO		NO	NO
Coking	CO ₂	1.A.1.c ⁽¹⁾	NO	NS	NO
	CH ₄			1.B.1c ⁽³⁾	NO
	N ₂ O			NO	NO
Coke pushing	CO ₂	NO	NO	NS	NO
	CH ₄	NO	NO	1.B.1c ⁽³⁾	NO
	N ₂ O	NO	NO	NO	NO
Coke quenching	CO ₂	NO	NO	NS	NO
	CH ₄	1.A.1.c ⁽¹⁾	NO	1.B.1c ⁽³⁾	NO
	N ₂ O	NO	NO	NO	NO
Emergencies and COG consumer maintenance among other reasons	CO ₂	NO	NO	NS	1.B.1c ⁽³⁾ and 1.A.1.c ⁽¹⁾
	CH ₄	NO	NO	1.B.1c ⁽³⁾	1.B.1c
	N ₂ O	NO	NO	NS	
Note: NS: Not significant, NO: not occurring ⁽¹⁾ Methodology described in this chapter ⁽²⁾ Methodology described in Chapter 2, Volume 2 of 2006 IPCC Guidelines ⁽³⁾ Methodology described in Chapter 4 Volume 2 of the 2019 Refinement					

4.2.2.1 CHOICE OF METHOD: METALLURGICAL COKE PRODUCTION THROUGH CARBONISATION

This section outlines three Tiers for calculating CO₂ and CH₄ emissions from metallurgical coke production.

The Tier used to estimate emissions will depend on the quantity and quality of data that is available for national inventory compilers. The decision tree in Figure 4.6 will help select the Tier to be used to estimate CO₂ emissions. For CH₄ emissions, the decision tree is presented in Figure 4.8a.

There are two Tier 1 method options to estimate CO₂ emissions, depending on the activity data that are available:

- Tier 1 a: Where only metallurgical coke production data are available, the methodology applies a default emission factor given in Table 4.1, corresponding to the type of coke production technology. This methodology takes into consideration default emission factors derived from stack measurements, comprising the emissions from carbonisation (fuel transformation) and combustion, reflecting that there is no practical way to measure the two parameters separately. Where this method is applied, the

Final Draft

corresponding CO₂ fugitive emissions should be estimated according to the methodology described in Section 4.3.2.2 Chapter 4 Volume 2 of the *2019 Refinement* (category 1.B.1c).

- Tier 1 b: Where, in addition to data on metallurgical coke production, the country also has data on the consumption of metallurgical coal, then it is *good practice* to use the simplified carbon mass balance approach, assuming that all coke oven gas is combusted for coke production. This simple carbon balance method encompasses all carbon that may be released via fugitive emissions (including unintended releases, flaring) and from the consumption of coke oven by-products. In most countries with coke production, the required activity data for this method are readily available from national statistics and/or operators, and as this method is associated with lower uncertainty than the Tier 1a approach, it is the preferred Tier 1 method where the activity data are available.

The Tier 2 method to estimate CO₂ emissions is based on the carbon mass balance approach, using national statistical data on the inputs and outputs of carbonaceous materials to coke production. Where country-specific carbon content data derived from national fuel characteristics are available, it is *good practice* to use them. Otherwise, a hybrid methodology¹ can be used, selecting the default carbon content data provided in Table 4.3, provided that coke production is not a *key category*, in which case country-specific data are required.

The Tier 3 method to estimate CO₂ emissions requires plant-specific emissions measurement data or modelling results, combined with plant-specific activity data and plant-specific carbon content data for the carbon mass balance approach, for those sources where measurement data are not available. Where models are used to estimate emissions (for example, a model that combines a carbon mass balance with measurements), it is *good practice* to conduct model verification to present evidence to justify that the model outputs reflect the facility performance. Further, it is *good practice* to fully document the data and assumptions applied within the model, the sensitivity of the model to key data and assumptions, and the associated uncertainty with modelling results.

Where stack emission measurements are used, it is *good practice* for inventory compilers to document the sampling protocols and analytical methods applied, and to present supporting information to justify that the measurement results reflect plant performance, such as information on the frequency and duration of the measurements and whether the plant was operating under normal conditions.

BOX 4.0 (NEW)

FLARING ACTIVITIES IN METALLURGICAL COKE AND IRON AND STEEL PRODUCTIONS

Gaseous products from metallurgical coke and iron and steel production are mainly used for the generation of heat and electricity, and in some cases as reducing agents. There is a minor proportion of the total gas produced, usually less than 5%, which is lost from the production stream and flared, mainly during emergencies or consumer maintenance.

Integrated facilities usually flare a mix of the gases produced, including coke oven gas (COG), blast furnace gas (BFG) and converter gas (LDG), at the same stacks. This situation represents a challenge for the GHG emissions reporting, because:

- GHG emissions from COG flaring should be reported under the Energy Sector;
- GHG emissions from BFG and LDG flaring should be reported under IPPU.

COG has a high energy content and losses to flaring are minimised as a result, to typically less than 2% of COG production.

BFG is also used widely for heat and power-raising, with flaring activity often determined by gas demand on plant, and typically up to 20% flared. LDG may be captured and used around the facility to meet fuel combustion demand, but is often completely flared and in some cases may be directly vented to atmosphere.

The typical industry flaring rates are: COG 0.3-2%; BFG 0.5-20%; LDG 5-100%.

¹ 'Hybrid' refers to a methodology based on the complete carbon balance approach, with the use of default carbon content data.

Table 4.1b summarizes the activity data and the emission factors to be used to estimate CO₂ emissions for the different Tiers.

TABLE 4.1B (NEW)					
TIERs TO ESTIMATE CO₂ EMISSIONS FROM METALLURGICAL COKE PRODUCTION – CARBONISATION PROCESS					
Method	AD	EF	Technology	Limitations/Comments	Tier
Production-based	Metallurgical coke produced in the country	Default EF (Table 4.1)	This method can be applied to technologies with and without by-product recovery.	The production-based method should not be used to estimate emissions in conjunction with the carbon balance approach for iron and steel production, where the coke ovens operate within an integrated steelworks, to avoid double-counting.	Tier 1a
Simplified carbon balance (where only limited AD are available)	Coking coal consumed and metallurgical coke produced in the country	Carbon content of coking coal and coke (Defaults are presented in Table 4.3)	This method assumes 100% consumption of COG within the coke making process, thus it is more applicable to cases where by-products are not recovered.	If this method is applied, do not also calculate CO ₂ emissions from fugitives and flaring using the methods described in the Energy volume, to avoid double-counting.	Tier 1b
National Carbon Balance method (country-specific EFs)	National data on all inputs (raw materials and fuels, i.e. coking coal) and on all outputs (products and by-products: coke, COG, tars and benzenes, flaring)	Country-specific carbon contents of inputs and outputs	All technologies	If country-specific carbon contents are not available for all inputs and outputs, the default carbon contents from Table 4.3 may be applied with the hybrid method, but this will be considered a Tier 1 / Tier 2 approach which is not appropriate for a <i>key category</i> .	Tier 2
Aggregated plant-specific carbon balance method (country-specific EFs)	Installation-level data on all inputs (<i>as described above</i>) and outputs (<i>as described above</i>)	Plant-specific carbon contents of inputs and outputs	All technologies	n/a	Tier 3a
Installation-level measurement data or plant specific modelling data	n/a	n/a	All technologies	Emissions measurement data and/or modelling results must be complete for all emission sources at the coke plant and must comply with measurement protocols and/or verification processes for modelling.	Tier 3b

The methodologies to estimate CH₄ emissions relate to emissions from stacks, using default emission factors (Tier 1a), country specific emission factors (Tier 2) or measurements/models (Tier 3). The methodology to estimate CH₄ fugitive emissions is described in Section 4.3.2.2 Chapter 4 Volume 2 of the *2019 Refinement* (IPCC category 1.B.1c).

Final Draft

TIER 1 METHOD**Tier 1 a: Production based method**

Applying this method requires the amount of coke produced (tonnes) in the country and a default emission factor, given in Table 4.1. The following equations are used:

EQUATION 4.1 (UPDATED)
CO₂ EMISSIONS FROM COKE PRODUCTION (TIER 1A)

$$E_{CO_2,energy} = CK \bullet EF_{CO_2}$$

EQUATION 4.1A (NEW)
CH₄ EMISSIONS FROM COKE PRODUCTION (TIER 1A)

$$E_{CF_4,energy} = CK \bullet EF_{CF_4}$$

Where:

$E_{CO_2,energy}$ or $E_{CH_4,energy}$ = emissions of CO₂ or CH₄ from coke production, in kg CO₂ or kg CH₄, to be reported under the Energy Sector, category 1.A.1c.

CK = quantity of coke produced nationally, tonnes.

EF = emission factor, tonnes CO₂/tonne coke produced or tonnes CH₄/tonne coke produced (Table 4.1).

Tier 1 b: Simplified carbon balance method

The Tier 1 b method assumes that all of the coke oven by-products are transferred off site and that all of the coke oven gas produced is burned on-site for energy recovery. Applying this method requires data on the amount of coking coal used as raw material and the amount of metallurgical coke produced. The following equation, with a default carbon content given in Table 4.3, is used:

EQUATION 4.1B (NEW)
CO₂ EMISSIONS FROM METALLURGICAL COKE PRODUCTION (TIER 1B)

$$E_{CO_2,energy} = (CC \bullet C_{cc} - CK \bullet C_{CK}) \bullet \frac{44}{12}$$

Where:

$E_{CO_2,energy}$ = CO₂ emissions to be reported in the Energy Sector category 1.A.1c, tonnes.

CC = quantity of coking coal consumed for coke production in the country, tonnes.

CK = quantity of coke produced in the country, tonnes.

C_{cc} = default carbon content of coking coal (tonnes C/tonne coal).

C_{CK} = default carbon content of metallurgical coke (tonnes C/tonne coke).

TIER 2 METHOD

The Tier 2 method to estimate CO₂ emissions is appropriate where national statistics on process inputs and outputs from integrated and non-integrated coke production processes are available, and where country-specific carbon contents for process inputs and outputs are available

EQUATION 4.2 (UPDATED)
CO₂ EMISSIONS FROM METALLURGICAL COKE PRODUCTION

$$E_{CO_2,energy} = [CC * C_{cc} + \sum_a (PM_a * C_a) + BG * C_{BG} - CO * C_{CO} - COG * C_{COG} - \sum_b (COB_b * C_b) - E_{flaring}] * \frac{44}{12}$$

Where:

$E_{CO_2,energy}$ = CO₂ emissions to be reported in the Energy Sector category 1.A.1c (tonnes).

CC = quantity of coking coal consumed in the country (tonnes).

PM_a = quantity of process materials *a*, other than those listed as separate terms, i.e. natural gas, fuel oil or converter gas, consumed in the country for metallurgical coke production (tonnes).

BG = quantity of blast furnace gas consumed in coke ovens in the country (tonnes).

CO = quantity of metallurgical coke produced in the country (tonnes).

COG = quantity of coke oven gas produced but not recirculated and therefore not consumed for metallurgical coke production (tonnes).

COB_b = quantity of coke oven by-product *b* (e.g. COG, coal tar, light oil) produced, and either transferred offsite or to other facilities or flared (tonnes).

$E_{flaring}$ = CO₂ emissions from flaring (tonnes), deducted from the carbon mass balance, as the corresponding emissions are estimated as fugitive emissions using the methodology described in Section 4.3.2.2 Chapter 4 Volume 2 of the *2019 Refinement*.

C_x = country specific carbon content of material input or output *x*, (tonnes C/tonne material).

[“C_x” is a generic term intended to cover parameters above such as “C_{cc}” – coking coal; “C_{co}” – metallurgical coke; etc.]

If country specific carbon contents for all the input and output materials included in Equation 4.2 are not available, default carbon content from Table 4.3 could be used. In this case the methodology is a hybrid between Tier 1 and Tier 2, and is not appropriate if the metallurgical coke production is a *key category*.

For CH₄, in Tier 2 methodology inventory compilers can use the amount of coke produced, in combination with country specific emission factor.

TIER 3 METHOD

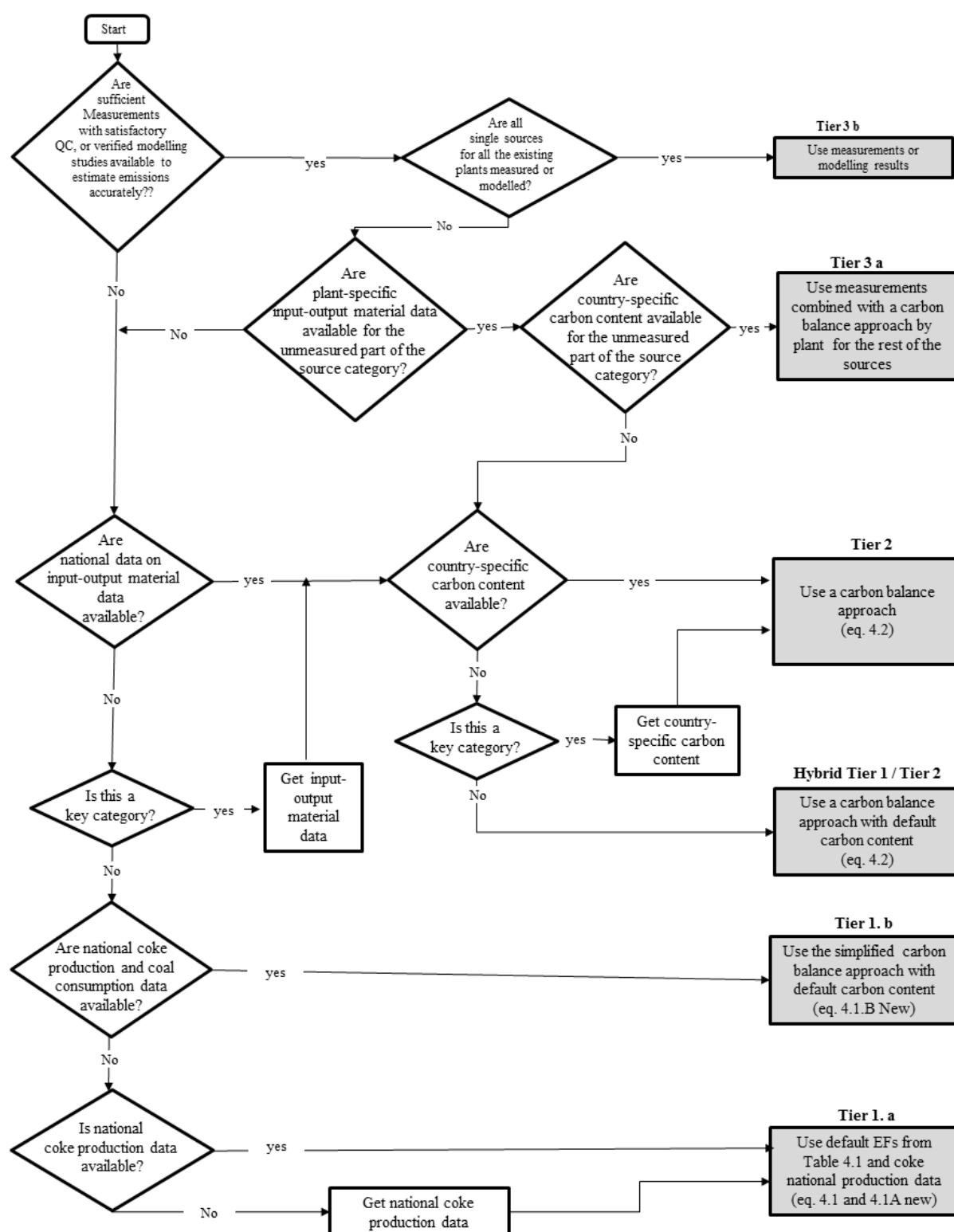
Unlike the Tier 2 method, Tier 3 uses plant specific data, considering that plants can differ substantially in their technology and process conditions.

Tier 3 comprises two approaches for CO₂ and only one for CH₄:

- For CO₂ and CH₄:
 - monitoring data or modelling of stack emissions, from both carbonisation and from fuel combustion; flaring of COG is excluded, as it is included in Section 4.3. Chapter 4 Volume 2 of the *2019 Refinement* (category 1.B.1c).
- For CO₂
 - the carbon mass balance approach, with plant-specific carbon contents of all the materials used and produced.

If actual measured CO₂/CH₄ emissions data are available from all the stacks present in all the coke production plants in the country, these data could be aggregated and used directly to account for the national emissions from metallurgical coke production. The total national emissions will be equal to the sum of emissions reported from each facility. It is a *good practice* to apply QA/QC to the monitoring data, following the recommendations included in Volume 1 Chapter 6 of the *2019 Refinement*.

A Tier 3 approach for one or more plants could be combined with lower Tiers approaches for other plants to derive a national estimate. In case the plant-specific CO₂ emissions data are not available for part or for all sources in the country, the CO₂ emissions for the unmeasured sources could be estimated using plant specific activity data applying a carbon mass balance with country specific carbon contents, using Equation 4.2.

453 **Figure 4.6 (updated) Estimation of CO₂ emissions from metallurgical coke production**

Notes:

⁽¹⁾ Measurements corresponding to fugitive emission emissions should be estimated and reported with the methodology described in Chapter 4 Volume 2 of the 2019 Refinement.

4.2.2.2 CHOICE OF METHOD: IRON AND STEEL PRODUCTION

This section outlines three Tiers for calculating CO₂ and CH₄ emissions and two Tiers N₂O emissions from iron and steel production. Decision trees are presented in Figures 4.7, 4.8a, 4.8b and 4.8c.

The Tier 1 method is based on national production data and default emission factors. The method derives estimates of CO₂ emissions based on assumptions regarding the quantity of material inputs to sinter production and to iron and steel production, to generate the reported production outputs, rather than through use of more detailed activity data on process inputs. Therefore, the method is associated with higher uncertainties, due to the reliance on these assumptions. Consequently, the Tier 1 method is only appropriate where sinter production and iron and steel production are not a *key category(ies)*.

The Tier 3 method is based on the use of stack measurements and/or modelling results:

- Where stack emission measurements are used, it is good practice for inventory compilers to document the sampling protocols and analytical methods applied, and to present supporting information to justify that the measurement results reflect plant performance, such as information on the frequency and duration of the measurements and whether the plant was operating under normal conditions.
- Where models are used to estimate emissions, it is good practice to conduct model verification to present evidence to justify that the model outputs reflect the facility performance. Further, it is good practice to fully document the data and assumptions applied within the model, the sensitivity of the model to key data and assumptions, and the associated uncertainty with modelling results.

METHODOLOGY FOR ESTIMATING CO₂ EMISSIONS

Tier 1 method – production-based emission factors

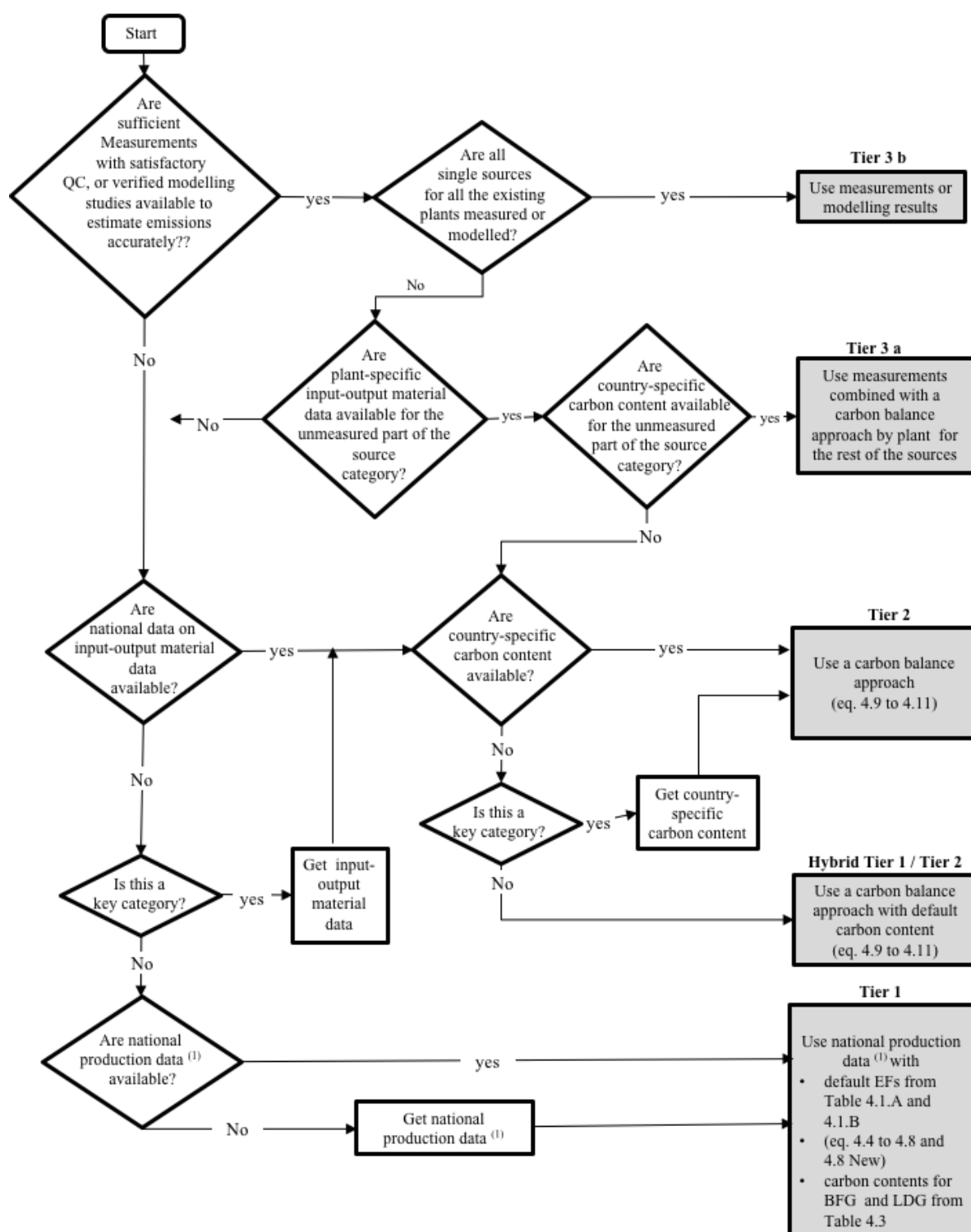
The Tier 1 approach for emissions from iron and steel production is to multiply default emission factors by national production data, as shown in Equation 4.4. Because emissions per unit of steel production vary widely depending on the method of steel production, it is *good practice* to determine the share of steel produced in different types of steelmaking processes, calculate emissions for each process, and then sum the estimates. Equation 4.4 considers steel production from Basic Oxygen Furnaces (BOF), Electric Arc Furnaces (EAF), and Open Hearth Furnaces (OHF). In the event that activity data for steel production for each process is not available, default allocation of total national steel production among these three steelmaking processes is provided in Table 4.1 in Section 4.2.2.3.

Equation 4.5 calculates emissions from the blast furnace production of pig iron that is not converted into steel. It is preferable to estimate emissions from this production separately because the emission factors for integrated iron and steel production (BOF and OHF processes) take into account emissions from both iron production and steel production.

A blast furnace is a closed system into which iron-bearing materials (iron ore lump, sinter and/or pellets), additives (slag formers such as limestone) and reducing agents (i.e. coke) are continuously fed from the top of the furnace shaft through a charging system that prevents the escape of blast furnace gas (BFG). A hot air blast, enriched with oxygen and auxiliary reducing agents is injected on the tuyere level providing a counter current of reducing gases. The air blast reacts with the reducing agents to produce mainly carbon monoxide (CO), which in turn reduces iron oxides to metal iron. The liquid iron is collected in the hearth along with the slag and both are cast on a regular basis. The liquid iron is transported in torpedo vessels to the steel plant, and the slag is processed to produce aggregate, granulate or pellets. The blast furnace gas is collected at the top of the furnace. It is treated and distributed around the works to be used as a fuel for heating or for electricity production. The vast majority of GHGs are emitted from the blast furnaces' stove stacks where the combustion gases from the stoves are discharged.

The objective in oxygen steelmaking is to burn (i.e. oxidise) the undesirable impurities contained in the hot metal feedstock. The main elements thus converted into oxides are carbon, silicon, manganese and phosphorus. The purpose of this oxidation process is to reduce the carbon content to a specified level (from approximately 4 – 5% to typically 0.01 – 0.4%), adjust the contents of desirable foreign elements and to remove undesirable impurities to the greatest possible extent, which are oxidised with the subsequent removal of the off-gas or slag. During the process, a number of additives are used to adjust steel quality and to form slag. The major emission point for GHGs from the BOF is the furnace exhaust gas that is discharged through a stack after gas cleaning. The gases produced during oxygen blowing (converter gas) contain large amounts of carbon monoxide. In most steelmaking plants, measures have been taken to recover the converter gas and use it as an energy source. The CO-rich flue-gas can be collected, cleaned and buffered for subsequent use as fuel. The carbon is removed as CO and CO₂ during the oxygen blow. Carbon may also be introduced to a much smaller extent from fluxing materials and other process additives that are charged to the furnace.

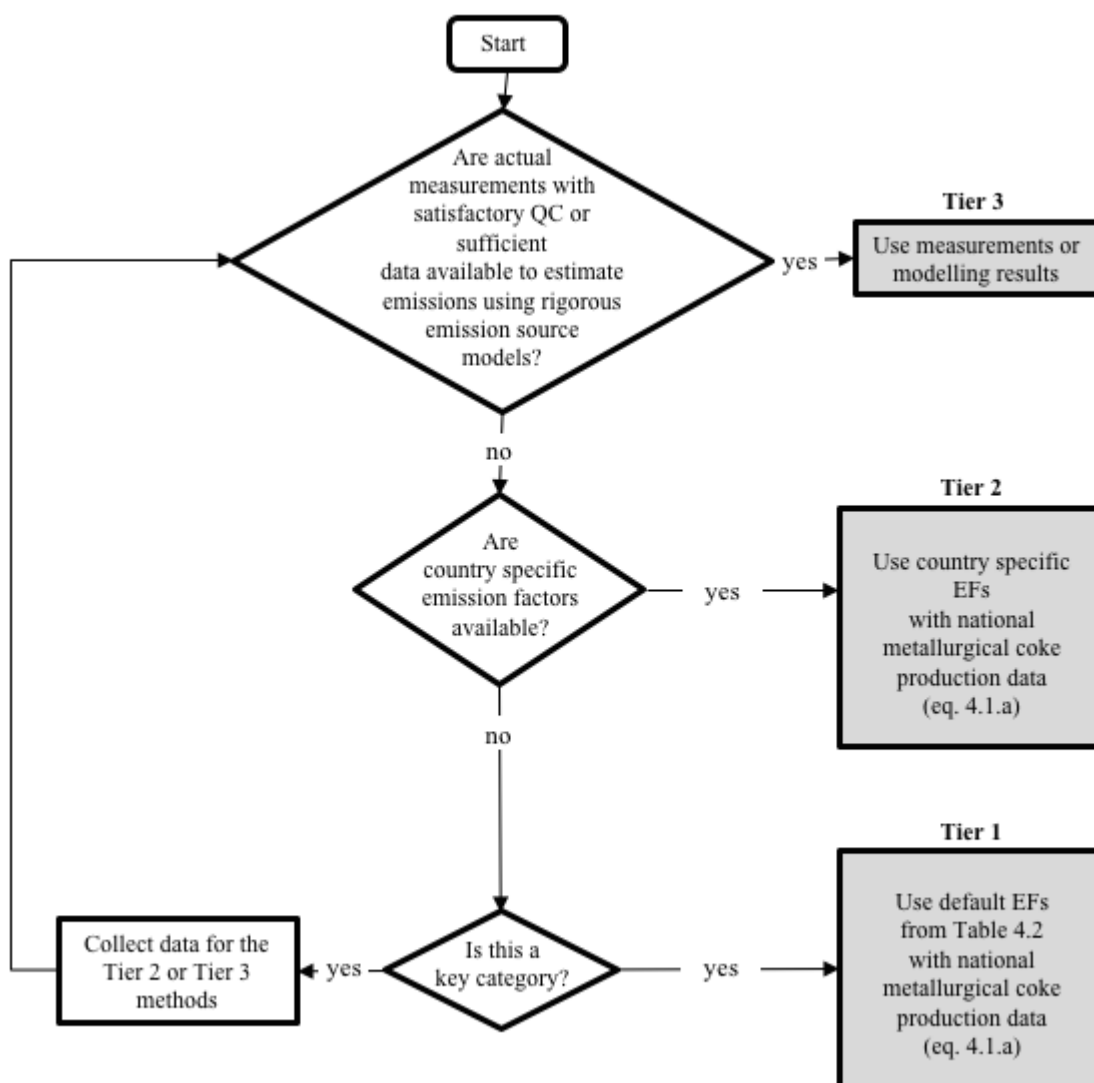
Final Draft

Figure 4.7 (updated) Decision tree for estimation of CO₂ emissions from iron and steel production

Note:

⁽¹⁾ National production data refers to the productions of (1) steel; (2) pig iron not processed into steel; (3) direct reduced iron; (4) sinter; (5) pellet; (6) blast furnace gas and (7) converter gas.

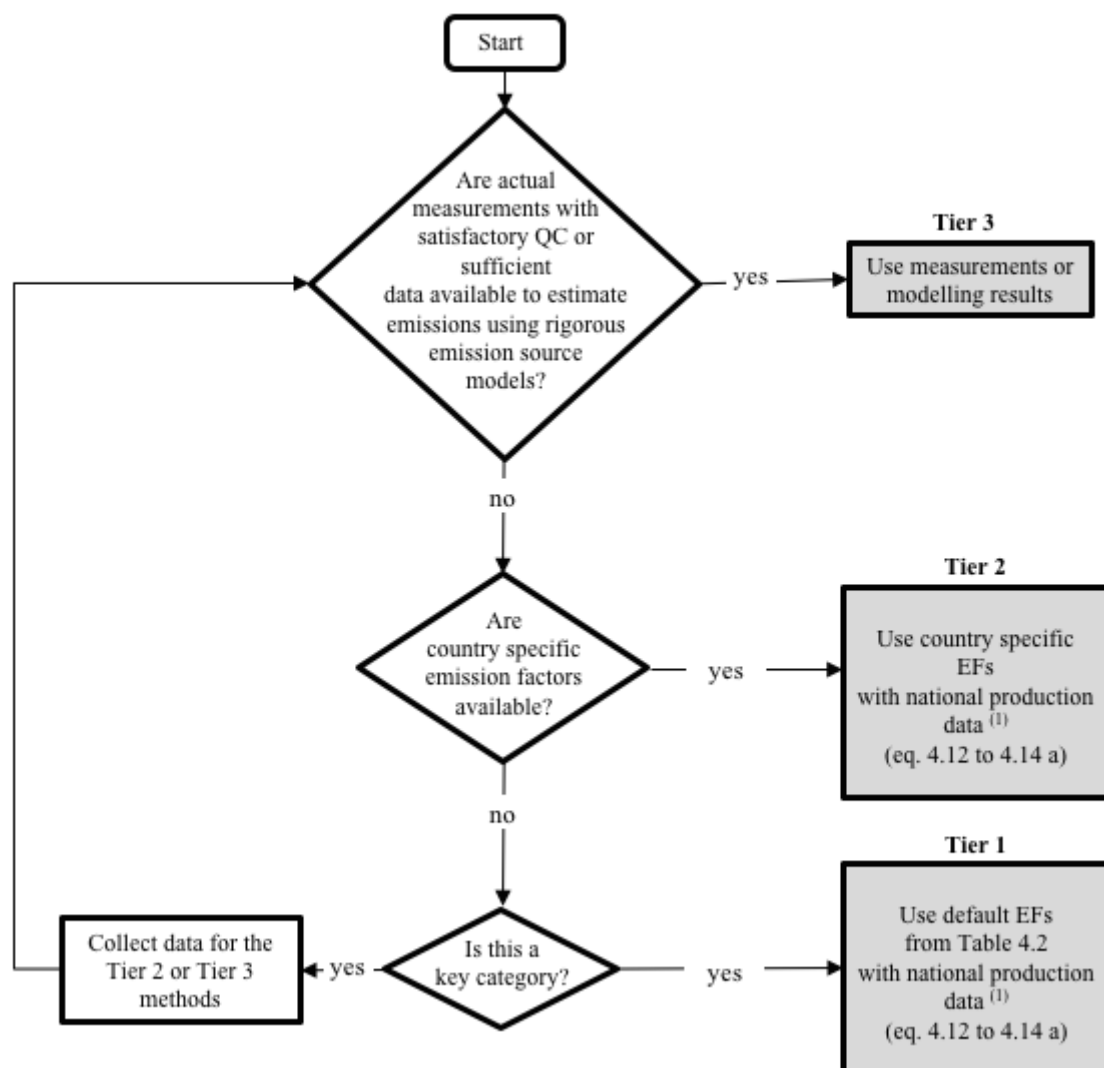
515 **Figure 4.8a (new) Decision tree for estimation of CH₄ emissions from coke production**



516
517
518

Final Draft

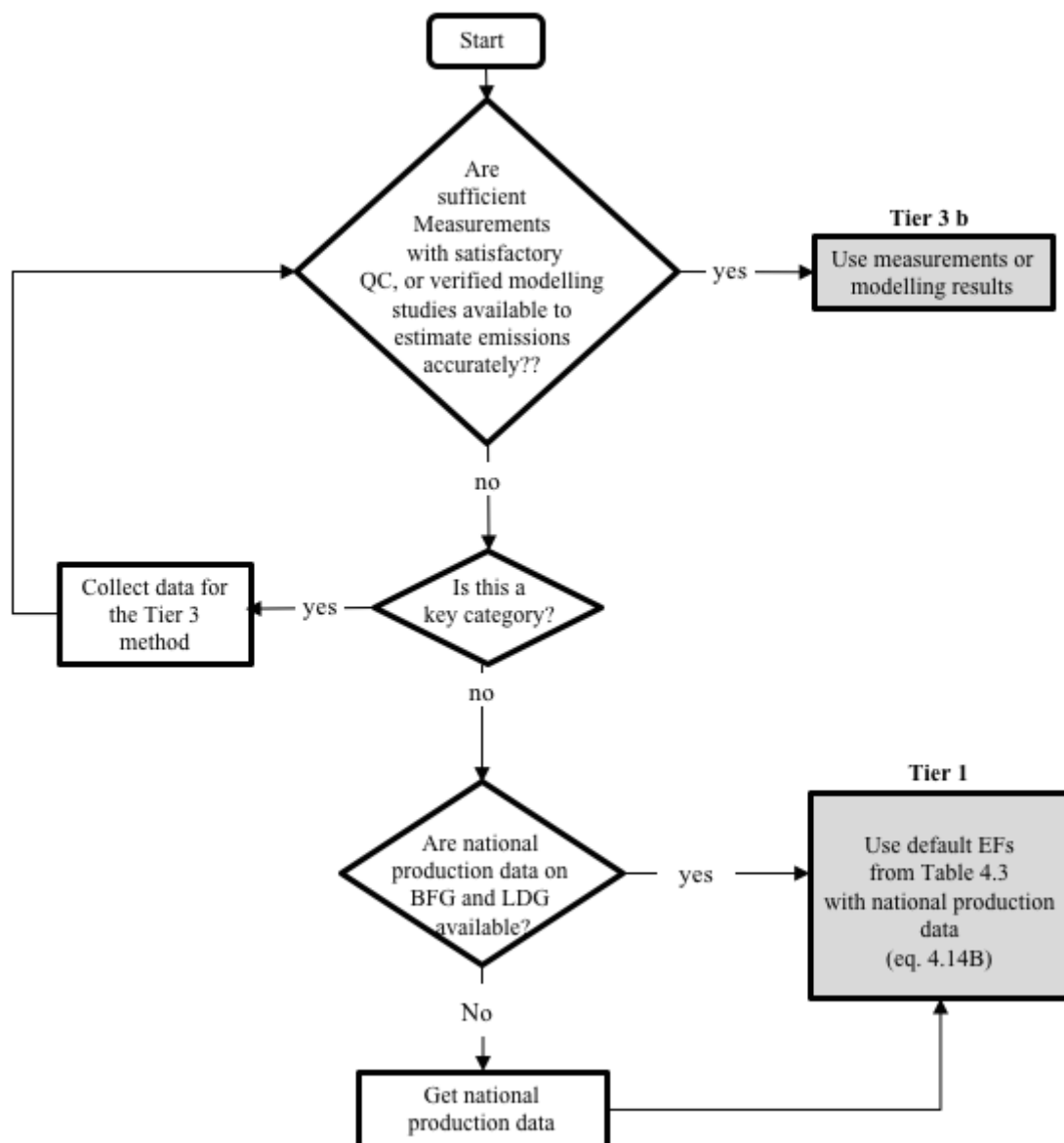
Figure 4.8b (updated) Decision tree for estimation of CH₄ emissions from iron and steel production



Note:

(1) National production data refers to the productions of (1) sinter; (2) pig iron; (3) direct reduced iron; (4) blast furnace gas and (5) converter gas.

Figure 4.8c (new) Decision tree for estimation of N₂O emissions from iron and steel production



Final Draft

Equation 4.6 calculates CO₂ emissions from production of Direct Reduced Iron (DRI) for the Tier 1 method using a CO₂ emission factor.

In sinter plants CO₂ emissions occur during fuel combustion in burners and as a result of leakages from the feed materials, including coke fines and other carbonaceous materials. It is *good practice* to estimate separately the emissions from national sinter production and national pellet production, using Equations 4.7 and 4.8. which should be used if the inventory compiler does not have detailed information about the process materials used. If the process materials are known, emissions should be calculated using the Tier 2 method.

Equation 4.8a calculates CO₂ emissions from blast furnace gas (BFG) and converter gas (LDG) flaring, considering that 20% (vol) of the BFG is removed from the production stream and then flared, and that all (100%) of the LDG is also flared. (see Box 4.0)

Total emissions are the sum of Equations 4.4 to 4.8 (including the Equation 4.8a).

EQUATION 4.4 (UNCHANGED)

CO₂ EMISSIONS FROM IRON AND STEEL PRODUCTION (TIER 1)

$$\text{Iron \& Steel: } E_{CO_2, non-energy} = BOF \bullet EF_{BOF} + EAF \bullet EF_{EAF} + OHF \bullet EF_{OHF}$$

EQUATION 4.5 (UNCHANGED)

CO₂ EMISSIONS FROM PRODUCTION OF PIG IRON NOT PROCESSED INTO STEEL (TIER 1)

$$\text{Pig Iron Production: } E_{CO_2, non-energy} = IP \bullet EF_{IP}$$

EQUATION 4.6 (UNCHANGED)

CO₂ EMISSIONS FROM PRODUCTION OF DIRECT REDUCED IRON (TIER 1)

$$\text{Direct Reduced Iron: } E_{CO_2, non-energy} = DRI \bullet EF_{DRI}$$

EQUATION 4.7 (UNCHANGED)

CO₂ EMISSIONS FROM SINTER PRODUCTION (TIER 1)

$$\text{Sinter Production: } E_{CO_2, non-energy} = SI \bullet EF_{SI}$$

EQUATION 4.8 (UNCHANGED)

CO₂ EMISSIONS FROM PELLET PRODUCTION (TIER 1)

$$\text{Pellet Production: } E_{CO_2, non-energy} = P \bullet EF_P$$

EQUATION 4.8A (NEW)

CO₂ EMISSIONS FROM FLARING (TIER 1)

$$\begin{aligned} \text{BFG and LDG flaring: } E_{CO_2, non-energy} &= BFG \bullet (EF_{CO_2})_{BFG \text{ flaring}} + \\ &LDG \bullet (EF_{CO_2})_{LDG \text{ flaring}} = BFG \bullet (0.2 \bullet CC_{BFG} \bullet \frac{44}{12}) + LDG \bullet (CC_{LDG} \bullet \frac{44}{12}) \end{aligned}$$

Where:

$E_{CO_2, non-energy}$ = emissions of CO₂ to be reported in IPPU Sector, tonnes

BOF= quantity of BOF crude steel produced, tonnes

EAF = quantity of EAF crude steel produced, tonnes

OHF = quantity of OHF crude steel produced, tonnes

IP = quantity of pig iron production not converted to steel, tonnes

DRI = quantity of Direct Reduced Iron produced nationally, tonnes

SI = quantity of sinter produced nationally, tonnes

P = quantity of pellet produced nationally, tonnes

EF_x = emission factor, tonnes CO₂/tonne *x* produced

$(EF_{CO_2})_{BFG\ flaring}$ = emission factor, tonnes CO₂/tonnes of BFG produced

$(EF_{CO_2})_{LDG\ flaring}$ = emission factor, tonnes CO₂/tonnes of LDG produced

BFG = blast furnace gas produced nationally, tonnes

LDG = converter gas produced nationally, tonnes

CC_{BFG} = carbon content of blast furnace gas, tonnes C/tonne

CC_{LDG} = carbon content of converter gas, tonnes C/tonne

Tier 2 method

The Tier 2 method is appropriate where the inventory compiler has access to national data on the use of process materials for iron and steel production, sinter production, pellet production and direct reduced iron production. In addition, as discussed in Section 4.2.2.5, there are several other process inputs and outputs that could be considered under Tier 2. This data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations or individual iron and steel companies. The Tier 2 method will produce a more accurate estimation compared to the Tier 1 method, as it considers the actual quantity of inputs that contribute to CO₂ emissions.

Total emissions are the sum of Equations 4.9, 4.10 and 4.11. for those processes that occur in the country.

EQUATION 4.9 (UNCHANGED) CO₂ EMISSIONS FROM IRON AND STEEL PRODUCTION (TIER 2)

$$E_{CO_2, non-energy} = \left[PC \cdot C_{PC} + \sum_a (COB_a \cdot C_a) + CI \cdot C_{CI} + L \cdot C_L + D \cdot C_D + CE \cdot C_{CE} + \sum_b (O_b \cdot C_b) + COG \cdot C_{COG} - S \cdot C_S - IP \cdot C_{IP} - BG \cdot C_{BG} \right] \cdot \frac{44}{12}$$

EQUATION 4.10 (UPDATED) CO₂ EMISSIONS FROM SINTER PRODUCTION (TIER 2)

$$E_{CO_2, non-energy} = \left[CBR \cdot C_{CBR} + COG \cdot C_{COG} + BG \cdot C_{BG} + \sum_a (PM_a \cdot C_a) \right] \cdot \frac{44}{12}$$

Where, for iron and steel production:

E_{CO₂, non-energy} = emissions of CO₂ to be reported in IPPU Sector, tonnes

PC = quantity of coke consumed in iron and steel production (not including sinter production), tonnes

COB_a = quantity of onsite coke oven by-product *a*, consumed in blast furnace, tonnes

CI = quantity of coal directly injected into blast furnace, tonnes

L = quantity of limestone consumed in iron and steel production, tonnes

D = quantity of dolomite consumed in iron and steel production, tonnes

CE = quantity of carbon electrodes consumed in EAFs, tonnes

Final Draft

O_b = quantity of other carbonaceous and process material b , consumed in iron and steel production, such as sinter or waste plastic, tonnes

COG = quantity of coke oven gas consumed in stationary combustion equipment in iron and steel production (such as cowpers, pre-heating ladles etc.), tonnes (or other unit such as GJ. Conversion of the unit should be consistent with Volume 2 Energy)

S = quantity of steel produced, tonnes

IP = quantity of iron produced not converted to steel, tonnes

BFG = quantity of blast furnace gas transferred off site, tonnes (or other unit such as GJ. Conversion of the unit should be consistent with Volume 2 Energy)

C_x = carbon content of material input or output x , tonnes C/(unit for material x) [e.g., tonnes C/tonne]

Where, for sinter production:

$E_{CO_2, \text{non-energy}}$ = emissions of CO_2 to be reported in IPPU Sector, tonnes

CBR = quantity of purchased and on-site produced coke breeze used for sinter production, tonnes

COG = quantity of coke oven gas consumed in sinter production, tonnes (or other unit such as GJ. Conversion of the unit should be consistent with Volume 2 Energy)

BFG = quantity of blast furnace gas consumed in sinter production, tonnes (or other unit such as GJ. Conversion of the unit should be consistent with Volume 2 Energy)

PM_a = quantity of process material a , other than those listed as separate terms, such as anthracite, consumed for sinter production in integrated iron and steel production facilities, tonnes

C_x = carbon content of material input or output x , tonnes C/(unit for material x) [e.g., tonnes C/tonne]

In an integrated plant, the emissions from the combustion of blast furnace gas, coke oven gas and converter gas to produce heat for different needs within the steelworks (rolling mills, hot rolling mill, plate mill, bar mill, cold rolling mill, coating, pipe) and to produce electricity at the internal power plant to cover the internal needs should be reported under IPPU (see Section 4.2.2.5). The methodology for these estimations is described in Chapter 2 Volume 2 of the 2006 IPCC Guidelines.

Equation 4.11 calculates CO_2 emissions from the production of direct reduced iron for the Tier 2 method based on reducing agents consumption and its carbon contents. Emissions from DRI production are derived from combusting fuel, coke breeze, metallurgical coke or other carbonaceous materials.

EQUATION 4.11(UNCHANGED)
 CO_2 EMISSIONS FROM DIRECT REDUCED IRON PRODUCTION (TIER 2)

$$E_{CO_2, \text{non-energy}} = (DRI_{NG} \bullet C_{NG} + DRI_{BZ} \bullet C_{BZ} + DRI_{CK} \bullet C_{CK}) \bullet \frac{44}{12}$$

Where:

$E_{CO_2, \text{non-energy}}$ = emissions of CO_2 to be reported in IPPU Sector, tonnes

DRI_{NG} = amount of natural gas used in direct reduced iron production, GJ

DRI_{BZ} = amount of coke breeze used in direct reduced iron production, GJ

DRI_{CK} = amount of metallurgical coke used in direct reduced iron production, GJ

C_{NG} = carbon content of natural gas, tonne C/GJ

C_{BZ} = carbon content of coke breeze, tonne C/GJ

C_{CK} = carbon content of metallurgical coke, tonne C/GJ

Note: Natural Gas has a double role, to provide heat and act as a reducing agent in DRI furnaces.

If country specific carbon contents for all the input and output materials included in Equations 4.9, 4.10 and 4.11 are not available, default carbon contents from Table 4.3 could be used. In this case, the methodology is a hybrid between Tier 1 and Tier 2 and is not appropriate if the iron and steel production is a *key category*.

Tier 3 method

Unlike the Tier 2 method, the Tier 3 method uses plant specific data. The Tier 3 method provides an even more accurate estimate of emission than the Tier 2 method because plants can differ substantially in their technology and process conditions. If actual measured CO₂ emissions data are available from iron and steelmaking facilities, these data can be aggregated to account for national CO₂ emissions. If facility-specific CO₂ emissions data are not available, CO₂ emissions can be calculated from plant-specific activity data for individual reducing agents, exhaust gases, and other process materials and products. The total national emissions will equal the sum of emissions reported from each facility. Equations 4.9 through 4.11 describe the parameters that are necessary for an accounting of plant-specific emissions using the Tier 3 method and plant-specific activity data at a facility level. Plant-specific carbon contents for each material are required for the Tier 3 method.

METHODOLOGY FOR CH₄

When carbon-containing materials are heated in the furnace for sinter production or iron production, the volatiles, including methane, are released. With open or semi-covered furnaces, most of the volatiles will burn to CO₂ above the charge, in the hood and off-gas channels, but some will remain un-reacted as CH₄ and non-methane volatile organic compounds (NMVOC). The amounts depend on the operation of the furnace. Sprinkle-charging will reduce the amounts of CH₄ compared to batch-wise charging. Increased temperature in the hood (less false air) will reduce the content of CH₄ further.

This section describes a Tier 1 default method and a more advanced Tier 2 and Tier 3 methods for CH₄ emissions from iron and steel production.

The Tier 1 method covers CH₄ emissions from sinter production and from iron production, multiplying default emission factors by national production data. Emissions from flaring are considered negligible, as CH₄ in blast furnace gas and in converter gas not significant. The guidance in this section does not cover the release of CH₄ from pelletisation, although the associated emissions may be relevant when anthracite is used. CH₄ may be emitted from steel making processes as well, however those emissions are assumed to be negligible.

Equation 4.12 calculates CH₄ emissions from sinter production, Equation 4.13 from pig iron production and Equation 4.14 from direct reduced iron production.

The total CH₄ emissions are the sum of Equations 4.12, 4.13, 4.14 and 4.14a, for the processes that occur in the country.

$$\begin{aligned} &\text{EQUATION 4.12 (UNCHANGED)} \\ &\text{CH}_4 \text{ EMISSIONS FROM SINTER PRODUCTION (TIER 1)} \\ &\text{Sinter Production: } E_{CH_4, non-energy} = SI \bullet EF_{SI} \end{aligned}$$

$$\begin{aligned} &\text{EQUATION 4.13 (UNCHANGED)} \\ &\text{CH}_4 \text{ EMISSIONS FROM BLAST FURNACE PRODUCTION OF PIG IRON (TIER 1)} \\ &\text{Pig Iron Production: } E_{CH_4, non-energy} = PI \bullet EF_{PI} \end{aligned}$$

$$\begin{aligned} &\text{EQUATION 4.14 (UNCHANGED)} \\ &\text{CH}_4 \text{ EMISSIONS FROM DIRECT REDUCED IRON PRODUCTION (TIER 1)} \\ &\text{Direct Reduced Iron Production: } E_{CH_4, non-energy} = DRI \bullet EF_{DRI} \end{aligned}$$

Where:

$E_{CH_4, non-energy}$ = emissions of CH₄ to be reported in IPPU Sector, kg

SI = quantity of sinter produced nationally, tonnes

PI = quantity of iron produced nationally including iron converted to steel and not converted to steel, tonnes

EF_{SI} = emission factor for sinter production, kg CH₄/tonne sinter produced

Final Draft

EF_{PI} = emission factor for pig iron production, kg CH₄/tonne pig iron produced

EF_{DRI} = emission factor for steel by direct reduced iron production, kg CH₄/tonne DRI steel produced

In Tier 2 methodology inventory compilers can use the amount of sinter, pig iron from blast furnace and iron from direct reduction produced nationally, in combination with the corresponding country specific emission factors.

The Tier 3 method uses plant specific emissions data from stack emissions monitoring, or modelling results. The total national emissions will equal the sum of emissions reported from each facility.

METHODOLOGY FOR N₂O

This section describes a Tier 1 default method and a more advanced Tier 3 plant level method for N₂O emissions from iron and steel production. There is no Tier 2 method.

The Tier 1 method covers only N₂O emissions from flaring, multiplying default emission factors by national production data. The guidance in this section does not cover the release of N₂O from other processes, as these emissions are assumed to be negligible.

Equation 4.14b calculates N₂O emissions from blast furnace gas (BFG) and converter gas (LDG) flaring, considering that 20% of the BFG is removed from the production stream and then flared, and that all (100%) of the LDG is also flared (see Box 4.0).

<p style="text-align: center;">EQUATION 4.14A (NEW) N₂O EMISSIONS FROM FLARING (TIER 1) BFG and LDG flaring: $E_{N2O, non-energy} = BFG \bullet 0.2 \bullet EF_{N2O \text{ BFG Flare}} + LDG \bullet EF_{N2O \text{ LDG Flare}}$</p>

Where:

E_{N₂O, non-energy} = emissions of CH₄ to be reported in IPPU Sector, tonne

BFG = blast furnace gas produced, tonne

LDG = converter gas produced, tonne

EF_{N₂O BFG flare} = emission factor for BFG flared, tonne N₂O/tonne BFG produced

EF_{N₂O LDG flare} = emission factor for LDG flared, tonne N₂O/tonne LDG produced

The Tier 3 method uses plant specific emissions data or modelling results.

The total national emissions will equal the sum of emissions reported from each facility.

4.2.2.3 CHOICE OF EMISSION FACTORS

This section provides default emission factors for CO₂ and CH₄ to be used in Tier 1a and provides a discussion on carbon contents to be used in the carbon balance approach at higher Tiers.

TIER 1A METHOD

Carbon dioxide emission factors

Tables 4.1, 4.1a, 4.1b provide default emission factors for coke, sinter, pellet, iron and steel production from direct emission sources. The emission factors for the three steelmaking methods are based on measurements and expert judgment using typical practice for the different steel production scenarios.

Table 4.1 includes CO₂ emission factors for both coke production technology types, i.e. *with* and *without* by-product recovery. In the first case, the CO₂ EF 0.51 t CO₂/t coke was calculated as the mean value from the wide range of sources analysed and chosen to be the Tier 1 EF as a conservative factor, not comprising energy saving technologies, such as Coke Dry Quenching (CDQ), Coal moisture control etc. If these energy efficiency

technologies are in use at a country's coke plants, the inventory compiler may choose a lower EF, e.g. 0.30 t CO₂/t coke. The wide range for by-product recovery coke plants, whose variability reflects not only different operational and maintenance practices, but also, and foremost, the types of fuels used as primary for coke production (including different combinations of coal, natural gas, fuel oil, coke oven gas, converter or blast furnace gas and other fuels).

TABLE 4.1 (UPDATED)
TIER 1 DEFAULT CO₂ EMISSION FACTORS FOR COKE PRODUCTION

Process	Emission Factor	Source
Coke production using by-product recovery technology (tonne of CO ₂ /tonne of coke)	0.51	<ul style="list-style-type: none"> – (EU IPPC BREF 2013), Table 5.2 Page 224 (0.16-0.86 t CO₂/t coke) – (Official Journal of the European Union 2011a) (0.286 t CO₂/ t coke) – (Fruehan et al. 2000) page 33, Table A-10,(0.3-0.34 t CO₂ /t coke) – (US EPA 2012) p. D-9, section D.2.5 (0.21 tCO₂/ t coke) – (Zhang et al. 2012) p. 2026, Table 4 (0.518 t CO₂ /t coke)
Coke production without by-product recovery (tonne of CO ₂ /tonne of coke)	1.23	– (US EPA 2012) p. D-9, section D.2.5

Table 4.1a includes CO₂ default emissions factor for sinter production, which represents the mean value based on the sources studied and refers to sinter plants which do not use carbonate ores. However, for those sinter plants which do use carbonate ores this CO₂ EF average can be up to twice as high. Moreover, this value can also vary widely depending on the kind of fuel gases used in the ignition oven.

For pellet production the scarce set of CO₂ EFs reported present a wide range of values. The default EF for Tier1 approach, included in Table 4.1.A, has been chosen as the maximum value reported. Similarly, for EAFs the CO₂ EF chosen corresponds to the maximum value reported.

TABLE 4.1A(NEW)
TIER 1 DEFAULT CO₂ EMISSION FACTORS FOR SINTER AND PELLET PRODUCTION

Sinter production (tonne of CO ₂ /tonne of sinter)	0.21	<ul style="list-style-type: none"> – (Fruehan et al. 2000), Table 4.1 (0.17-0.19 t CO₂/t sinter) – (Zhang et al. 2012), p. 2026, Table 4 (0.21 t CO₂/t sinter) – (EU IPPC BREF 2013), Table 3.4, p. 96 (0.162-0.368 t CO₂/t sinter) – (Official Journal of the European Union 2011a) (0.171t CO₂/ t sinter)
Pellet production (tonne CO ₂ /tonne pellet produced)	0.19	– (EU IPPC BREF 2013), Chapter 4, Table 4.1 Page 188.

Final Draft

762

TABLE 4.1b (NEW) TIER 1 DEFAULT CO ₂ EMISSION FACTORS FOR IRON AND STEEL PRODUCTION		
Iron production (tonne CO ₂ /tonne of hot metal)	1.43	<ul style="list-style-type: none"> – (Fruehan et al. 2000), p. 33, Table A-11. (1.447-1.559 t CO₂/t hot metal). – (Zhang et al. 2012), p. 2026, Table 4 (1.375 t CO₂/t hot metal). – (Official Journal of the European Union 2011a), Annex 1, (1.328 t CO₂/t hot metal).
Direct Reduced Iron production (tonne CO ₂ per tonne DRI produced)	0.70	Direct Reduced Iron Production: European IPPC Bureau (2001), Integrated Pollution Prevention and Control (IPPC) Best Available Techniques Reference Document on the Production of Iron and Steel, December 2001, Table 10.1 Page 322 and Table 10.4 Page 331. http://eippcb.jrc.es/pages/FActivities.htm
Steelmaking Method		
Electric Arc Furnace (EAF) (tonne CO ₂ /tonne of steel produced) ¹	0.18	– (EU IPPC BREF 2013), Chapter 8, Table 8.1 p.429 (0,072-0,180 t CO ₂ /t of steel produced)
Basic Oxygen Furnace (BOF) (tonne CO ₂ /tonne of steel produced) ^{2,3}	1.58	<ul style="list-style-type: none"> – (Fruehan et al. 2000), p.33 Table A-11. Comparison of theoretical minimum and actual CO₂ emissions for selected processes comes up with a range of 0.189-0.207 t CO₂/t liquid steel, without considering blast furnace emissions. – (Joint Research Center 2013), Table 7.3, p. 369 (22.6-174 kg CO₂/t liquid steel), without considering blast furnace emissions.
Open Hearth Furnace (OHF) (tonne CO ₂ per tonne of steel produced) ^{2,4}	1.72	Steel Production: Consensus of experts and IISI Environmental Performance Indicators 2003 STEEL (International Iron and Steel Institute, 2004)
<p>¹ The emission factor for EAF steelmaking does not include emissions from iron production. This factor is based on production of steel from scrap metal, and therefore the EAF emission factor does not account for any CO₂ emissions from blast furnace iron making. Therefore is not applicable to EAFs that use pig iron as a raw material.</p> <p>² The emission factors for BOF and OHF steelmaking do include emissions from blast furnace iron production, and are consistent with Equation 4.4</p> <p>³ The emission factors for BOF represents the mean value of (Blast Furnace + BOF) CO₂ emissions across the sources studied.</p>		

763

764 **Methane emission factors**765 Default CH₄ emission factors are provided in Table 4.2 below.

TABLE 4.2 (UPDATED) TIER 1 DEFAULT CH ₄ EMISSION FACTORS FOR COKE PRODUCTION (NON FUGITIVES), IRON AND STEEL PRODUCTION		
Process	Emission Factor	Source
Coke Production (kg CH ₄ /tonne of coke produced)	0.089	<ul style="list-style-type: none"> – (Japan NIR 2018) (0,089 kg CH₄/t coke produced) – (EU IPPC BREF 2013), Chapter 8, Table 8.1 Page 429 (0,001- 0,080 kg CH₄/t coke produced)
Sinter Production (kg CH ₄ /tonne of sinter produced)	0.07	EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005). Processes With Contact: <i>Sinter and Pelletizing Plants: Sinter and Pelletizing Plants (Except Combustion 030301)</i> Table 8.2a Emission factors for gaseous compounds
DRI Production kg CH ₄ /TJ (on a net calorific basis)	1	Energy Volume default emission factor for CH ₄ Emissions from natural gas combustion. [See Table 2.3 of Volume 2, Chapter 2.]

766

767

Nitrous oxide

Due to the absence of emission factor values reported in literature, the approach described in US CFR (2018), that estimate N₂O emission factors on the basis of CO₂ emission factors, is adopted, according with Equation 4.14b.

EQUATION 4.14B (NEW)
N₂O EMISSION FACTORS FROM FLARING OF BLAST FURNACE GAS AND CONVERTER GAS

$$(EF_{N_2O})_{BFG_flaring} = (EF_{CO_2})_{BFG_flaring} \bullet \left[\left(\frac{EF_{CO_2}}{EF_{N_2O}} \right)_{Oil_and_gas_production} \right]$$

$$(EF_{N_2O})_{LDG_flaring} = (EF_{CO_2})_{LDG_flaring} \bullet \left[\left(\frac{EF_{CO_2}}{EF_{N_2O}} \right)_{Oil_and_gas_production} \right]$$

Where:

$(EF_{CO_2})_{BFG_flaring}$ = 0.125 tonne CO₂/ tonne BFG produced, (equation 4.14a, with CC_{BFG} from Table 4.3)

$(EF_{CO_2})_{LDG_flaring}$ = 1.28 tonne CO₂/ tonne LDG produced, (equation 4.14a, with CC_{LDG} from Table 4.3)

EF_{CO₂} and EF_{N₂O} for oil and gas production are set as 3.0 E-03 and 3.3 E-08 Gg gas per 10⁶ m³ gas produced, taken from Table 4.2.5, Volume 2, Chapter 4 *2006 IPCC Guidelines*.

N₂O emission factors estimated on the basis of this equation, are provided in Table 4.2b below.

TABLE 4.2B (NEW) TIER 1 DEFAULT N₂O EMISSION FACTORS FOR COKE PRODUCTION AND IRON AND STEEL PRODUCTION		
Process	Emission Factor	Source
Blast furnace gas flaring ton N ₂ O / ton BFG produced	1.37 E-06	Equation 4.14b
Converter gas flaring ton N ₂ O / ton LDG produced	1.41 E-05	Equation 4.14b

TIER 1B AND TIER 2 METHODS

The default carbon contents in Table 4.3 should be used if there is no information on average country specific carbon contents. Carbon contents in Table 4.3 are based on expert judgment, complementing those provided in Table 1.2 and 1.3 in Chapter 1 Volume 2 of the *2006 IPCC Guidelines*. It is a *good practice* to use country-specific values, based on measurements or other well-documented data. The Emission Factor Database (EFDB) provides a variety of well-documented emission factors and other parameters that may be better suited to national circumstances than the default values, although the responsibility to ensure appropriate application of material from the database remains with the inventory compiler.

TIER 3 METHODS

The Tier 3 method is based on aggregated plant-specific emission estimates or the application of the carbon balance approach at the plant specific level. The inventory compiler should ensure that each facility has documented the emission factors and carbon contents used, and that these emission factors are indicative of the processes and materials used at the facility. The Tier 3 method requires carbon contents and production/consumption mass for all process materials and off-site transfers such as those listed in Table 4.3. While this Table provides default carbon contents, it is *good practice* under Tier 3 to adjust these values to reflect variations at the plant level. The

Final Draft

carbon contents listed in Table 4.3 are only appropriate for the Tier 3 method if plant-specific information indicates that they correspond to actual conditions. It is anticipated that for the Tier 3 method the plant-specific data would include both carbon content data and production/consumption mass rate data, and that therefore the default values in Table 4.3 would not be applied to the Tier 3 method in most instances.

TABLE 4.3 (UPDATED) TIER 2 MATERIAL-SPECIFIC CARBON CONTENTS FOR IRON AND STEEL PRODUCTION (TONNES C/TONNE)	
Process Materials	Carbon Content
Blast Furnace Gas	0.17
Charcoal*	0.91
BF injection coal	0.806
Steam coal (combustion coal)	0.671
Coal Tar	0.62
Coke	0.83
Coke Oven Gas	0.47
Coking Coal	0.73
Direct Reduced Iron (DRI, Gas-based)	0.020
Direct Reduced Iron (DRI, Coal-based)	0.020
Dolomite/Crude dolomite	0.13
EAF Carbon Electrodes ¹	1.00
EAF coal	0.89
Heavy oil	0.793
Light oil	0.709
Kerosene	0.858
LPG	0.814
Hot Briquetted Iron ²	0.02
Limestone	0.121
Natural Gas	0.73
Oxygen Steel Furnace Gas or Converter gas	0.35
Petroleum Coke ²	0.87
Purchased Pig Iron	0.047
Scrap Iron ²	0.04
Steel ²	0.01
Note: 1 Assuming 80 percent petroleum coke and 20 percent coal tar 2 Source: table.4, page 13 of ISO14404-1 & ISO14404-2 with conversion from CO ₂ to C (multiplied by 12/44). * The amount of CO ₂ emissions from charcoal can be calculated by using this carbon content value, but it should be reported as zero in national greenhouse gas inventories. (See Section 1.2 of Volume 1)	

4.2.2.4 CHOICE OF ACTIVITY DATA

TIER 1 METHOD

The Tier 1 method requires only the amount of steel produced in the country by process type, the total amount of pig iron produced that is not processed into steel, and the total amount of coke, direct reduced iron, pellets, and sinter produced; in this case the total amount of coke produced is assumed to be produced in integrated coke production facilities. These data may be available from governmental agencies responsible for manufacturing statistics, business or industry trade associations, or individual iron and steel companies. If a country only has aggregate data available, a weighted factor should be used. Total crude steel production is defined as the total output of usable lingots, continuously-cast semi-finished products, and liquid steel for castings.

TIER 2 METHOD

The Tier 2 method requires the total amount of iron and steel, coke oven gas, blast furnace gas, and process materials such as limestone used for iron and steel production, direct reduced iron production, and sinter production in the country, in addition to onsite and offsite production of coke. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual iron and steel companies. These amounts can then be multiplied by the appropriate default carbon contents in Table 4.3 and summed to determine total CO₂ emission from the sector. However, activity data collected at the plant-level is preferred (Tier 3). If this is not a *key category* and data for total industry-wide reducing agents and process materials are not available, emissions can be estimated using the Tier 1 approach.

TIER 3 METHOD

The Tier 3 method requires collection, compilation, and aggregation of facility-specific measured emissions data or facility-specific process material production/consumption mass data and carbon content data. The Tier 3 method can be based on a plant-specific mass balance approach (for CO₂ emissions) or on plant-specific direct emissions monitoring data (for both CO₂ and CH₄ emissions). In this case, it is a *good practice* to apply a QA/QC for the monitoring data, following the recommendations included in Chapter 6 Volume 1 of the *2019 Refinement*. The Tier 3 method also may require activity data to be collected at the plant level and aggregated for the sectors. The plant-specific data should preferably be aggregated from data furnished by individual iron and steel and coke production companies. The amounts of process materials are more accurately determined in this manner. These data may also be available from governmental agencies responsible for manufacturing or energy statistics, or from business or industry trade associations. The appropriate amounts can then be multiplied by facility specific carbon content data and summed to determine total CO₂ emissions from the sectors, and the total emissions will be more accurate than when using the Tier 2 method. This approach also allows for additional accuracy by allowing individual companies to provide more accurate plant-specific data and/or to use more relevant carbon contents that may differ from the default factors used in Tier 2 method.

4.2.2.5 COMPLETENESS

RELATIONSHIP TO THE ENERGY SECTOR

Iron and steel production consists of many production processes (occurring at different facilities), such as coking, sintering, iron-making, blast furnace steelmaking and rolling. These processes are connected among each other with the pipeline network which carries by-product gases, such as coke oven gas, blast furnace gas and basic oxygen furnace gas. This complexity creates the risk of double counting of emissions or omission of emissions. Additionally, when there are many different types of steelworks in a particular country, it may be difficult to calculate CO₂ emissions for the Energy Sector and the Industrial Processes Sector separately without ambiguities.

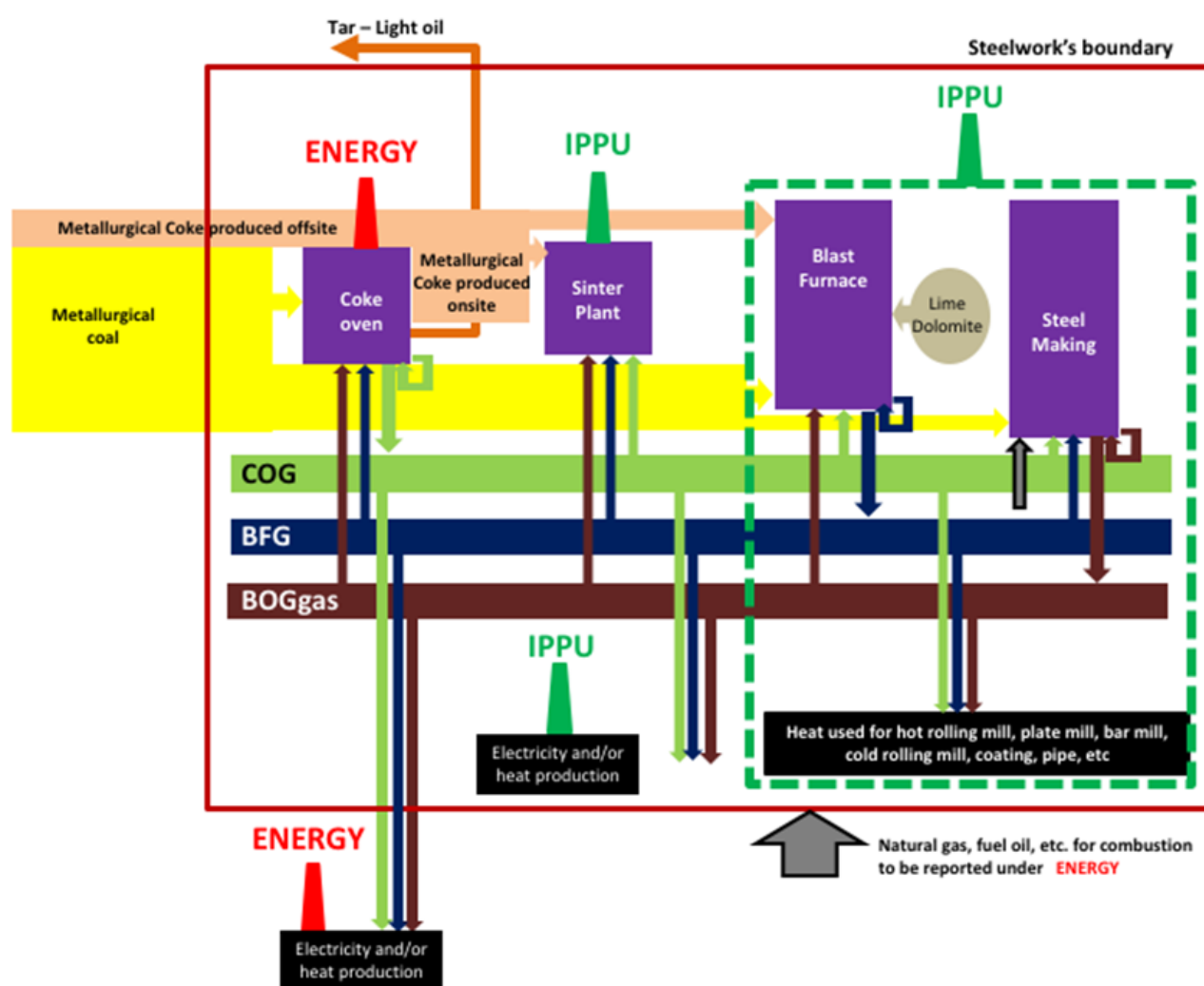
Because of the dominant role of coke, it is important to consider the existence of coke making at a facility and define the boundary limits of the carbon balance at an iron and steelmaking facility to assure that CO₂ emissions are not double-counted. The combustion emissions from fuels obtained directly or indirectly from the feedstock for an IPPU process will normally be allocated to the part of the source category in which the process occurs (see Box 1.1 Chapter 1 Volume 3 of the *2006 IPCC Guidelines*). Following this criterion, the emissions from iron and steel production for the case of an integrated iron and steel plant should be reported under IPPU or under Energy, as shown in Figure 4.8a, with the following peculiarities:

- The emissions from the combustion of blast furnace gas, coke oven gas and converter gas for sintering in the blast furnace and for steel making should be reported under IPPU.
- The emissions from the combustion of blast furnace gas, coke oven gas and converter gas to produce heat for different uses within the steelworks (rolling mill, hot rolling mill, plate mill, bar mill, cold rolling mill, coating, pipe) should be reported under IPPU.

Final Draft

- The emissions from the combustion of derived gases (including blast furnace gas, coke oven gas and converter gas) to produce electricity in an internal power plant should be reported under IPPU
- Consistent with the guidance in Box 1.1. Chapter 1 Volume 3 of the *2006 IPCC Guidelines*, where the derived gases are exported off-site for subsequent combustion at another facility, then if the gas is delivered to (for example) a nearby brick works for heat production or a main electricity producer then the emissions are reported in the appropriate source subcategories (1A2f or 1A1a).
- The emissions from flaring or venting of gases at coke ovens are allocated to the Energy (Fugitives) section 4.3.2.2 Chapter 4 Volume 2 of the *2019 Refinement*, whilst the emissions from flaring or venting of gases elsewhere in the I&S sector (e.g. blast furnace, sinter plant, basic oxygen furnace) are reported under IPPU.

Figure 4.8d (new) Energy or IPPU CO₂ emissions allocation in an integrated iron and steel facility



RELATION TO OTHER METHODOLOGICAL APPROACHES

In the iron and steel industry there has been a global effort to establish a common methodology for the calculation of CO₂ emissions and the energy intensity of steelworks as well as to conduct continuous data collection with the purpose of performance tracking and promoting international cooperation in reducing CO₂ emissions. The World Steel Association established the first method of this kind in 2007, and since then, has conducted yearly confidential CO₂ data collection from steelworks across the world. The method was refined further and was established as ISO 14404 “Calculation method of carbon dioxide emission intensity from iron and steel production” in 2013. This methodology is appropriate for CO₂ and energy management in the steel industry, and it is in line with national policies of many governments. The calculation method establishes clear boundaries for the collection of CO₂ emissions data (Reference ISO 14404 “Calculation method of carbon dioxide emission intensity from iron and steel production”). The net CO₂ emissions and production from a steel plant are calculated using all the parameters within the boundaries. The CO₂ emission intensity is calculated as the net CO₂ emission from the plant using the boundaries divided by the amount of crude steel produced by the plant. With this methodology, the CO₂ emission intensity of steel plants is calculated irrespective of the type of process used, products manufactured and geographic characteristics. This calculation method only uses primary inputs to the plant and primary outputs from the plant that are commonly measured and recorded by the plants; thus, the method requires neither the measurement of the specific efficiency of individual equipment or processes nor dedicated measurements of the complex flow and recycling of materials and waste heat. In this way, the calculation method ensures its simplicity and universal applicability without requiring steel plants to install additional dedicated measuring devices or to collect additional dedicated data other than those commonly used for plant management. However, since different regions have different energy sources and raw materials available, the resulting calculations cannot be used to determine the benchmark for free allocation under emissions trading schemes, for example in Europe, but they can be used to compare the performance of steel plants globally and to help plant staff determine their own position in energy and CO₂ efficiency.

There is a difference between the *2019 Refinement* and ISO 14404 “Calculation method of carbon dioxide emission intensity from iron and steel production”, dealing with the allocation of CO₂ emissions to the IPPU and Energy sectors, as in ISO 14404 the emissions from coking, sintering, blast furnacing, direct reduction, coke making processes, reheating furnaces and rolling are reported under Energy, and only the emissions from the use of limestone and dolomite are reported under IPPU.

OTHER FORMS OF CARBON

Although the dominant means of producing crude iron, or pig iron, is blast furnacing using coke, other forms of carbon (e.g., pulverized coal, coal derivatives, recycled plastics or tires, natural gas, or fuel oil) can also be used to substitute for some portion of the coke in the blast furnace. In these cases, the materials should be accounted for as process sources of carbon in the same manner as coke, and care should be taken to deduct these materials from any general energy statistics, if they are included there. Iron can also be produced in other types of iron-making processes besides blast furnacing, such as direct reduced iron processes, often using natural gas or coal instead of coke, and these carbon sources should be accounted for in the same manner as coke, as they serve the same purpose.

In most blast furnaces, the iron making process is aided by the use of carbonate fluxes (limestone or dolomite). Because these materials are necessary raw materials for the process, they should be accounted for as part of the iron and steelmaking inventory. Again, however, care should be taken not to double-count emissions associated with limestone and dolomite usage if accounted for separately in the minerals sector. (See Section 2.5, Other Process Uses of Carbonates, in this volume.)

SINTER

Some integrated facilities also utilize sinter plants to convert iron-bearing fines into an agglomerate (or sinter) suitable for use as a raw material in the blast furnace. Typically, coke fines (or coke breeze) are used as a fuel in the sintering process and are a source of CO₂ and CH₄ emissions. If the coke fines are produced at a coke plant within the facility and the CO₂ and CH₄ emissions are accounted for in the coal entering the facility, or if the coke breeze is otherwise accounted for as purchased coke, the CO₂ and CH₄ emissions from coke used in sintering should not be double-counted. Emissions from sinter production are categorised as IPPU emissions and should be reported as such.

EXHAUST GASES

It is important to avoid double counting blast-furnace-derived by-product gases such as blast furnace gas, or recovered converter off-gas, if they have been accounted for as process emissions. Process emissions should include all carbon inputs in the blast furnace, used as the primary reductant. In a typical fully integrated coke, iron and steel plant situation, adjustments may need to be made for coke oven by-products and the carbon content of shipped steel, which should be clearly mentioned in the description of the sources. In some cases, it may also be

Final Draft

necessary to make adjustments for blast furnace gas or iron that may be sold or transferred off site. The process flow of exhaust gases is clearly illustrated in Figures 4.1-4.5.

The use of a default emission factor for CO₂ emission estimates with Tier 1a for metallurgical coke production and Tier 1 for iron and steel production assumes an average mix of fuel between coke oven gas, blast furnace gas and, in some cases, converter off-gas. On the other hand, the Tiers based on the carbon balance approach consider the actual flow of these gases used and produced. Therefore, the combined use of Tier 1a to estimate CO₂ from metallurgical coke production and Tier 2 or 3 to estimate CO₂ from iron and steel production in integrated plants can lead to double counting or underestimation of some of the gases used. Similarly, the combined use of Tier 1 to estimate CO₂ from iron and steel production and Tier 2 or 3 to estimate CO₂ from metallurgical coke production can lead to double counting or underestimation of some of the gases used. The inventory compiler should take this into consideration when choosing the Tiers to estimate CO₂ emissions from integrated iron and steel plants.

ELECTRODE CONSUMPTION

Electrode consumption amounts to about 3.5 kg/tonne for EAF furnaces. However, depending upon the characteristics of the charged materials, some carbon may be added to the EAF (typically about 20 kg/tonne) for process control purposes or may be contained in the charged materials themselves as iron substitutes, an increasingly more frequent trend. In these cases, CO₂ and CH₄ emissions from these additional carbon-bearing materials should be considered process-related and accounted for in the inventory because their carbon content is not as likely to have been accounted for elsewhere in the inventory. In addition, if natural gas is used to enhance reactions in an EAF as reducing agent it should be accounted for as a carbon source as all process materials used in iron and steel manufacturing are reported as IPPU emissions.

Some specialty steel production takes place in electric induction furnaces, in which case the charge is 100 percent steel scrap and where there are no carbon electrodes. There are no appreciable CO₂ or CH₄ emissions from this steelmaking process.

OHF PROCESS

Although the OHF is no longer prevalent, it may be necessary to inventory CO₂ and CH₄ emissions from this steelmaking process in some countries. An open hearth furnace is typically charged with both molten iron and scrap as in the case of a BOF, and oxygen is injected into the furnace, but reduction of carbon in the iron and melting of the charge also takes place by firing fossil fuels (e.g., natural gas, fuel oil, coal or tar) across the surface of the raw material bath. Carbon in the iron may be ignored, as in the case of the BOF, because it has been accounted for as a source of carbon for iron-making. However, carbon in the fuels used in the open hearth process should be accounted for as IPPU emissions.

4.2.2.6 DEVELOPING A CONSISTENT TIME SERIES

No refinement

4.2.3 Uncertainty assessment

The default emission factors for coke production and iron and steel production used in Tier 1 may have an uncertainty of ± 10 percent. Tier 2 material-specific carbon contents would be expected to have an uncertainty of 10 percent. Tier 3 emission factors would be expected to be within 5 percent if plant-specific carbon content and mass rate data are available. Table 4.4 provides an overview of the uncertainties for emission factors, carbon contents and activity data.

TABLE 4.4 (UPDATED) UNCERTAINTY RANGES		
Method	Data Source	Uncertainty Range
Tier 1	CO ₂ Default Emission Factors	$\pm 10\%$
	CH ₄ Default Emission Factors	$\pm 400\%$
	N ₂ O Default Emission Factors	$\pm 300\%$
	National Production Data	$\pm 10\%$
	Material-Specific Default Carbon Contents	$\pm 10\%$
Tier 2	Material Country Specific Carbon Contents	$\pm 10\%$
	National Reducing Agent & Process Materials Data	$\pm 10\%$
Tier 3	Company-Derived Process Materials Data	$\pm 5\%$
	Company-Specific Measured CO ₂ and CH ₄ Data	$\pm 5\%$
	Company-Specific Emission Factors	$\pm 5\%$

4.2.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation

No refinement

Final Draft

981 **4.3 FERROALLOY PRODUCTION**

982 No refinement

983

984

985

4.4 PRIMARY ALUMINIUM PRODUCTION

This sub-chapter 4.4 “Primary Aluminium Production” Chapter 4 Volume 3 of the *2019 Refinement* is an update of sub-chapter 4.4 Chapter 4 Volume 3 of the *2006 IPCC Guidelines* and should be used *instead of* the sub-chapter 4.4 in the *2006 IPCC Guidelines*, with two exceptions relating to accounting of CO₂ emissions from the primary aluminium smelting process:

- Section 4.4.2.1 – ‘Choice of method for CO₂ emissions from primary aluminium production’,
- Section 4.4.2.2 – ‘Choice of emission factors for CO₂ emissions from primary aluminium production’.

For these two sections, the existing *2006 IPCC Guidelines* should be used. No refinements have been made to guidance on CO₂ emissions from primary aluminium smelting.

Updates and new guidance since the *2006 IPCC Guidelines* include the following:

- Section 4.4.1 is an updated introduction to GHG emissions from primary aluminium production, including alumina refining via alternative Bayer-Sinter and Nepheline technologies.
- Sections 4.4.2.3 to 4.4.2.7 and sections 4.4.3 to 4.4.4 provide new and updated guidance for accounting of PFC emissions from the primary aluminium smelting process.
 - (i) Updated technology classes – addition of ‘PFPB_L’, ‘PFPB_M’, ‘PFPB_{MW}’ – to replace the ‘CWPB’ class in existing *2006 IPCC Guidelines* for accounting PFC emissions only. For accounting of CO₂ emissions from primary aluminium smelting, the ‘CWPB’ class should still be used.
 - (ii) Updated guidance (including updated Tier 1 and Tier 2 default factors and uncertainties) on PFC emissions from ‘high voltage anode effects’ (HVAE), previously termed ‘anode effects’ in the *2006 IPCC Guidelines*. This includes new Tier 2b and Tier 3b methods for estimating PFC emissions from HVAE, using *individual* anode effect durations, rather than overall anode effect performance. Existing methods based on *overall* anode effect performance have been relabelled as Tier 2a and Tier 3a.
 - (iii) New guidance on PFC emissions from ‘low voltage anode effects’ (LVAE), using either default (Tier 1) or facility-specific (Tier 3) emission factors.
 - (iv) New guidance on accounting PFC emissions during cell start-up (CSU) periods.
 - (v) New guidance on Total PFC emissions, being the sum of HVAE, LVAE and CSU emissions (if applicable).
 - (vi) A new Tier 3_{DM} facility-specific method for total PFC emissions by direct gas measurement.
 - (vii) Corresponding updates relating to Time-Series Consistency, Uncertainty Assessment and QA/QC Reporting and Documentation sections.
- Sections 4.4.5 to 4.4.7 provide new guidance on accounting GHG emissions from alumina production via alternative refining processes: ‘Bayer-sintering parallel’ (BSP), ‘Bayer-sintering sequential’ (BSS) and ‘Nepheline processing’ (NP) processes:
 - (i) This includes a Tier 1 and facility-specific Tier 3 method to account for CO₂ emissions for BSP, BSS and NP production routes.
 - (ii) Note that no new guidance is required for the alumina production via the conventional ‘Bayer’ process.

4.4.1 Introduction to Primary Aluminium

This section covers emissions from primary aluminium production processes including, alumina refining using the Bayer-Sinter and Nepheline alternative refining technology¹. A number of refinements and updates have been made to the *2006 IPCC Guidelines* and are detailed in the following sections.

Primary aluminium production typically begins with the mining of aluminium-containing ores (bauxites). Most bauxite is refined through the Bayer Process, which thermo-chemically extracts aluminium oxide (alumina) from the ore. The main sources of greenhouse gas emissions from the Bayer Process are covered by existing guidance in the *2006 IPCC Guidelines* for lime production (Volume 3, Section 2.3) and fossil fuel combustion associated with alumina hydrate calcination and heat production for hydrochemical processes (Volume 2: Energy). A small proportion of alumina (<6% in 2015) is produced from the Bayer-Sinter process or nepheline ore refining process using alternative technology. New guidance has been included in this chapter for emissions from sub-processes related to the Bayer-Sinter process and nepheline ore processes only.

Alumina is reduced to molten aluminium metal via the electrolytic Hall-Héroult process. In this process, electrolytic reduction cells can differ in the form and configuration of the carbon anode and alumina feed system and are typically grouped by technology accordingly. In the *2006 IPCC Guidelines*, four technology types were defined, representing the technology in place at the time (% global production): Centre-Worked Prebake – *CWPB* (82% including Point-Fed Prebake, *PFPB*), Side-Worked Prebake – *SWPB* (2%), Horizontal Stud Söderberg – *HSS* (3%) and Vertical Stud Söderberg – *VSS* (13%).

Since 2006, the technological landscape has changed, a result of the closure of older technology facilities and significant investment in new, larger state-of-the-art facilities. Point-Fed Prebake Technology for example has increased from <80% share of global production in 2006 to >90% in 2017 but more significantly, the growth in technology without fully automated anode effect intervention strategies for perfluorocarbon (PFC) GHG emissions has risen from <30% in 2006 to >60% in 2017. As such, the technology types have been redefined as follows:

- (iii) *Legacy Point-Fed Prebake (PFPB_L)* – older cell designs with line currents of less than 350kA;
- (iv) *Modern Point-Fed Prebake (PFPB_M)* – new cell technologies² that operate at line currents in excess of 350kA including: AP3X/AP4X, APXe/AP60, EGA DX and DX+;
- (v) *Modern Point-Fed Prebake without fully automated anode effect intervention strategies for PFC emissions (PFPB_{MW})* – new cell technologies operating with large cells with line currents often in excess of 350kA, with no automatic anode effect intervention capacity (refer to Box 4.1a description) or with non-standard HVAE definitions, i.e. where HVAEs are not counted until the cell voltage has exceeded the threshold for 15 to as many as 120 seconds (Marks & Nunez 2018b; Wong *et al.* 2018) vs. 3 seconds for the rest of the industry (refer to Box 4.2 for typical definition);
- (vi) *Side-Worked Prebake (SWPB)* technology;
- (vii) *Horizontal Stud Söderberg (HSS)* technology; and
- (viii) *Vertical Stud Söderberg (VSS)* technology.

The three new Prebake technology classes – *PFPB_L*, *PFPB_M* and *PFPB_{MW}* – should be used for accounting of PFC emissions from primary aluminium smelting, in place of the previous *CWPB* class in the *2006 IPCC Guidelines*. However, for accounting CO₂ emissions from primary aluminium smelting, the previous *CWPB* class should still be used.

¹ Emissions from the combustion of fossil fuels associated with primary aluminium production, bauxite mining, and aluminium production from recycled sources are covered in Volume 2: Energy. Also, carbon dioxide emissions associated with the production of electricity from fossil fuel combustion to produce aluminium are also covered in Volume 2.

² Details on some of these newest cell technologies are available on the following references: (Bardai *et al.* 2009; Rio Tinto Alcan 2013; Emirates Global Aluminium 2017)

BOX 4.1A (NEW)**FULLY AUTOMATED ANODE EFFECT INTERVENTION STRATEGIES FOR PFC EMISSIONS**

Many Point-Fed Prebake (PFPB) aluminium smelters employ fully automated control strategies to reduce PFC emissions, otherwise known as ‘*automatic anode effect intervention or termination*’ strategies. These are strategies that rapidly terminate high voltage anode effects (HVAE) when they are detected, using both: (i) automated up/down movements of carbon anodes and (ii) automated feeding of alumina to rapidly increase dissolved alumina levels in the cell; in most cases, no manual intervention is required.

However, these automated strategies are not employed in one technology class – *Modern Point-Fed Prebake without fully automated anode effect intervention strategies for PFC emissions (PFPB_{MW})* – where anode effects are terminated through manual operator intervention, which can result in higher PFC emissions. This technology class is also characterised by the use of HVAE definitions that differ significantly from that used in the rest of industry (see Box 4.2).

Although smelting technology has changed somewhat, the most significant process emissions have not. They are:

- (i) Carbon dioxide (CO₂) emissions from the consumption of carbon anodes in the reaction to convert aluminium oxide to aluminium metal (for which no refinements are included in this update for primary aluminium smelting);
- (ii) Emissions of the perfluorocarbons (PFCs) tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆) during process upset conditions known as ‘anode effects’ (for which refinements for aluminium smelting are included in the following sections).

Also emitted are less significant process emissions: Carbon Monoxide (CO), Sulphur Dioxide (SO₂), and Non-Methane Volatile Organic Carbon (NMVOC). Sulfur hexafluoride (SF₆) is not emitted during the electrolytic process and is only rarely used when fluxing specialized, high magnesium aluminium alloys, from which small quantities can be released as fugitive emissions.

The decision trees in Figure 4.11 (refer to the *2006 IPCC Guidelines*) and Figure 4.12 provides guidance for selecting a methodology estimating CO₂ and PFC emissions from aluminium production, respectively. All inventory compilers in countries with aluminium production should be able to implement at least the Tier 1 method and thereby ensure completeness of reporting. Although this chapter presents default emission factors, countries should make every effort to use higher Tier methods because emission rates can vary greatly, and the uncertainty associated with Tier 1 factors is very high. Most aluminium smelters routinely collect the process data needed for calculation of Tier 2 emissions factors. The sole exception is estimation of PFC emissions from facilities with PFPB_{MW} technology, whose process data (specifically, accounting of HVAEs) is not currently compatible with the Tier 2 emission factors presented here. For these smelters, it is still possible to implement Tier 3 methods – for example, production-based emission factors (for HVAE and LVAE emission sources, or total PFC emissions) or direct PFC gas measurements (Tier 3_{DM}). Furthermore, use of Tier 3 methods for HVAE emissions (based on HVAE performance) is also possible for PFPB_{MW} facilities, provided conventional definitions of HVAEs (refer to Box 4.2) are adopted.

4.4.2 Methodological issues for primary aluminium production

4.4.2.1 CHOICE OF METHOD FOR CO₂ EMISSIONS FROM PRIMARY ALUMINIUM PRODUCTION

No refinement

4.4.2.2 CHOICE OF EMISSION FACTORS FOR CO₂ EMISSIONS FROM PRIMARY ALUMINIUM PRODUCTION

No refinement

4.4.2.3 CHOICE OF METHOD FOR PFCs

BOX 4.2 (UPDATED)

HIGH AND LOW VOLTAGE ANODE EFFECT DESCRIPTION

An anode effect is a process upset condition where an insufficient amount of alumina is dissolved in the electrolyte, resulting in the emission of PFC gases. This often causes cell voltage to be elevated above the normal operating range. However, PFC gases can also be generated without elevated cell voltage.

A high voltage anode effect (HVAE) is typically identified as an anode effect where the voltage exceeds the specific voltage threshold defined at the facility for a specific duration. The typical voltage threshold of the industry, and used within this guideline, is 8 volts (Tabereaux 2004; US Environmental Protection Agency & International Aluminium Institute 2008) while the typical duration is 3 seconds (Wong *et al.* 2015).

A low voltage anode effect (LVAE) is typically identified as emission of PFC gases in cases where the cell voltage does not exceed the voltage threshold.

During electrolysis, alumina (Al_2O_3) is dissolved in a fluoride melt comprising 80% by weight cryolite (Na_3AlF_6). Perfluorocarbons (PFCs) are formed from the reaction of the carbon anode with the cryolite melt during a process upset condition known as an ‘anode effect’ (see Box 4.2). An anode effect occurs when the concentration of alumina in the electrolyte is too low to support the standard anode reaction. When the 2006 IPCC Guidelines were developed, anode effects were characterised by a sudden increase in voltage generally greater than 8V (US Environmental Protection Agency & International Aluminium Institute 2008) for a period of approximately 3 seconds. These anode effects are now known as a ‘high voltage anode effects’ (HVAE), which release both CF_4 and C_2F_6 .

Since the late 2000s, driven by the development of more productive, high-amperage cell technology with many large anodes, ‘low voltage anode effect’ (LVAE) emissions of CF_4 have been identified. These LVAE emissions have been the focus of much research and occur as result of the same process upset condition as HVAE emissions but often at a smaller, localised scale. Guidance on estimating LVAE C_2F_6 emissions has not been provided here as C_2F_6 concentrations from LVAE are most of the time undetectable (within the noise level of the measuring instrument) or at low ppb levels. During LVAE, the cell voltage typically remains below the formation voltage of C_2F_6 . Some research (Asheim *et al.* 2014; Dion *et al.* 2016) has even concluded that formation of C_2F_6 from LVAE does not occur, or occurs at level so low, it is considered negligible.

LVAE emissions have not been included in national GHG inventories to date because the information and methodology for their estimation was not available, but estimates should now be included to ensure GHG inventories are as complete as possible. Therefore, it is *good practice* to estimate and report *Total PFC emissions*, i.e. the sum of HVAE and LVAE emissions combined. The methodologies for HVAE and LVAE are presented separately to allow for different Tiers to be adopted for each element if necessary.

The decision tree shown in Figure 4.12 describes *good practice* in choosing the PFC inventory methodology appropriate for national circumstances. Table 4.14a provides a summary of all methods in this guidance for estimating PFC emissions at Tiers 1 to 3.

For HVAE emissions, the Tier 2 (2a and 2b) and Tier 3 (3a_{HVAE} and 3b_{HVAE}) methods are based on plant-specific process data for HVAEs, which are regularly collected by smelters. In choosing a method for estimating PFCs, it should be noted that the uncertainty associated with higher tier methodologies is generally significantly lower than that for Tier 1, and therefore it is *good practice* to use Tier 2 and Tier 3 methodologies if this is a *key category*. There is an exception for countries where the prevailing technology is PFPB_{MW}, whose current definitions (and therefore accounting) of HVAEs are not compatible with the Tier 2a, 2b, 3a_{HVAE}, or 3b_{HVAE} methods in this guidance. In these cases, the Tier 1 method is acceptable for estimating emissions from HVAE even if the source is *key*, although use of Tier 3 methods (e.g. production-based facility-specific factors, or direct measurement Tier 3_{DM}) will significantly reduce uncertainty.

The Tier 3 methodologies for HVAE PFC emissions should be utilized with coefficients calculated from measurement data obtained using good measurement practices (US Environmental Protection Agency & International Aluminium Institute 2008). Communication with primary aluminium producers will determine the availability of process data, which, dictates the method used to calculate emissions. Plants other than PFPB_{MW}

1167 routinely measure HVAE performance as ‘anode effect minutes per cell-day’. HVAE PFC emissions are directly
1168 related to anode effect performance via a coefficient specific to technology or plant.

1169 In the *2006 IPCC Guidelines*, two methods for calculating coefficients for HVAE PFCs were outlined: slope and
1170 overvoltage. The overvoltage method is not widely used anymore so this update will focus on the slope method
1171 only. If the overvoltage method is still used, it should be adopted at the Tier 3 level only. If Tier 3 is not possible
1172 then it is *good practice* to adopt the Tier 2a slope method.

1173 For LVAE emissions, the Tier 3 methodology calculates PFCs by multiplying a facility-specific factor (ratio of
1174 LVAE to HVAE emissions, based on prior measurements) by the HVAE emissions (Marks & Nunez 2018b). This
1175 takes into account plant-specific performance at the HVAE level. The alternative is to use a facility-specific,
1176 production-based emission factor for LVAE emissions. There is currently no generally recognised means to
1177 calculate LVAE CF₄ emissions from the process control data that is normally recorded during primary aluminium
1178 production. The most accurate approach to date is to directly measure both LVAE and HVAE PFC emissions at
1179 the individual facility level (Tier 3_{DM} methodology for total PFC emissions), but this is not widely or regularly
1180 practiced by industry. Moreover, there is currently no official methodology to standardise the measurement of
1181 LVAE PFC emissions. Until an official methodology is released, the ‘Protocol for Measurement of
1182 Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions from Primary Aluminum Production’ ((US
1183 Environmental Protection Agency & International Aluminium Institute 2008) can be used as guidance for total
1184 emissions measurement. It should be noted that there is ongoing work within industry to provide an updated
1185 measurement protocol. The LVAE methodologies proposed here provide a first step towards total emissions
1186 reporting but inventory compilers should be aware of the very high level of uncertainty that accompanies these
1187 estimates and that work is ongoing within the aluminium industry to provide good practice guidelines to
1188 complement these methodologies. It is *good practice* to check the Emissions Factor Database (EFDB) as a source
1189 for future LVAE factors.

1190 PFC emissions can also occur during cell start-up (CSU) – refer to Box 4.3 for a description. If they are not already
1191 included in normal HVAE and LVAE accounting, then HVAE emissions during cell start-up can be estimated via
1192 a Tier 2 approach (2b_{HVAE} methodology, based on individual anode effect durations) or a Tier 3 approach using
1193 facility-specific emission factors or coefficients (Tier 3a_{HVAE}, 3b_{HVAE} or 3_{CSU}).

1194 For all facilities, the Tier 3 approach is preferred because plant-specific coefficients will lead to estimates that are
1195 more accurate. If no PFC measurements have been made to establish a plant-specific coefficient, the Tier 2 method
1196 can be used until measurements have been made and Tier 3 coefficients are established. Countries can use a
1197 combination of methodologies depending on the type of data available from individual facilities.

1198 ACCOUNTING FOR ALL SOURCES OF PFC EMISSIONS

1200 In the following sections, a number of different methodologies with differing levels of uncertainty are proposed to
1201 estimate PFC emissions. To obtain the total respective emissions of CF₄ and C₂F₆, the various sources of PFC
1202 should be summed using Equation 4.24a. This equation is applicable for estimating total PFC emissions for all
1203 Tier methods – the only exception being Tier 3_{DM} direct gas measurement as this already provides total PFC
1204 emissions from all sources.

$$\begin{aligned}
 &\text{EQUATION 4.24A (NEW)} \\
 &\text{TOTAL PFC EMISSIONS} \\
 &\text{Total } E_{CF_4} = (HVAE E_{CF_4} + LVAE E_{CF_4} + CSU E_{CF_4}) \\
 &\quad \text{and} \\
 &\text{Total } E_{C_2F_6} = (HVAE E_{C_2F_6} + CSU E_{C_2F_6})
 \end{aligned}$$

1211 Where:

1212 Total E_{CF₄} = Total CF₄ from aluminium production, kg CF₄

1213 Total E_{C₂F₆} = Total C₂F₆ from aluminium production, kg C₂F₆

1214 HVAE E_{CF₄} = HVAE emissions of CF₄ from aluminium production, kg CF₄

1215 HVAE E_{C₂F₆} = HVAE emissions of C₂F₆ from aluminium production, kg C₂F₆

1216 LVAE E_{CF₄} = LVAE emissions of CF₄ from aluminium production, kg CF₄

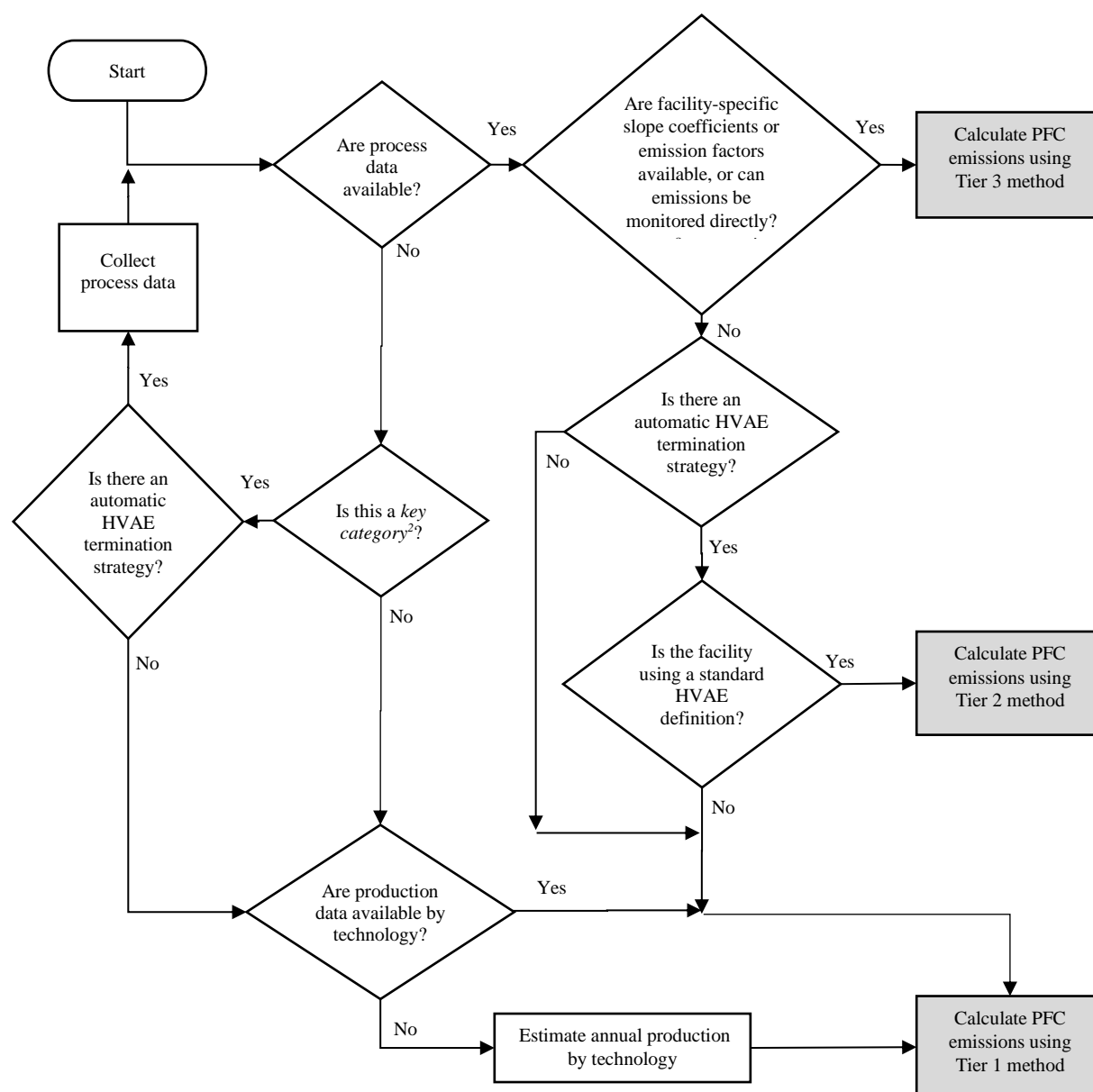
1217 CSU E_{CF₄} = Total amount of CF₄ produced during cell start-ups for a specific period, kg CF₄

1218 CSU E_{C₂F₆} = Total amount of C₂F₆ produced during start-ups for a specific period, kg C₂F₆

Final Draft

Note that the last terms in Equation 4.24a, $CSU\ EC_{CF_4} = 0$ and $CSU\ EC_{C_2F_6} = 0$, where cell start-up emissions are already accounted for by normal accounting of HVAE and LVAE emissions. Care should be taken not to double count emissions from cell start-ups.

Figure 4.12 (updated) Decision tree for calculation of total PFC emissions from primary aluminium production



Notes:

¹Good practices for obtaining facility specific PFC emission coefficients are detailed in the Protocol for Measurement of Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions from Primary Aluminum Production (US Environmental Protection Agency & International Aluminium Institute 2008).

² See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

TABLE 4.14A (NEW)
SUMMARY OF ACCOUNTING METHODS FOR PFC EMISSIONS

Tier		Emission Source	PFC Gas	Method description	By	Applicable for:	
						Normal Operations	Start-Up? ^a
1	1 _{HVAE}	HVAE	CF ₄ , C ₂ F ₆	Production-based default emission factor	Technology class	Yes	Yes
	1 _{LVAE}	LVAE	CF ₄	Production-based default emission factor	Technology class	Yes	Yes
2	2a _{HVAE}	HVAE	CF ₄ , C ₂ F ₆	Slope method ^b	Technology class ^e	Yes	Yes ^g
	2b _{HVAE}	HVAE	CF ₄ , C ₂ F ₆	Non-linear method ^{c,d}	Technology class ^e	Yes	Yes
3	3a _{HVAE}	HVAE	CF ₄ , C ₂ F ₆	Slope ^b or Overvoltage ^f method	Facility specific ^e	Yes	Yes ^h
	3b _{HVAE}	HVAE	CF ₄ , C ₂ F ₆	Non-linear method ^c	Facility specific ^e	Yes	Yes
	3 _{LVAE}	LVAE	CF ₄	LVAE/HVAE ratio or production-based factor	Facility specific	Yes	Yes
	3 _{CSU}	CSU	CF ₄ , C ₂ F ₆	Cell start-up emission factor	Facility specific	-	Yes
	3 _{DM}	Total	CF ₄ , C ₂ F ₆	Direct gas measurement	Facility specific	Yes	Yes ⁱ

Notes:

^a For separate accounting of cell ‘start-up’ emissions, *only if* these are not already accounted in emissions during normal operations.

^b The slope method is where HVAE emissions are estimated based on *overall* anode effect performance.

^c Non-linear methods refer to the Tier 2b or 3b (Marks & Nunez 2018a) and (Dion *et al.* 2018a) methods, where HVAE emissions are estimated based on *individual* anode effect measurement.

^d Tier 2b methods for HVAE emissions are only applicable for PFPB_M, PFPB_L and SWPB technologies; alternative methods should be used for VSS, HSS and PFPB_{MW} technologies.

^e The Tier 2a/3a and 2b/3b methods for HVAE emissions are *not* applicable for PFPB_{MW} technology, due to inconsistencies in defining an HVAE. However, if consistent definitions (refer to Box 4.2) are adopted, then use of Tier 3a or 3b for PFPB_{MW} technology is possible.

^f The overvoltage method is an alternative to the slope method, where HVAE emissions are estimated based on *overall* anode effect performance; however this method should only be adopted a Tier 3 facility-specific level, since Tier 2 default emission coefficients have not been updated here in the 2019 Refinement.

^g Use of the Tier 2a slope method for HVAE emissions during cell start-up (CSU) periods is possible, however, this may lead to overestimates of emissions.

^h To use the Tier 3a method for CSU emissions, it is *good practice* to use individual facility slope or overvoltage coefficients specifically for cell start-ups (as opposed to coefficients for normal operations, which may result in overestimates of emissions).

ⁱ The Tier 3_{DM} direct gas measurement method at individual facilities should provide emission factors that are inclusive of HVAE and LVAE emissions during normal operations as well as CSU emissions (during cell start-up).

ESTIMATING EMISSIONS FROM HIGH VOLTAGE ANODE EFFECTS

Tier 1 method for High Voltage Anode Effect (HVAE) emissions: Use of technology-based default emission factors

The Tier 1_{HVAE} method uses technology-based default emission factors for the main production technology types (Legacy PFPB, Modern PFPB, Modern PFPB_{MW}, SWPB, HSS and VSS). PFC emissions can be calculated according to Equation 4.25. The level of uncertainty in the Tier 1 method is much greater because individual facility anode effect performance, which is the key determinant of anode effects and thus PFC emissions, is not directly taken into account. Tier 1 can be consistent with *good practice* when PFCs from primary aluminium is not a *key category*, when pertinent process data are not available from operating facilities.

Tier 1 can also be consistent with *good practice* when the cell technology is PFPB_{MW} as the process data required for Tier 2 (e.g. anode effect frequency and duration) is typically not comparable to data for other technologies (Marks & Nunez 2018b) and could therefore lead to inaccurate results; however, if facility-specific emission factors (e.g. production-based factors to use in Equation 4.25), coefficients or direct measurements (Tier 3_{DM}) are available for PFPB_{MW} technology facilities, it is *good practice* to adopt a Tier 3 method.

Final Draft

$$\begin{aligned} &\text{EQUATION 4.25 (UPDATED)} \\ &\text{HVAE PFC EMISSIONS (TIER 1 METHOD)} \\ &HVAE E_{CF_4} = (HVAE EF_{CF_4} \bullet MP) \\ &\text{and} \\ &HVAE E_{C_2F_6} = (HVAE EF_{C_2F_6} \bullet MP) \end{aligned}$$

Where:

HVAE E_{CF_4} = HVAE emissions of CF_4 from aluminium production, kg CF_4 HVAE $E_{C_2F_6}$ = HVAE emissions of C_2F_6 from aluminium production, kg C_2F_6 HVAE EF_{CF_4} = default HVAE emission factor by cell technology type for CF_4 , kg CF_4 /tonne AlHVAE $EF_{C_2F_6}$ = default HVAE emission factor by cell technology type for C_2F_6 , kg C_2F_6 /tonne Al

MP = metal production by cell technology type, tonnes Al

Tier 2a and Tier 3a methods for High Voltage Anode Effect (HVAE) emissions: Based on overall anode effect performance and slope coefficient

The equation for estimating individual plant have CF_4 emissions is based on the relationship between anode effect emissions and performance. The slope coefficient is based on direct measurements of PFCs. Tier 2a makes use of average coefficients from measurements at numerous facilities. Tier 3a_{HVAE} is based on measurements at the individual facility. Because the process mechanisms that produce PFC emissions during HVAE are similar for CF_4 and C_2F_6 , the two gases should be considered together when estimating PFC emissions. C_2F_6 emissions are calculated in the HVAE methods described herein as a fraction of CF_4 emissions.

With an established relationship between anode effect process data and PFC emissions, process data collected on an on-going basis can be used to calculate PFC emissions in lieu of direct measurement of PFCs. Equation 4.26 should be used when anode effect minutes per cell day are recorded. For individual high voltage anode effects, the reported anode effect duration (AED) is the sum of every second where the measured cell voltage is higher than the trigger threshold. The anode effects minutes per cell day (AEM) are calculated based on the sum (in minutes) of all the recorded anode effect minutes divided by the product of the number of cells in the considered section and the respective time in days (US Environmental Protection Agency & International Aluminium Institute 2008).

Because PFPB_{MW} smelters currently do not record shorter-duration anode effects that nevertheless can result in significant PFC emissions, the Tier 2a and 3a_{HVAE} methods are not recommended for PFPB_{MW} smelters; however, if these facilities adopt consistent definitions for HVAEs (refer to Box 4.2), then it is possible to use Tier 3a.

Slope Coefficient: The coefficient characterises the kg of CF_4 per tonne of aluminium produced, divided by anode effect minutes per cell-day¹. Since PFC emissions are measured per tonne of aluminium produced, it includes the effects of cell amperage and current efficiency, the two main factors determining the amount of aluminium produced in the cell. Equation 4.26 describes the method for both CF_4 and C_2F_6 .

$$\begin{aligned} &\text{EQUATION 4.26 (UPDATED)} \\ &\text{HVAE PFC EMISSIONS BY SLOPE METHOD (TIER 2A AND TIER 3A METHODS)} \\ &HVAE E_{CF_4} = S_{CF_4} \bullet AEM \bullet MP \\ &\text{and} \\ &HVAE E_{C_2F_6} = HVAE E_{CF_4} \bullet F_{C_2F_6 / CF_4} \end{aligned}$$

Where:

HVAE E_{CF_4} = HVAE emissions of CF_4 from aluminium production, kg CF_4 HVAE $E_{C_2F_6}$ = HVAE emissions of C_2F_6 from aluminium production, kg C_2F_6

S_{CF_4} = slope coefficient for CF_4 by cell technology type (Tier 2a) or smelter specific emission ratio (Tier 3a) (kg CF_4 /tonne Al)/(AE-Mins/cell-day)

¹ The term 'cell-day' refers to the number of cells operating multiplied by the number of days of operation.

AEM = anode effect minutes per cell-day, AE-Mins/cell-day

MP = metal production, tonnes Al

$F_{C_2F_6/CF_4}$ = weight fraction of HVAE C_2F_6/CF_4 , kg C_2F_6 /kg CF_4

Tier 3a method for High Voltage Anode Effect (HVAE) emissions: Based on overall anode effect performance and overvoltage coefficient

Overvoltage Coefficient: Some process control systems characterize high voltage anode effects by calculating an Anode Effect Overvoltage¹ (AEO) statistic. AEO is defined as the extra cell voltage above the target operating voltage, and this parameter has been shown to be a good predictor of PFC emissions when recorded by the process control system. The AEO process control technology is in use at a few modern smelters. AEO is calculated by summing the product of time and voltage above the target operating voltage and dividing this figure by the time over which data were collected. As noted above, for years beyond 2019, it is *good practice* to adopt this overvoltage method only at a Tier 3 level; alternatively, if facility-specific overvoltage coefficients are unavailable, it is *good practice* to use the Tier 2a or 3a_{HVAE} slope method.

EQUATION 4.27 (UPDATED) HVAE PFC EMISSIONS BY OVERVOLTAGE METHOD (TIER 3A METHOD)

$$HVAE E_{CF_4} = OVC \cdot \frac{AEO}{CE / 100} \cdot MP$$

and

$$HVAE E_{C_2F_6} = HVAE E_{CF_4} \cdot F_{C_2F_6 / CF_4}$$

Where:

$HVAE E_{CF_4}$ = HVAE emissions of CF_4 from aluminium production, kg CF_4

$HVAE E_{C_2F_6}$ = HVAE emissions of C_2F_6 from aluminium production, kg C_2F_6

OVC = Overvoltage coefficient for CF_4 , (kg CF_4 /tonne Al)/mV

AEO = anode effect overvoltage, mV

CE = aluminium production process current efficiency expressed, percent (e.g., 95 percent)

MP = metal production, tonnes Al

$F_{C_2F_6/CF_4}$ = weight fraction of C_2F_6/CF_4 , kg C_2F_6 /kg CF_4

Tier 2b and Tier 3b method for High Voltage Anode Effect (HVAE) emissions: Based on individual anode effect duration

An alternative way to quantify PFC emissions from HVAE for PFPB technology was proposed by (Marks & Nunez 2018a) and by (Dion *et al.* 2018a). This approach considers that the PFC generation rate is not constant throughout the duration of the HVAE but declines as the HVAE continues. Therefore, PFCs are estimated for *each individual* HVAE (based on its duration) and the summation of individual HVAE emissions gives total HVAE emissions.

In general, the Tier 2b method is expected to be more accurate than the Tier 2a method, and the Tier 3b_{HVAE} method is similarly expected to be more accurate than the Tier 3a_{HVAE} method. The Tier 2b and 3b_{HVAE} methods are considered particularly useful for facilities with a low HVAE frequency or when considerable change in the distribution of HVAE duration can be observed (e.g. years when an important relining and start-up of electrolysis cells is expected). Both approaches quantify the PFC emissions from individual HVAEs based on process parameters that are known or calculated by the cell control system.

¹ Computer control systems report either 'positive' or 'algebraic' overvoltage depending on the version of software used. Use of the expression 'overvoltage' should not be confused with the classical electrochemical terminology, which usually means the extra voltage needed for an electrochemical reaction to occur.

Final Draft

Tier 2b emission rate coefficients (K_1 , K_2 for the Marks & Nunez 2018a method; C_1 , C_2 , C_3 and C_4 for the Dion *et al.* 2018a method) were calculated based on a set of data collected from different facilities. The Tier 3b methodology uses the same equations as presented below with facility-specific coefficients, based on the results of extensive gas monitoring measurement campaigns. A significant number of individual HVAE, with various durations, should be monitored to obtain accurate coefficients. There is currently no measurement protocol available to determine Tier 3 coefficients based on individual anode effect measurement but there is ongoing work within industry towards publication of an updated protocol.

The Tier 2b and 3b_{HVAE} methods require extraction and use of performance data for individual HVAEs to calculate PFC emissions (an alternative would be for cell control systems to automatically calculate and report total emissions from individual HVAEs using the Tier 2b/3b_{HVAE} methods). If HVAE performance data is unavailable, an alternative method should be used.

At the Tier 2b level, the choice of method can be based on the following considerations:

1. *Technology Class* – The Marks and Nunez approach is applicable for PFPB_L and PFPB_M technologies; the Dion *et al.* approach is applicable for PFPB_M, PFPB_L as well as the SWPB technology class. However, based on the lowest uncertainties for each technology (refer to Table 4.16b), the Marks and Nunez method is recommended for PFPB_L technology, whereas the Dion *et al.* approach is recommended for the PFPB_M and SWPB technology classes. For all other technology classes, it is *good practice* to employ facility-specific Tier 3b coefficients or alternative methods.
2. *Distribution of individual HVAE durations (AED) at the facility* – The Dion *et al.* approach is limited to AEDs up to 1000 s for estimating CF₄ and 150 s for C₂F₆, whereas the Marks & Nunez approach has the advantage of no limitations on AED. Therefore, if a facility has a substantial proportion of HVAEs (e.g. more than 5%) with AED greater than 150s, it is *good practice* to use the Marks and Nunez method or alternative methods.

Marks & Nunez approach: The approach proposed by (Marks & Nunez 2018a) uses different coefficients depending on individual anode effect durations (AED), as presented in Equation 4.27a. Note that for the Tier 2b approach, Tier 2b emission rate coefficients (K_1 and K_2) are presented in Table 4.16a; these coefficients apply only to PFPB_M and PFPB_L technologies. For Tier 2, weight fractions of C₂F₆/CF₄ by technology class are given in Table 4.16 (these are the same weight fractions as for the Tier 2a method).

EQUATION 4.27A (NEW)
HVAE PFC EMISSIONS (TIER 2B AND TIER 3B METHOD – (MARKS & NUNEZ 2018A))

$$HVAE E_{CF_4} = \sum [(K_1 \bullet AED_i^{K_2}) \bullet \frac{kA_i}{1000}]$$

and

$$HVAE E_{C_2F_6} = HVAE E_{CF_4} \bullet F_{C_2F_6 / CF_4}$$

Where:

HVAE E_{CF₄} = Total HVAE CF₄ produced during the considered period, as the sum of all individual ‘i’ HVAE emissions, kg CF₄

HVAE E_{C₂F₆} = HVAE emissions of C₂F₆ from aluminium production, kg C₂F₆

AED_i = Total duration of each individual ‘i’ HVAE, during which the cell voltage is above the HVAE detection threshold, s

kA_i = Average potline current during each individual ‘i’ HVAE, kA

K_1 = Emission rate coefficient dependant on the AED, dimensionless

K_2 = Emission rate coefficient dependant on the AED, dimensionless

F_{C₂F₆/CF₄} = weight fraction of HVAE C₂F₆/CF₄, kg C₂F₆/kg CF₄

Dion *et al.* approach: The approach proposed by (Dion *et al.* 2018a) to quantify total CF₄ and C₂F₆, from the sum of emissions from individual HVAEs is presented in Equation 4.27b. Tier 2b emission rate coefficients (C_1 , C_2 , C_3 and C_4) are calculated using Equation 4.27f. Note that use of the Tier 2b emission rate coefficients are

only for (i) PFPB_M and PFPB_L and SWPB technology classes and (ii) HVAEs with durations (AED) *below* 1000 s for CF₄ estimation and *below* 150 s for C₂F₆ estimation, based on the data set used by (Dion *et al.* 2018a). For other technologies or longer duration HVAEs, it is *good practice* to employ Tier 3b coefficients or an alternative method.

EQUATION 4.27B (NEW)
HVAE PFC EMISSIONS (TIER 2B AND TIER 3B METHOD – (DION *ET AL.* 2018A))

$$HVAE E_{CF_4} = \sum [(C_1 \bullet AED_i^{C_2}) \bullet MP_{Day}] / 1000$$

and

$$HVAE E_{C_2F_6} = \sum [(C_3 \bullet AED_i^{C_4}) \bullet MP_{Day}] / 1000$$

Where :

HVAE E_{CF₄} = Total HVAE CF₄ produced during the considered period, as the sum of all individual HVAE emission, kg CF₄

HVAE E_{C₂F₆} = Total HVAE C₂F₆ produced during the considered period, as the sum of all individual HVAE emission, kg C₂F₆

AED_i = Total duration of each individual ‘i’ HVAE during which the cell voltage is above the HVAE detection threshold, s

MP_{Day} = Average daily metal production per cell¹, tonnes Al

C₁ = Emission rate coefficient for CF₄ dependant on the metal production of the cell, kg CF₄ /s-tonne Al

C₂ = Emission rate coefficient for CF₄ dependant on the metal production of the cell, dimensionless.

C₃ = Emission rate coefficient for C₂F₆ dependant on the metal production of the cell, kg C₂F₆/s-tonne Al

C₄ = Emission rate coefficient for C₂F₆ dependant on the metal production of the cell, dimensionless.

ESTIMATING EMISSIONS FROM LOW VOLTAGE ANODE EFFECTS²

Tier 1 method for Low Voltage Anode Effect (LVAE) emissions

The Tier 1_{LVAE} method uses technology-based default emission factors for the main production technology types (PFPB_L, PFPB_M, SWPB, VSS and HSS). PFC emissions can be estimated according to Equation 4.27c. There is no Tier 1_{LVAE} default emissions factor for PFPB_{MW} as an estimate for LVAE emissions is already included in the Tier 1_{HVAE} default emissions factor as this value was derived from *total* PFC measurement data. The level of uncertainty in the Tier 1 method is much greater than the level of uncertainty in the Tier 3 methods because individual facility operating characteristics are not taken into account. Tier 1 is consistent with *good practice* when PFCs from primary aluminium is not a *key category* or when smelter specific LVAE emissions data are not available from operating facilities.

¹ MP_{Day} in Equation 4.27b is the average metal production *per cell per day* – it can be estimated from potline data or from the line amperage and average current efficiency of the potline. Care should be taken not to confuse this with the variable ‘MP’ – total metal production from the facility over the accounting period – used in other equations.

² C₂F₆ emissions were not considered in the estimation of LVAE as C₂F₆ concentrations from LVAE are most of the time undetectable. The level of these emissions is in the low ppb and within the noise level of the measuring instrument. Some research (Asheim *et al.* 2014; Dion *et al.* 2016) has even concluded that formation of C₂F₆ from LVAE does not occur, or occurs at level so low, it is considered negligible.

Final Draft

$$\text{EQUATION 4.27C (NEW)}$$

$$\text{LVAE PFC EMISSIONS (TIER 1 AND TIER 3 METHODS – PRODUCTION-BASED)}$$

$$LVAE E_{CF_4} = (LVAE EF_{CF_4} \bullet MP)$$

Where:

LVAE E_{CF_4} = LVAE emissions of CF_4 from aluminium production, kg CF_4 LVAE EF_{CF_4} = LVAE emission factor for CF_4 (Tier 1 default by cell technology type, or Tier 3 facility-specific), kg CF_4 /tonne Al

MP = metal production by cell technology type, tonnes Al.

Tier 3 methods for Low Voltage Anode Effect (LVAE) emissions

The Tier 3 methods for estimating LVAE emissions multiply facility-specific factors either by (i) metal production (Equation 4.27c) or (ii) as a ratio of HVAE emissions (Equation 4.27d). The method based on metal production is analogous to the Tier 1 method for LVAE. The method based on ratio of HVAE emissions assumes that HVAE emissions reflect the overall performance and process control of the smelter. For both methods, it is *good practice* to define the facility-specific emission factor (LVAE EF_{CF_4}), or emission ratio of LVAE to HVAE emissions ($ER_{LV\ CF_4}$) based on direct PFC measurements at the facility. Preliminary testing of both methods produced results that were broadly aligned and consistent with the direct measurements of PFCs (Marks & Nunez 2018b).

A Tier 2 method for LVAE emissions has not been provided, since use of $ER_{LV\ CF_4}$ emission ratios for different technology classes would *not* reduce uncertainty levels compared to a Tier 1 approach. This is because a Tier 2 $ER_{LV\ CF_4}$ emission ratio approach cannot capture all the underlying factors that drive LVAE emissions in one smelter versus another of the same technology class. Therefore, this method is only recommended at a Tier 3 individual facility level.

$$\text{EQUATION 4.27D (NEW)}$$

$$\text{LVAE PFC EMISSIONS (TIER 3 METHOD – AS RATIO OF HVAE EMISSIONS)}$$

$$LVAE E_{CF_4} = HVAE E_{CF_4} \bullet ER_{LV\ CF_4}$$

Where:

LVAE E_{CF_4} = low voltage anode effect emissions of CF_4 from aluminium production, kg CF_4 HVAE E_{CF_4} = high voltage anode effect emissions of CF_4 from aluminium production by cell technology, kg CF_4 $ER_{LV\ CF_4}$ = Smelter-specific ratio of LVAE/HVAE CF_4 emissions**ESTIMATING EMISSIONS FROM CELL START-UP****Tier 2 and 3 methods for Cell Start-Up (CSU) emissions**

For completeness, it is *good practice* to always include cell start-up (CSU) emissions (refer to Box 4.3) in total PFC emissions estimates. There are various ways CSU emissions can be included depending on the methodological Tier selected. The Tier 1 HVAE and LVAE default emission factors implicitly include CSU emissions; therefore, where the Tier 1 methods are used, there is no need to estimate CSU emissions separately. The Tier 2a and 2b HVAE methods and the Tier 3a and 3b_{HVAE} methods can account for CSU emissions if data on anode effect duration and frequency are collected during CSUs and are included in the emissions calculations. As discussed below, this may lead to a slight overestimate of emissions if the Tier 2a or 3a slope factor method is used. Finally, the Tier 3_{DM} direct measurement method includes CSU emissions as long as the continuous emissions monitoring occurs during CSU periods.

BOX 4.3 (NEW)**PFC EMISSIONS DURING START-UP OF ELECTROLYSIS CELLS**

New electrolysis cells undergo a ‘start-up’ process prior to normal operation. The ‘start-up’ period can vary from one facility to another, e.g. from the first few hours of a cell’s life to a month.

HVAEs can occur during start-ups of electrolysis cells – from the moment when the anode beam is first raised on the cell and metal starts being produced – leading to generation of PFC emissions (International Aluminium Institute 2006; Dando *et al.* 2008; Xu *et al.* 2008; Dando *et al.* 2009; Maltais *et al.* 2010). While some researchers (Kristensen *et al.* 2007; Reny *et al.* 2016) have shown that cell start-ups can be done without HVAE, it is not common practice and PFC emissions from cell start-ups may contribute to a significant proportion of a facility’s total PFC emissions during certain periods, especially when the aluminium smelter is annually carrying out a large number of cell start-ups.

While some facilities have historically included the start-up period in accounting HVAE emissions, others have excluded it given that it does not represent normal operations. It is thought that LVAE emissions may also occur during the start-up period.

Furthermore, new cells following start-up typically operate with a higher cell voltage than during normal operation. For this reason, some smelters use a different HVAE detection threshold (e.g. 9.5 volts instead of 8 volts) for a specific period to reduce the risk of falsely detecting HVAE (Dando *et al.* 2008). This detection threshold is specific to each facility (based on historical data) and should be used for calculating HVAE performance at the facility when estimating cell start-up emissions.

HVAE PFC emissions measured during CSU events have demonstrated lower emission rates than during normal operations. For this reason, accounting for these HVAEs using the standard slope or overvoltage coefficient during normal operations for the technology class (Tier 2a) or facility (Tier 3a) may lead to an overestimation of these PFC emissions (Dando *et al.* 2008; Xu *et al.* 2008; Maltais *et al.* 2010).

To avoid overestimating emissions from CSUs through use of the Tier 2a or 3a_{HVAE} methods, inventory compilers have three options. Lowest uncertainties will be obtained with the second and third options proposed below as it is based on specific measurements during CSU. However, as a significant amount of CSU measurements may prove difficult to acquire, it is *good practice* to consider the first option when no facility-specific data for cell start-up is available. First, to take into consideration the different process dynamics of HVAEs during the start-up of cells, compilers can use the Tier 2b or 3b_{HVAE} non-linear approach (Equations 4.27a or 4.27b) when no facility-specific measurement data for cell start-up is available. LVAE emissions during cell-start-up can then be estimated using either a production-based Tier 1 or Tier 3 approach (Equation 4.27c), or Tier 3 ratio of HVAE emissions approach (Equation 4.27d).

Second, inventory compilers using the Tier 3a method can avoid overestimates by developing and applying slope or overvoltage coefficients specifically for CSUs at the facility (in addition to the coefficients for normal operation).

Third, when data is available, compilers may determine a facility-specific Tier 3 emission factor based on the total emissions of PFC per cell start-up at the facility. This Tier 3_{CSU} method accounts for both HVAE and LVAE emissions during the start-up process, as given in Equation 4.27e:

EQUATION 4.27E (NEW)**TOTAL PFC EMISSIONS FOR START-UP OF ELECTROLYSIS CELLS (TIER 3_{CSU} METHOD)**

$$CSU E_{CF_4} = (EF_{CSU CF_4} \bullet N_{CSU})$$

And

$$CSU E_{C_2F_6} = (EF_{CSU C_2F_6} \bullet N_{CSU})$$

Where:

E_{CF_4} = Total amount of CF_4 produced during start-ups for a specific period, kg CF_4

$E_{C_2F_6}$ = Total amount of C_2F_6 produced during start-ups for a specific period, kg C_2F_6

$EF_{CSU CF_4}$ = Average amount of CF_4 produced during the cell start-up period, kg CF_4 / cell start-up.

$EF_{CSU C_2F_6}$ = Average amount of C_2F_6 produced during the cell start-up period, kg C_2F_6 / cell start-up.

Final Draft

N_{CSU} = Total number of cell start-ups during the specific period considered, cell start-up

Note that Equation 4.27e should be used to estimate CSU emissions *only if* CSU emissions are excluded from normal HVAE and LVAE accounting. Care should be taken not to double count CSU emissions if they are already included in the normal accounting of HVAE and LVAE emissions.

DIRECT MEASUREMENT OF TOTAL EMISSIONS

Tier 3_{DM} method for Total PFC emissions: Based on direct gas measurement

The Tier 3_{DM} method is based on direct measurement of *total* PFC gases (CF₄ and C₂F₆) at individual facilities, rather than estimating emissions through emission factors or coefficients and process data (e.g. anode effect minutes per cell-day). As total emissions are measured, there is no need to account for PFCs from high and low voltage anode effects (HVAE and LVAE) separately. Furthermore, cell start-up (CSU) emissions are included since direct measurements should provide representative coverage of emissions from all operations. The Tier 3_{DM} method, following industry best practices, provides the lowest of uncertainty level for all accounting methods, since the only sources of uncertainty is related to sampling procedures and measurement error.

Measurement approaches are only briefly described here. For detailed guidance on direct measurement of PFCs, refer to established standard measurement practices and the latest industry protocols (e.g. (US Environmental Protection Agency & International Aluminium Institute 2008)). The inventory compiler should also consult guidance on plant-level measurements outlined in Volume 1, Chapter 2, and on QA/QC of measurements in Volume 1, Chapter 6. Two common approaches for direct PFC measurements are (i) *time-integrated* measurements and (ii) *continuous* measurements.

Time-integrated measurements are periodic measurements where PFCs from the facility are collected in sampling containers over set time-intervals; gas samples are then analysed ‘off-line’ in a laboratory. Examples of analysis techniques include: Gas Chromatography with Mass Spectrometry (GC/MS) and Fourier Transform Infrared Spectrometry (FTIR). Time-integrated measurements are typically simpler and more cost-effective to operate and often provide more accurate (with lower limits of detection) than *continuous* measurement approaches (US Environmental Protection Agency & International Aluminium Institute 2008; Fraser *et al.* 2013). For time-integrated measurements, it is *good practice* to provide continuous coverage over time as this ensures measurements are representative of all smelter operations. For more details, refer to the latest industry measurement protocol for PFC measurements.

Continuous measurements are those where PFCs are measured continuously by *in-situ* instruments at the facility. These have advantages of: (i) providing continuous coverage of total emissions and (ii) allowing emissions from high vs. low voltage anode effects (HVAE and LVAE) to be accounted for separately (US Environmental Protection Agency & International Aluminium Institute 2008). However, this approach can be more cost-intensive and may require specialist expertise to operate and maintain. Examples of measurement techniques include: FTIR, Mass Spectrometry (MS), Photoacoustic Spectrometry (PAS), Tunable-Diode Laser Absorption Spectrometry (TDLAS) and Quantum-Cascade Lasers (QCL) (Aarhaug *et al.* 2018). For accurate capture of LVAE emission components, an important consideration is the detection limit of measuring instrumentation, given that LVAE emissions are typically at low concentrations (as low as ppb levels); this introduces a further level of uncertainty for continuous measurement approaches.

To ensure the accuracy of emissions accounting by direct measurement, it is *good practice* to employ established measurement practices and the latest industry protocols (US Environmental Protection Agency & International Aluminium Institute 2008). There is ongoing work to develop an updated measurement protocol for total PFC emissions (particularly LVAE emissions) to improve consistency and alignment across the industry.

4.4.2.4 CHOICE OF EMISSION FACTORS FOR PFCs

Tier 1: Technology based default emission factors

Default emission factors for the Tier 1 method are provided in Table 4.15. These are for estimation of both HVAE emissions (Equation 4.25) and LVAE emissions (Equation 4.27c). Aluminium production data by technology is usually available through national statistics publications or through publicly available company reports and websites.

Note that for the PFPB_{MW} technology class, the HVAE-CF₄ emission factor in Table 4.15 includes LVAE emissions and therefore represents total CF₄ emissions.

TABLE 4.15 (UPDATED) TECHNOLOGY SPECIFIC DEFAULT EMISSION FACTORS FOR THE CALCULATION OF HVAE AND LVAE EMISSIONS FROM ALUMINIUM PRODUCTION (TIER 1 METHOD) (MARKS & NUNEZ 2018B)						
Technology	HVAE				LVAE	
	CF ₄		C ₂ F ₆		CF ₄	
	EF _{CF4} (kg/tonne Al)	Uncertainty Range (%) ^b	EF _{C2F6} (kg/tonne Al)	Uncertainty Range (%)	EF _{CF4} (kg/tonne Al)	Uncertainty Range (%)
PFPB _L	0.016 ^a	-82/+126 ^a	0.001	-74/+109 ^a	0.009 ^a	+99/-61
PFPB _M	0.011	-90/+213	0.001	-90/+256	0.018	+247/-98
PFPB _{MW}	0.161 ^b	-85/+476	0.013 ^b	-98/+864	-	-
SWPB	0.354	-76/+116	0.093	-89/+68	0.010	+69/-69
VSS	0.159 ^c	-94/+580 ^c	0.009 ^c	-94/+525	0.001	+61/-52
HSS	0.477	-79/+112	0.033	-76/+86	0.026	- ^d
Notes:						
^a PFPB _L emission factors and uncertainties reported in (Marks & Nunez 2018b) erroneously included data from another technology class (PFPB _M). This has since been corrected in the emission factor and uncertainty values reported here (expert opinion – Dr Jerry Marks).						
^b PFPB _{MW} emission factor (EF) is based on total emissions measurement data which includes LVAE emissions.						
^c VSS emission factors (EF) and uncertainties here incorporate data sets from (Marks & Nunez 2018b) and (Burkat, V.S. et al. 2018)						
^d Single data point – no uncertainty range calculated.						

Final Draft

Tier 2a: HVAE-PFC emission factor based on technology specific relationship between overall anode effect performance and PFC emissions

The Tier 2a slope method (Equation 4.26) is based on using technology specific coefficients for the applicable reduction cell and process control technology as listed in Table 4.16.

TABLE 4.16 (UPDATED) TECHNOLOGY SPECIFIC COEFFICIENTS FOR THE CALCULATION OF HVAE PFC EMISSIONS FROM ALUMINIUM PRODUCTION USING SLOPE ¹ METHODOLOGY (TIER 2A METHOD) (MARKS & NUNEZ 2018B)				
Technology	CF ₄		Weight Fraction C ₂ F ₆ /CF ₄	
	SC _{CF₄} (kg CF ₄ /tonne Al)/(AE-Mins/cell-day) ^a	Uncertainty Range (%)	C ₂ F ₆ /CF ₄	Uncertainty range (%)
PFPB _L	0.122	-48/+45	0.097	-35/+31
PFPB _M	0.104	-27/+32	0.057	-55/+55
PFPB _{MW} ^a	-	-	-	-
SWPB	0.233	-27/+44	0.280	-55/+58
VSS	0.058	-53/+130	0.086	-76/+236
HSS	0.165	-47/+28	0.077	-61/+48
Note: ^a Tier 2 default coefficients are not available for PFPB _{MW} technology class (Modern PFPB without fully automated anode effect intervention strategies for PFC emissions) because process data for anode effect frequency and duration was either not available, or, not comparable to traditional definitions or thresholds associated with anode effects.				

Tier 2b: HVAE-PFC emission rate coefficients based on individual anode effect durations

Marks & Nunez approach: The Tier 2b method proposed by (Marks & Nunez 2018a) (Equation 4.27a) uses different emission rate coefficients to estimate HVAE-CF₄ emissions, based on the anode effect duration (AED) of individual high voltage anode effects, as listed below in Table 4.16a.

For estimation of HVAE-C₂F₆ emissions, the Tier 2a technology-specific weight fractions of C₂F₆/CF₄ ($F_{C_2F_6/CF_4}$) should be used – refer to Table 4.16.

TABLE 4.16A (NEW) SPECIFIC HVAE-CF ₄ EMISSION RATE COEFFICIENTS BASED ON THE ANODE EFFECT DURATION AS CALCULATED BY (MARKS & NUNEZ 2018A) (TIER 2B METHOD).		
AED ^a	Value of K ₁	Value of K ₂
1s < AED ≤ 5s	0.0341	0.756
5s > AED ≤ 200s	0.0473	0.693
AED > 200 s	0.1661	0.479
^a In the rare occurrences where AED is equivalent to 0s, the equation that should be used is: kg CF ₄ = 0.576 · kA / 1000		

Dion et al. approach: For the Tier 2b method proposed by (Dion et al. 2018a) to calculate HVAE emissions (Equation 4.27b), emission rate coefficients C₁, C₂, C₃ and C₄ are defined in Equation 4.27f below for the generic smelter, based on the daily metal production per cell.

¹ The ‘Overvoltage method’ (Equation 4.27) is no longer widely adopted within the aluminium industry. Therefore, there is insufficient data available to update the overvoltage coefficients related to the overvoltage methodology. It is *good practice* to compile PFC inventories using the slope model for recent and future calculations. Tier 3 overvoltage coefficients can still be used as they are facility-specific (Dion et al. 2017; Marks & Bayliss 2012).

EQUATION 4.27F (NEW)
EMISSION RATE COEFFICIENTS FOR HVAE PFC (TIER 2B METHOD – (DION *ET AL.* 2018A))

$$C_1 = 0.6415 \bullet MP_{Day} + 5.878$$

$$C_2 = -0.0972 \bullet MP_{Day} + 0.8905$$

$$C_3 = 0.238MP_{Day}^2 - 1.407 \bullet MP_{Day} + 2.342$$

$$C_4 = -0.0981MP_{Day}^2 + 0.381 \bullet MP_{Day} + 0.3413$$

Where :

C_1 = Emission rate coefficient for CF_4 dependant on the metal production of the cell, kg CF_4 / s · tonne Al

C_2 = Emission rate coefficient for CF_4 dependant on the metal production of the cell, dimensionless

C_3 = Emission rate coefficient for C_2F_6 dependant on metal production of the cell, kg C_2F_6 / s · tonne Al

C_4 = Emission rate coefficient for C_2F_6 dependant on the metal production of the cell, dimensionless.

MP_{Day} = Average daily metal production per cell¹, for the cell technology, tonnes Al

Uncertainty levels when calculating PFCs from individual HVAE: The uncertainty range of each Tier 2b methodology was estimated for both PFPB_M and PFPB_L technologies in order to facilitate the choice of one of the two methods. These are shown in Table 4.16b.

TABLE 4.16B (NEW) UNCERTAINTY RANGE ^c (%) IN ESTIMATING PFC EMISSIONS FROM INDIVIDUAL HVAES (TIER 2B METHODS)				
Technology	CF_4 ^{a,b}		C_2F_6 ^{a,b}	
	Marks & Nunez approach	Dion <i>et al.</i> approach	Marks & Nunez approach	Dion <i>et al.</i> approach
SWPB and PFPB _L	-47 / +29	-36 / +51	-52 / +39	-42 / +68
PFPB _M	-16 / +134	-33 / +61	-54 / +152	-24 / +13

Note:

^a Uncertainty ranges were evaluated for total emissions across multiple measurement campaigns and facilities (expert opinion). Overall, 11 measurement campaigns for PFPB_M and 10 measurements campaigns for PFPB_L and SWPB technology classes were used to estimate the uncertainties related to CF_4 , while 5 measurement campaigns for PFPB_M and 4 measurements campaigns for PFPB_L and SWPB technology classes were used to estimate the uncertainties related to C_2F_6 .

^b Uncertainty ranges were calculated for HVAE emissions, where HVAEs were within the recommended HVAE duration (AED) limits of the (Dion *et al.* 2018a) method. It is possible that the uncertainty increases if the AED exceeds recommended limits when using the (Dion *et al.* 2018a) method, i.e. 1000 s and 150 s for CF_4 and C_2F_6 estimations, respectively.

^c The uncertainty range calculated in Table 4.16B is based on a comparison with direct measurements and should not be compared to the reported Tier 2a uncertainty range from table 4.16 which compares variations of EF. For comparison, the calculated CF_4 uncertainty range for Tier 2a based on direct measurements is (-44% / + 388%) for legacy facilities and (-22% / + 256%) for modern facilities. The calculated C_2F_6 uncertainty range for Tier 2a based on direct measurements is (-58% / + 8%) for legacy facilities and (-19% / +97 %) for modern facilities.

Tier 3: PFC emission factors based on a facility specific relationship between HVAE and LVAE performance and PFC emissions

Tier 3 methods are based on facility-specific coefficients or emission factors to estimate PFCs:

- For HVAE emissions, Tier 3a_{HVAE} and 3b_{HVAE} coefficients characterize the relationship between facility HVAE performance and measured PFC emissions from periodic or continuous measurements that are consistent with established measurement practices and latest industry protocols (US Environmental Protection Agency & International Aluminium Institute 2008).

¹ MP_{Day} in Equation 4.27g is the average metal production *per cell per day* – it can be estimated from potline data or from the line amperage and average current efficiency of the potline. Care should be taken not to confuse this with the variable ‘ MP ’ – total metal production from the facility over the accounting period – used in other equations.

Final Draft

- For *LVAE emissions*, facility-specific Tier 3_{LVAE} LVAE/HVAE emission ratios or LVAE emission factors can be established based on direct measurement of HVAE and LVAE for a period of time. There is ongoing work to develop an updated measurement protocol for LVAE emissions to improve consistency and alignment across the industry.
- For *cell start-up (CSU) emissions*, Tier 3_{CSU} production-based emission factors can be established based on direct measurement of HVAE and LVAE emissions during the start-up of electrolysis cells; alternatively, direct measurements can also be used to define Tier 3_{HVAE} or 3_{bHVAE} and 3_{LVAE} coefficients for emissions estimation (described above) specifically for cell start-up periods.

Tier 3_{DM} is based on direct measurement at facilities, rather than estimation using on emission factors or coefficients.

4.4.2.5 CHOICE OF ACTIVITY DATA

Production statistics should be available from every facility to enable use of Tier 1 methods for both CO₂ and PFC emissions. Uncertainty in the tonnages of aluminium produced is likely to be low in most countries. Given the expected universal availability of production data, production capacity data should only be used as a check on production statistics.

For CO₂ emissions, all aluminium smelters collect data to support Tier 2 or Tier 3 methods. Söderberg smelters collect anode paste consumption data while Prebake smelters record baked anode consumption. The Tier 2 and Tier 3 methods use the same equation for calculation of CO₂ emissions; however, the Tier 3 method uses facility specific composition data for anode materials while the Tier 2 method uses industry average anode composition data.

Good practice methods for PFC emissions resulting from high voltage anode effects (HVAE) require accurate HVAE minutes per cell day data for all cell types. Annual statistics should be based on the production-weighted average of monthly HVAE effect data. The Tier 2_{HVAE} and Tier 3_{HVAE} slope method utilizes *overall* performance statistics for HVAE minutes per cell day and aluminium production data and Tier 3_{HVAE} overvoltage method utilizes overall performance statistics for anode effect overvoltage and current efficiency. Similarly, Tier 2_{bHVAE} and Tier 3_{bHVAE} utilises data on *individual* HVAE performance (anode effect duration) and line amperage or daily average metal production at each facility.

Good practice methods for PFC emissions resulting from low voltage anode effects (LVAEs) require accurate aluminium production data for Tier 1 (based on production-based, default emission factors) and Tier 3 (based on production-based, facility-specific emission factors). For the alternative Tier 3 estimation based on the ratio of LVAE/HVAE emissions, *good practice* methods for HVAE should be adopted as these are used in the calculation of LVAE emissions.

Good practice methods for PFC emissions from cell start-up (CSU) requires the same activity data described above for HVAE and LVAE emissions (if using Tiers 2a, 2b, 3_{HVAE} or 3_{bHVAE} and Tiers 1_{LVAE} or 3_{LVAE}), however with a data set specific to cell start-ups. Alternatively, if using Tier 3_{CSU} facility-specific emission factors defined for cell start-ups, the only activity data required is the number of cell start-ups over the accounting period.

The direct measurement method for total PFCs (Tier 3_{DM}) is not based on estimation and no activity data is required.

Individual aluminium companies or industry groups, national aluminium associations or the International Aluminium Institute (IAI) should be consulted to ensure that the data are available and in a useable format for inventory estimation.

4.4.2.6 COMPLETENESS

Primary aluminium facilities will generally have good records of tonnes of aluminium produced throughout the entire time series covered by the inventory. In addition, carbon consumption data are typically available over the same period. Process data on high voltage anode effects may be incomplete over the entire time series and measures may have to be employed, such as those described in Section 4.4.2.7, Developing a Consistent Time Series, to calculate PFC emissions over some portions of the inventory period. Primary aluminium production also utilizes large amount of electricity and care should be exercised to avoid omissions of carbon dioxide associated with electricity input, or, to avoid double counting of this carbon dioxide.

Furthermore, updates here in the *2019 Refinement* provide significant advances in completeness, given the inclusion of accounting for: (i) PFC emissions from LVAEs from primary aluminium production and (ii) PFC emissions from cell start-ups (CSU), both of which were not previously accounted for in the *2006 IPCC*

Guidelines. Despite greater completeness compared to the 2006 Guidelines, a higher level of uncertainty overall is introduced in estimating total PFCs, given the higher uncertainties in accounting LVAE emissions. Finally, care should be exercised to avoid double counting of PFCs from cell start-ups, if these are already accounted for in normal HVAE and LVAE emissions.

4.4.2.7 DEVELOPING A CONSISTENT TIME SERIES

General guidance on managing time-series consistency is available in Volume 1, Chapter 5; however, the following provides guidance specific to aluminium production.

Time-series consistency for CO₂ emissions

Aluminium production statistics will typically be available for the entire history of the facility. Developing a consistent time series for carbon dioxide emissions should not be a problem since most facilities historically have measured and recorded anode or paste consumption. Where historic anode or paste consumption data are missing, carbon dioxide emissions can be estimated from aluminium production utilizing the Tier 1 method.

Time-series consistency for High Voltage Anode Effect (HVAE) PFC emissions

A complete time series of PFC related activity data such as high voltage anode effect (HVAE) minutes per cell day or overvoltage gives the best time series results. Because PFC emissions only became a major focus area in the early 1990s for the global aluminium industry, some facilities may have limited information about the required anode effect data to implement Tier 2 or Tier 3 PFC inventory practices over the entire time covered by the inventory. Substantial errors and discontinuities can be introduced by reverting to Tier 1 methods for PFC emissions for years for which activity data are not available. The appropriateness of applying Tier 2 or Tier 3 PFC emission factors back in time to a given facility and availability of detailed process data vary with the specific conditions. Generally, backcasting of Tier 2 or Tier 3 methods using splicing or surrogate data are preferred over use of Tier 1 emission factors. Specifically, where only HVAE frequency data are available and HVAE duration data are unavailable, it is *good practice* to splice or backcast PFC emissions per tonne aluminium based on HVAE frequency data (implicitly assuming that anode effect durations did not change). When going back in time using Tier 2 methodologies, it is important to take into consideration the reported change in slope coefficient for HVAEs. Hence, it is suggested that inventory compilers use the technology-specific slope coefficients from the 2006 IPCC Guidelines for annual inventories up to 2018 when using either the Tier 2a or the Tier 2b method. For the year 2019 and onwards, it is *good practice* to the methods and emission factors reported in the 2019 Refinement for quantification of PFCs using Tier 2.

Inventory compilers switching from the Tier 3_{HVAE} overvoltage methodology to the Tier 3_{HVAE} slope model should use both methods in parallel for a period of three years to evaluate the potential impact. However, publications demonstrated that the difference between both methods should be negligible with Tier 3 emission factors (Dion et al. 2017; Marks & Bayliss 2012). If the difference between both methods is greater than 5% over the transition period, then *good practices* would require contacting the International Aluminum Institute (IAI) to be directed to expert advice to determine the optimal course of action for the best representativeness.

For inventory compilers switching from Tier 2a-3_{HVAE} (slope/overvoltage) to the Tier 2b-3b_{HVAE} (non-linear) methodology to estimate HVAE emissions, it is consistent with *good practices* to adopt a similar protocol, i.e. evaluate both methods in parallel for three years to evaluate impacts and if greater than 5% differences are noted during the transition period, the IAI can be contacted for expert advice. Backcasting PFC emissions using Tier 2b in 2018 and prior years is also possible, provided historical data on individual HVAE durations is still available.

Currently many facilities are making PFC measurements that facilitate implementation of Tier 3 PFC inventory methods. There are a number of issues that impact on whether Tier 3 PFC emission factors can be extrapolated to past inventory periods. Factors that should be considered include: (i) whether any technology upgrades have been implemented at the facility, including significant amperage increase, new cell control system, or significant changes in alumina feed control strategy affecting the frequency of HVAEs, (ii) whether there have been substantial changes in work practices affecting the distribution of the HVAE durations, (iii) whether any changes in the calculation of underlying process data have occurred, and (iv) the quality of the measurements made to establish the Tier 3 factor or coefficient. It is *good practice* to consult with representatives from the operating facilities, either directly or through regional or international organizations representing the industry to develop the best strategy for the specific group of operating locations included in the national inventory. Additional information on splicing methods and details regarding constructing a time series for primary aluminium is available in The Aluminium Sector GHG Protocol (International Aluminium Institute 2006). Expert advice is also available from global and regional aluminium industry associations regarding greenhouse gas emissions and typical industry emissions from aluminium production.

Table 4.16b has been provided to facilitate the choice of the correct HVAE emission factor (EF) for time consistent inventories.

Time-series consistency for Low Voltage Anode Effect (LVAE) PFC emissions

Low voltage anode effects (LVAEs) became a concern for the aluminium industry in the early 2010s, due to an increase number of cell technologies with higher amperage and additional anodes (Chen *et al.* 2013; Wong & Marks 2013; Zarouni *et al.* 2013; Dando *et al.* 2015; Wong *et al.* 2015; International Aluminium Institute 2018). Actual data indicates that these PFC emissions are greater for specific cell technologies, usually with cell amperage higher than 350kA. Therefore, inventory compilers should backcast the LVAE PFC emissions, for national inventories, by using the respective Tier 1 coefficient specific to each category back to 2006. Since 2006, the global aluminium industry has undergone changes in operating conditions and factors that make LVAE emissions much more prevalent¹. Prior to 2006 therefore, LVAE could be considered as immaterial to the total PFC emissions from primary aluminium production (as suggested by the agreement in global top-down and bottom-up industry estimates of total PFCs prior to 2002 (Wong et al., 2015); hence it is *good practice* not to report LVAE before 2006.

If Tier 3 coefficients are available, it is *good practice* to use these coefficients for past inventory periods instead of using Tier 1 coefficients. There are several issues that impact the uncertainty of Tier 3 PFC emission factors when extrapolated to past inventory periods. The factors presented in the previous section on high voltage anode effects are also applicable when estimating the possibility of extrapolating LVAE estimations outside of the measured EF period. It is particularly important to consider any significant change in the alumina feeding strategy as it can significantly impact the LVAE emission coefficient. Finally, the study performed by (Dion *et al.* 2018b) highlighted the importance of considering numerous facilities when estimating LVAE emissions using Tier 1 emission factors. Inventory compilers should therefore be aware of the limitations associated with the Tier 1 coefficients included in this guidance when applying it to a limited number of smelters, or when used for a single facility. This is driven by the high uncertainty of LVAE PFC emissions from individual smelters and the possible variability of these emissions related to different control process parameters between the different facilities.

Table 4.16c has been provided to facilitate the choice of the correct LVAE emission factor (EF) for time consistent inventories.

TABLE 4.16C (NEW)			
SUMMARY OF WHICH GUIDELINES TO REFER TO, FOR TIME CONSISTENT PFC INVENTORIES			
For estimation of:	Time frame		
	Prior to 2006	2006 to 2019	2020 and beyond
HVAE emissions	Refer to 2006 IPCC Guidelines for methodology and adequate EF.	Refer to 2006 IPCC Guidelines for methodology and adequate EF.	Refer to 2019 Refinement for methodology and adequate EF.
LVAE emissions	LVAE are considered immaterial due to the high levels of HVAE from smelters during this period ¹ . It is <i>good practice</i> not to report LVAE.	Refer to 2019 Refinement for methodology and adequate EF.	Refer to 2019 Refinement for methodology and adequate EF.
¹ (International Aluminium Institute 2018). Refer to footnote 1 below, for factors that have led to LVAE emissions becoming more prevalent in the aluminium industry following the time of the 2006 IPCC Guidelines.			

4.4.3 Uncertainty assessment for primary aluminium production

¹ The fundamental factors that make LVAE emissions more prevalent in today's current smelting technologies were less significant prior to the 2006 IPCC Guidelines (expert judgement). These factors include: higher anode current density (Amps per cm² anode surface) to maximise cell productivity, lower anode-cathode distance to minimise cell voltage and hence energy use, larger anode dimensions which reduced the volume of liquid electrolyte to dissolve alumina, greater demand on transporting alumina to all anodes per point feeder (for PFPB technologies), and longer cells with significantly more anodes increasing the risk of localised issues in cells.

There are major differences in the uncertainty for PFC emissions depending on the choice of Tier 1, Tier 2, or Tier 3 methods. The differences in uncertainty resulting from choice of method for carbon dioxide emissions are much smaller than for PFC emissions. There is no basis for country or regional differences in emissions resulting from aluminium production other than the differences that result from the specific type of production technologies and work practices in use in the country or region. These differences are reflected in the calculation methodologies described above.

4.4.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for CO₂ emissions

The uncertainty in the emission factors for calculating carbon dioxide emissions from carbon anode or paste consumption should be less than ± 5 percent for both the Tier 2 and Tier 3 methods, and less than ± 10 percent for the Tier 1 method. The reactions leading to carbon dioxide emissions are well understood and the emissions are very directly connected to the tonnes of aluminium produced through the fundamental electrochemical equations for alumina reduction at a carbon anode and oxidation from thermal processes. Both of these fundamental processes producing carbon dioxide are included in process parameters routinely monitored at the production facilities, the net carbon consumed and/or paste consumption. The main source of uncertainty is in the net carbon consumed for Prebake technologies and paste consumption for Söderberg cells. These factors are both carefully monitored and are important factors in the economic performance of a facility. Improvements in accuracy of carbon dioxide emissions inventories can be achieved by moving from Tier 1 to Tier 2 methods because there is a range of performance of reduction facilities in the consumption of carbon anode materials. Less significant improvements in accuracy can be expected in choosing the Tier 3 method over the Tier 2 method. This is because the major factors in the calculation are the net anode carbon consumed or paste consumption and the production of aluminium. The uncertainty of both these components of the calculation equation is low, 2 to 5 percent, and these uncertainties dominate the overall calculation of carbon dioxide emissions in the Tier 2 and Tier 3 methods. Facility specific data are used in both Tier 2 and Tier 3 calculations for these parameters. The Tier 3 method refines the calculation to use actual composition of the carbon anode materials. While there can be considerable variability in the minor components of the anode materials this variability does not contribute significantly to the overall calculation of carbon dioxide emissions.

Uncertainties for PFC emissions

In considering changes in uncertainty in PFC emissions inventory when moving from Tier 1 to Tier 2 and Tier 3 methods, there are major reductions in uncertainty when choosing the Tier 2 or Tier 3 methods over the Tier 1 method.

For HVAE emissions, the high level of uncertainty in the Tier 1 method reflects the significant variability in HVAE performance from one facility to another within the same technology class. The Tier 1 method is based on using a single default coefficient for all operators by technology type. Since there can be variations in anode effect performance (frequency and duration) by factors of 10 among operators using the same technology (IAI, 2005c), use of the Tier 1 method can result in uncertainties of the same magnitude. There is less impact on uncertainty levels in choosing the Tier 3 methods (3a_{HVAE} and 3b_{HVAE}) over the Tier 2 methods (2a and 2b) for estimating HVAE. When using the Tier 2a or 2b methods, the level of uncertainty reduction depends on the cell technology type. For example, the uncertainty for Tier 2a industry slope coefficients for individual facilities ranges from -27 to +32 percent for PFPB_M, to -53 to +130 percent for VSS. Compared to Tier 2a, the Tier 2 method provides significantly lower levels of uncertainty (roughly 3-5 times less, expert opinion) for individual facilities in terms of estimated PFC emissions; however again, the level of uncertainty depends on technology type.

Both Tier 2 (2a and 2b) and Tier 3 (3a_{HVAE} and 3b_{HVAE}) methods are based on direct PFC measurements that establish a relationship between HVAE performance and PFC specific emissions. The Tier 2 methods use average equation coefficients by technology while the Tier 3a_{HVAE} and 3b_{HVAE} methods use facility-specific coefficients based on direct PFC measurements made at the facility. The lowest uncertainty for PFC emissions calculations from HVAE is from the use of the Tier 3b_{HVAE} method, followed by the Tier 3a_{HVAE} method. However, to achieve this lower uncertainty in Tier 3 PFC calculations it is important to use *good practices* in making facility specific PFC measurements. These measurement *good practices* have been established and documented in a protocol available globally (US Environmental Protection Agency & International Aluminium Institute 2008); it is *good practice* to check for updates to these protocols. When properly established these Tier 3 coefficients will have an uncertainty of ± 15 percent at the time the coefficients are measured.

For LVAE emissions, there is a high level of uncertainty associated with emission estimates using Tier 1. The Tier 3_{LVAE} method has a much lower uncertainty than Tier 1 as it is facility specific and based on a period of direct measurement at the site. LVAE is a relatively new discovery in the aluminium industry and as such, research continues on the best predictors and models to use to estimate LVAE emissions. There is also high variability observed between different facilities which results in large uncertainty ranges for the measured data that underpins

Final Draft

the emissions factors. A measurement protocol for LVAE measurements to support the Tier 3_{LVAE} methodology is still under development and it is expected that such industry guidance to align measurement procedures and processes will improve consistency across the industry. Furthermore, considering the typically low concentrations of LVAE emissions and the detection limits of measuring instruments, it is expected that the uncertainty of the Tier 3_{LVAE} method for LVAE emissions will be larger than that for Tier 3 methods (3a_{HVAE} and 3b_{HVAE}) to estimate HVAE emissions. Finally, while Tier 3_{LVAE} provides the lower uncertainty for LVAE estimations than Tier 1, the lowest overall uncertainty for total PFC emissions is from the Tier 3_{DM} method, i.e. direct measurement of total PFCs.

For CSU emissions, there is no specific methodology at the Tier 1 level, since CSU emissions are implicitly included in Tier 1 methods for estimating HVAE and LVAE emissions. However, given the wide variation in cell technologies and start-up operating practices from one facility to another, a higher level of uncertainty is expected at Tier 1 (as discussed previously for HVAE and LVAE emissions). If CSU emissions are accounted for separately, use of the Tier 2b method is likely to provide lower uncertainties compared to the Tier 2a method (with standard slope coefficients, which may overestimate HVAE emissions). Similarly, when facility-specific at Tier 3 coefficients are available, use of the Tier 3b_{HVAE} method is expected to provide lower levels of uncertainty than the Tier 3a_{HVAE} method. However, lowest uncertainties can be obtained through use of one of the following: (a) Tier 3a_{HVAE} or Tier 3b_{HVAE} emission coefficients for HVAE emissions, combined with Tier 3_{LVAE} coefficients determined specifically for CSU periods, or (b) use of Tier 3_{CSU} total emission factors determined specifically for CSU periods.

Finally, the Tier 3_{DM} direct measurement method, following industry best practices, provides the lowest of uncertainty level for all accounting methods for all PFC emissions (HVAE, LVAE and CSU), since the only sources of uncertainty is related to sampling procedures and measurement error.

4.4.3.2 ACTIVITY DATA UNCERTAINTIES

There is very little uncertainty in the data for the annual production of aluminium, less than 1 percent. The uncertainty in recording carbon consumption as baked anode consumption or coke and paste consumption is estimated to be only slightly higher than for aluminium production, less than 2 percent. For HVAE PFC emissions, the other component of calculated facility specific emissions using Tier 2a or Tier 3a_{HVAE} methods is the overall anode effect activity data, i.e.: anode effect minutes (AEM) per cell day for the slope method, or anode effect overvoltage (AEO) for overvoltage method. 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 also applies to the Tier 2b and 3b_{HVAE} approach where potline current and anode effect durations (AED) for individual HVAEs are precisely monitored by the cell control system; the only exception are cases where this individual AED data is automatically consolidated into overall anode effect performance statistics by the facility's software on a daily basis, or for different periods, which prevents the use of this method. Further activity data required for Tier 2b or 3b_{HVAE} method (Dion *et al.* approach) is the average daily metal production per cell, which has very little uncertainty in the data, less than 5 percent. For estimation of CSU emissions using the Tier 3_{CSU} method, there is very little uncertainty on the recorded number of cell start-ups (N_{CSU}) per accounting period, less than 2 percent.

4.4.4 Quality Assurance/Quality Control (QA/QC) Reporting and Documentation for primary aluminium production

4.4.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is *good practice* at all primary aluminium production facilities to maintain records of all of the necessary activity data to support calculations of emissions factors as suggested in these guidelines. These records will include production of aluminium, anode effect performance and consumption of carbon materials used in either Prebake or Söderberg cells. In addition, the International Aluminium Institute maintains global summaries of aggregated activity data for these same parameters and regional data are available from regional aluminium associations. It is *good practice* to aggregate emissions estimates from each smelter to estimate total national emissions. However, if smelter-level production data are unavailable, smelter capacity data may be used along with aggregate national production to estimate smelter production.

It is *good practice* to verify facility CO₂ emission factors per tonne aluminium by comparison with the expected range of variation that would be predicted from the variation noted in Tables 4.10 and 4.11 for carbon dioxide

specific emissions. Also, the underlying equation coefficients used for calculating PFC emission factors per tonne aluminium should be compared with those noted. It is suggested that any inventory value outside the 95 percent confidence range of the data population variance be confirmed with the data source.

Use of standard measurement methods improves the consistency of the resulting data and knowledge of the statistical properties of the data. For HVAE emissions from primary aluminium, the ‘*EPA/IAI Protocol for Measurement of Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions from Primary Aluminum Production*’ is the internationally recognized standard (US Environmental Protection Agency & International Aluminium Institute 2008). Significant differences between calculated Tier 3_{HVAE} or 3_{bHVAE} coefficients based on PFC measurements and the respective industry average Tier 2a or 2b coefficients for similar reduction technology should elicit further review and checks on calculations. Large differences should be explained and documented. The International Aluminium Institute (IAI) collects anode effect performance data from a number of smelters and can be consulted for assistance in identifying outlier data. . In addition, an up-to-date database of PFC measurements is also maintained by IAI and should be consulted when assessing the appropriateness of reported data. For LVAE emissions measurements which are relatively new and as yet, not widely measured, protocols are under development to improve consistency and alignment across the industry. Industry associations such as the IAI can be consulted for the latest developments.

Inter-annual changes in emissions of carbon dioxide per tonne aluminium should not exceed +/-10 percent based on the consistency of the underlying processes that produce carbon dioxide. In contrast, inter-annual changes in emissions of PFCs¹ per tonne of aluminium may change by values of up to +/- 100 percent. Increases in PFC specific emissions can result from process instability. Increases in anode effect frequency and duration can be the result of factors such as unanticipated power interruptions, changes in sources of alumina feed materials, cell operational problems, and increases in potline amperage to increase aluminium production. Decreases in PFC specific emissions can result from decreases in anode effect frequency and duration due to changes in the computer algorithms used in cell process control, upgrades in cell technology such as the installation of point feeders, improved work practices and better control of raw materials.

4.4.4.2 REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Chapter 6, Quality Assurance and Quality Control, Internal Documentation and Archiving. Some examples of specific documentation and reporting relevant to this source category are provided below.

It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced. To improve transparency, it is *good practice* to report emissions for PFCs from aluminium production separately from other source categories. Additionally, it is *good practice* that CF₄ and C₂F₆ emissions are reported separately on a *mass basis*.

The supporting information necessary to ensure transparency in reported emissions estimates is shown in Table 4.17, *Good practice* Reporting Information for PFC Emissions from Aluminium Production by Tier, below.

Much of the production and process data are considered proprietary by operators, especially where there is only one smelter in a country. It is *good practice* to exercise appropriate techniques, including aggregation of data, to ensure protection of confidential data.

¹ Reference to PFCs from this section applies to both HVAE and LVAE emissions.

Final Draft

TABLE 4.17 (UPDATED)								
GOOD PRACTICE REPORTING INFORMATION FOR CALCULATING CO ₂ AND PFC EMISSIONS FROM ALUMINIUM PRODUCTION BY TIER								
Data	Tier 1	Tier 2		Tier 3				
		2a HVAE	2b HVAE	3a HVAE	3b HVAE	3LVAE	3CSU	3DM
PFCs (CF ₄ , C ₂ F ₆ reported separately on mass basis)								
Annual national production (by technology)	X							
Annual production by smelter (by technology)		X		X		X		
Daily average production by smelter (by technology) ¹			X		X			
Annual current efficiency by smelter (by technology) ²				X				
Anode Effect Minutes per cell-day		X		X				
Anode Effect Overvoltage (mV)				X				
Anode Effect Duration for individual HVAE by smelter ³			X		X			
Line amperage (kA) during individual HVAE by smelter ^{3,4}			X		X			
Number of cell start-ups by smelter							X	
Default technology emission coefficients	X							
Technology specific emission coefficients linked to HVAE performance		X	X					
Facility specific emission coefficients linked to HVAE performance				X	X			
Facility specific emission coefficients linked to LVAE performance						X		
Facility specific emission coefficients linked to cell start-up							X	
Facility specific emission mass by direct measurement								X
Supporting documentation	X	X	X	X	X	X	X	X
CO ₂								
Annual national production (by Prebake or Søderberg technology)	X							
Annual production by smelter (by Prebake or Søderberg technology)			X			X		
Net anode consumption for Prebake cells or paste consumption for Søderberg cells			X			X		
Carbon material impurity levels and carbon dust for Søderberg cells						X		
Notes:								
¹ Daily average production data is only used in the Tier 2b/3b Dion <i>et al.</i> method, but not required for the Marks & Nunez method.								
² Current efficiency data used only in the Tier 3a Overvoltage Method, but not required for Tier 3a Slope Method.								
³ Given the total number of HVAEs that occur in a facility annually, it is not practical to report to individual anode effect data for all HVAEs by smelter in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.								
⁴ Line current data are only used in the Tier 2b/3b Marks & Nunez method, but not required for the Dion <i>et al.</i> method.								

4.4.5 Methodological issues for alumina production

This guidance does not consider any new methodological issues associated with GHG emission inventories for the production of alumina from the conventional Bayer process. Emissions from the Bayer process are covered by existing guidance for fossil fuel combustion (Volume 2, Chapter 2) and for lime production (Volume 3, Section 2.3).

Methodological issues for alumina production from *Bayer-sintering parallel* (BSP), *Bayer-sintering sequential* (BSS) and *Nepheline processing* (NP) only are considered in this section (see Figure 4.12a). In 2017, only around 3% of alumina was produced globally via the Bayer-sintering process and around 1% via the Nepheline processing mainly in 3 countries – Russia, Kazakhstan and China.

4.4.5.1 ALTERNATIVE ALUMINA REFINING PROCESSES

BAYER-SINTERING PROCESS

The Bayer-sintering process is an alternative process to the more conventional Bayer process and is used when the bauxite feed has a high silica content making processing by the conventional Bayer process uneconomical due to high soda and alumina loss. The Bayer-sinter process involves a sintering stage (either with soda or with soda and limestone) that produces a solid sodium aluminate sinter which is then leached to form the sodium aluminate liquor (green liquor).

The process to produce green liquor is an alternative process to bauxite digestion which takes place in the conventional Bayer process. Green liquors from both Bayer and sintering branches of the process are cooled and held in precipitator vessels which results in the precipitation of alumina hydrate that is filtered and washed.

The alumina hydrate is then passed through a rotary or stationary calciner at 1100°C to drive off the chemically combined water. The result is a white powder, pure calcined or ‘metallurgical’ grade alumina (Al₂O₃), which is the basic raw material for primary aluminium production.

Depending on bauxite quality there two variations of the Bayer-sintering process: *parallel* and *sequential*. In the case of the *parallel* process (BSP), a proportion of the bauxite feed (up to 20-30%) is processed in the sintering branch and the rest is effectively processed by the conventional Bayer process (Figure 4.12a). In the case of *sequential* process (BSS), all bauxite is Bayer digested and red mud is mixed with soda and limestone and fed to the sintering operation to recover soda and alumina from it.

The main sources of the greenhouse gases emissions of CO₂, NO₂ and CH₄ from the Bayer-sintering process are listed below, of which, the sintering step is the main focus of this section:

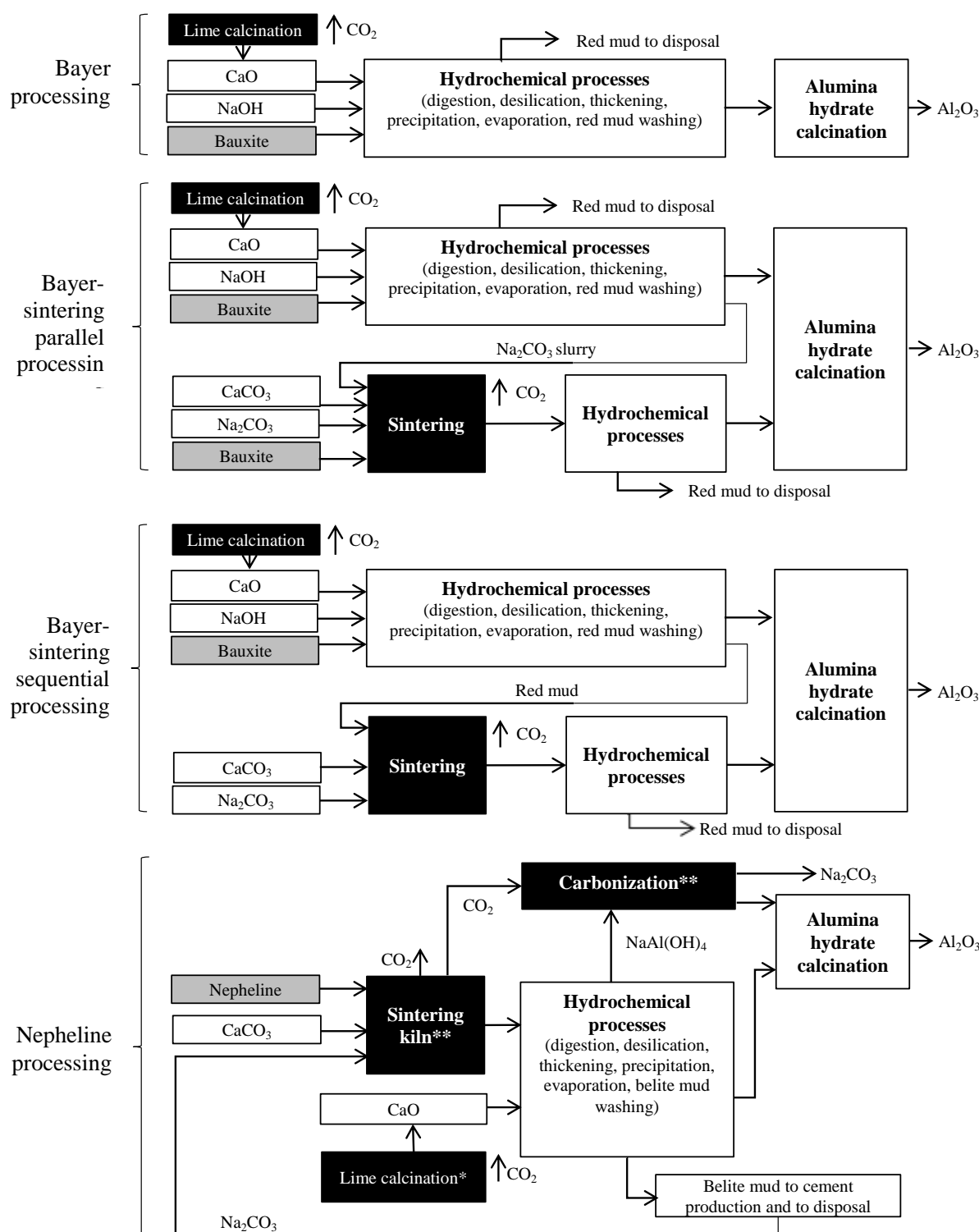
- Sintering (fuel combustion¹ and carbonates decomposition²)
- Power and heat production facilities (fuel combustion¹)
- Alumina hydrate calcination (fuel combustion¹)
- Lime calcination (fuel combustion and carbonates decomposition³).

¹ Calculation of GHG emissions shall be done in accordance to Volume 2 Energy, Chapter 2 Stationary Combustion for Fuel Burning.

² Emissions from carbonate decomposition shall be calculated in accordance to Section 4.4.5.2 of current chapter.

³ Calculation of GHG emissions shall be done in accordance to Volume 3 Industrial Processes and Product Use, Chapter 2 Mineral Industry Emissions, Section 2.3 Lime Production.

Final Draft

Figure 4.12a (new) Alumina production processes

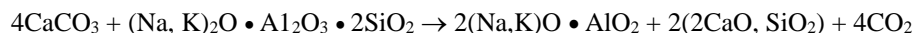
* Calculated in accordance to Volume 3 Industrial Processes and Product Use, Chapter 2 Mineral industry emissions, Section 2.3 Lime production.

** Calculated in accordance to Section 4.4.5.2 of the current chapter.

NEPHELINE PROCESS

The *Nepheline process* (NP) is another alternative route for alumina production (<1% of global production¹ in 2017), which uses nepheline as the raw material as opposed to bauxite in the conventional Bayer process. Nepheline ore is a sodium and potassium containing aluminosilicate that contains more silica than alumina. In order to make silica insoluble at the leaching process, it is combined with lime forming $2\text{CaO} \bullet \text{SiO}_2$ (belite) using the sintering process. The belite mud may be used in the cement production whereas sodium and potassium streams may be used to produce soda ash and potash resulting in complex processing of nepheline raw material.

The main steps in the process are (refer to Figure 4.12a): crushing and milling of nepheline with limestone and recycled soda liquor forming the raw mix; and sintering of the raw mix (at about 1300°C) in rotary kilns where calcium carbonate is decomposed and the following reaction between calcium oxide and nepheline takes place, forming CO_2 :



The nepheline sinter is leached with the dissolution of alkali aluminate. The sinter residue is separated and transported to be used in cement production and the aluminate liquor is passed on for desilication to remove partially dissolved silica from the liquor. Then, alumina hydrate is obtained from the green liquor partly by decomposition and partly by carbonisation. Carbonisation captures CO_2 in the process (Figure 4.12a).

The main sources of greenhouse gases emissions from the nepheline process are similar to the Bayer-sintering process. To avoid double counting CO_2 emissions related to by-products produced alongside alumina (i.e. belite mud for cement, soda ash, potash), shall be considered only in relation to the raw materials required for the aluminium production process.

OTHER GHG SOURCES AND CAPTURE

CO_2 and CH_4 are also produced during other sub-processes that are implemented or may be implemented at all alumina refineries but the emissions from such processes are currently considered to be negligible and not a main source of GHG emissions (<1%, expert judgement).

Examples of such sub-processes include: flue gas desulphurization, acid cleaning of process equipment, organic carbon in bauxite, liquor burning, etc.

There are also a number of CO_2 capture pathways to consider:

- Carbonization
- CO_2 absorption through use of bauxite residue for flue gas desulphurization
- CO_2 absorption through use of water collected from bauxite/nepheline storage residue area.

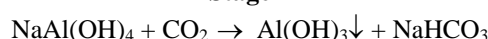
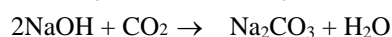
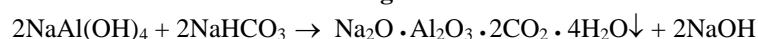
As noted throughout Volume 3 on Industrial Processes and Product Use (IPPU), the emission estimation methodologies outlined in this Chapter consider only process-related emissions and do not consider energy-related emissions. Inventory compilers should ensure that energy-related emissions are accounted for in the Energy Sector and that there is no double-counting of emissions between the Energy and IPPU Sectors. For example, the calculation of CO_2 emissions from fuel consumed in lime calcination, sintering, alumina hydrate calcination and electricity and heat production at a facility's own boilers, CHP or power plants should be considered using the guidance related to the combustion of fossil fuels.

¹ There is only a single alumina refinery that uses this technology (Russia) and estimate is based on its annual production as a proportion of total global alumina production.

Final Draft

CO₂ capture from carbonization in nepheline process

The main reactions of CO₂ capture by during the carbonization sub-process are:

Stage 1**Stage 2**

Part of CO₂ after Sintering is passed through gas treatment facilities to remove particles and other harmful components and then forwarded to carbonizers, where the carbonization reaction proceeds step by step. This is done in a two-stage process.

CO₂ absorption through use of circulating water collected from bauxite/nepheline storage residue area

If a refinery uses circulating water collected from bauxite/nepheline storage residue area, which contains a lot of sodium alkaline to treat flue gas to remove particles, SO₂ and other acid gases it should be assumed that the scrubbing system will also remove some CO₂ in the flue gas. The efficiency of CO₂ capture is very dependent on concentration of sodium alkaline in circulating water and type of scrubbing technology. If there is a lack of direct measurement data on CO₂/CO in flue gas where such scrubbing system is used, it is not recommended that CO₂ removal be considered in CO₂ calculations.

CO₂ absorption through bauxite residue neutralization

Carbonation of bauxite residue (red mud) can be carried out to utilize the capacity of this waste to capture CO₂ and in turn, the capacity of CO₂ to neutralize the highly alkaline red mud. The absorption of CO₂ is rapid and can be efficient if there is good contact between the residue and the CO₂. For high concentration CO₂ streams (90% or more) the reaction can be virtually 100% with a few seconds contact. Total alkalinity of red mud drops drastically with the added CO₂ recorded as an increase in bicarbonate alkalinity.

For lower concentrations of CO₂ such as flue gas where concentrations may be 12-15%, the reaction efficiency will be reduced. If CO₂ removal data is not available for bauxite residue contacted with gases containing less than 50% CO₂, then it is recommended that reaction efficiency of 35% be assumed by default.

CO₂ absorption can be estimated by multiplying the quantity of CO₂ injected into the process multiplied by the measured or assumed reaction efficiency.

Measurement of the increase in bicarbonate in the residue can also be used as a better measure of the amount of CO₂ actually absorbed in the neutralization process.

4.4.5.2 CHOICE OF METHOD FOR ALUMINA PRODUCTION

The decision tree in Figure 4.12b describes *good practice* in choosing the most appropriate method based on national circumstances.

In the Tier 1 method, emissions are estimated using alumina production data and national or default emission factors for the relevant technologies. The estimation of emissions directly from alumina production, without process specific information about raw materials and technology, is subject to high levels of uncertainty. This is because emissions from carbonates decomposition in the sintering and/or lime calcination processes can vary significantly.

Tier 2 implements method from Tier 1 but country-specific emission factors should be applied.

The Tier 3 approach relies on plant specific data. Tier 3 methods should also include a correction for emissions of dust. Tier 3 also includes a correction addition for emissions associated with dust not recycled to the kiln. Any uncalcined dust not recycled to the kiln should be subtracted from the total emissions estimate.

Should CO₂ capture technology be installed and used at a plant, it is *good practice* to deduct the CO₂ captured in a higher tier emissions calculation (Tier 3). The default assumption is that there is no CO₂ capture and storage (CCS) taking place. Any methodology taking into account CO₂ capture should consider that CO₂ emissions captured in the process may be both fuel combustion and process-related. In cases where combustion and process emissions are to be reported separately, e.g. for alumina production, inventory compilers should ensure that the same quantities of CO₂ are not double counted. In these cases, the total amount of CO₂ captured should preferably be reported in the corresponding energy combustion and IPPU source categories in proportion to the amounts of CO₂ generated in these source categories. For additional information on CO₂ capture and storage refer to Volume 3, Section 1.2.2 (under Industrial Processes and Product Use) and Volume 2, Section 2.3.4 (Under Energy).

TIER 1 METHOD FOR SINTERING

The Tier 1 method for lime production emissions is described in (Volume 3, Section 2.3.1.1). To avoid double counting, before applying this method it is essential to check whether lime production data from alumina plants is already considered in the inventory for lime production. If the lime production process at alumina plants has not been, included, the emissions associated with this process shall be considered as source related to alumina production. To attribute lime production emissions specifically to alumina production, it is necessary to gather data on how much of the national lime production occurs at alumina plants.

The Tier 1 method for the sintering process (including BSP, BSS and NP alumina production processes) is based on default emission factors, but requires country specific activity data on production mass produced by BSS, BSP and NP processes. If the Bayer-sinter (BS) process is used, the GHG emissions from the sintering are dependent on the quality of bauxite and the silica content of the bauxite. High silica content, low content of Al₂O₃ in ore leads to use of high carbonate content which results in greater GHG emissions. In case of Nepheline processing (NP), GHG emissions from the sintering are dependant on the Al₂O₃ content of the nepheline ore.

If detailed and complete data (including mass and composition) for the carbonates consumed in the sintering and lime production processes are not available, it is *good practice* to use aggregated national alumina production data, based on the technology applied, raw material and data on the proportion of Bayer and Bayer-sintering, expressed as an emission factor in the following Equation 4.27g:

EQUATION 4.27G (NEW)

TIER 1: SINTERING PROCESS EMISSIONS BASED ON ALUMINA PRODUCTION DATA

$$CO_2 \text{ Emissions} = M_{BS_Al_2O_3} \cdot S_{BS} \cdot EF_{BS_Sint} + M_{NP_Al_2O_3} \cdot S_{NP} \cdot EF_{NP_Sint} + M_{Lime} \cdot EF_{Lime}$$

Where:

$CO_2 \text{ Emissions}$ = emissions of CO₂ from sintering production, tonnes

$M_{BS_Al_2O_3}$ = mass of alumina produced by BSP and BSS processes, tonnes

$M_{NP_Al_2O_3}$ = mass of alumina produced by NP processes, tonnes

M_{Lime} = mass of lime produced, tonnes.

S_{BS} = mass fraction of alumina produced by BSP and BSS processes. The parameter can be varied from 0 to 1, where 1 is related to 100% of alumina produced by sintering process.

S_{NP} = mass fraction of alumina produced by NP process. The parameter can be varied from 0 to 1, where 1 is related to 100% of alumina produced by sintering process.

EF_{BS_Sint} = default emission factor for sintering BSP and BSS processes, tonnes CO₂/tonne alumina (see discussion under Section 4.4.6.3 Choice of Emission Factors), which is not corrected for dust.

EF_{NP_Sint} = default emission factor for sintering NP process, tonnes CO₂/tonne alumina (see discussion under Section 4.4.6.3 Choice of Emission Factors), which is not corrected for dust.

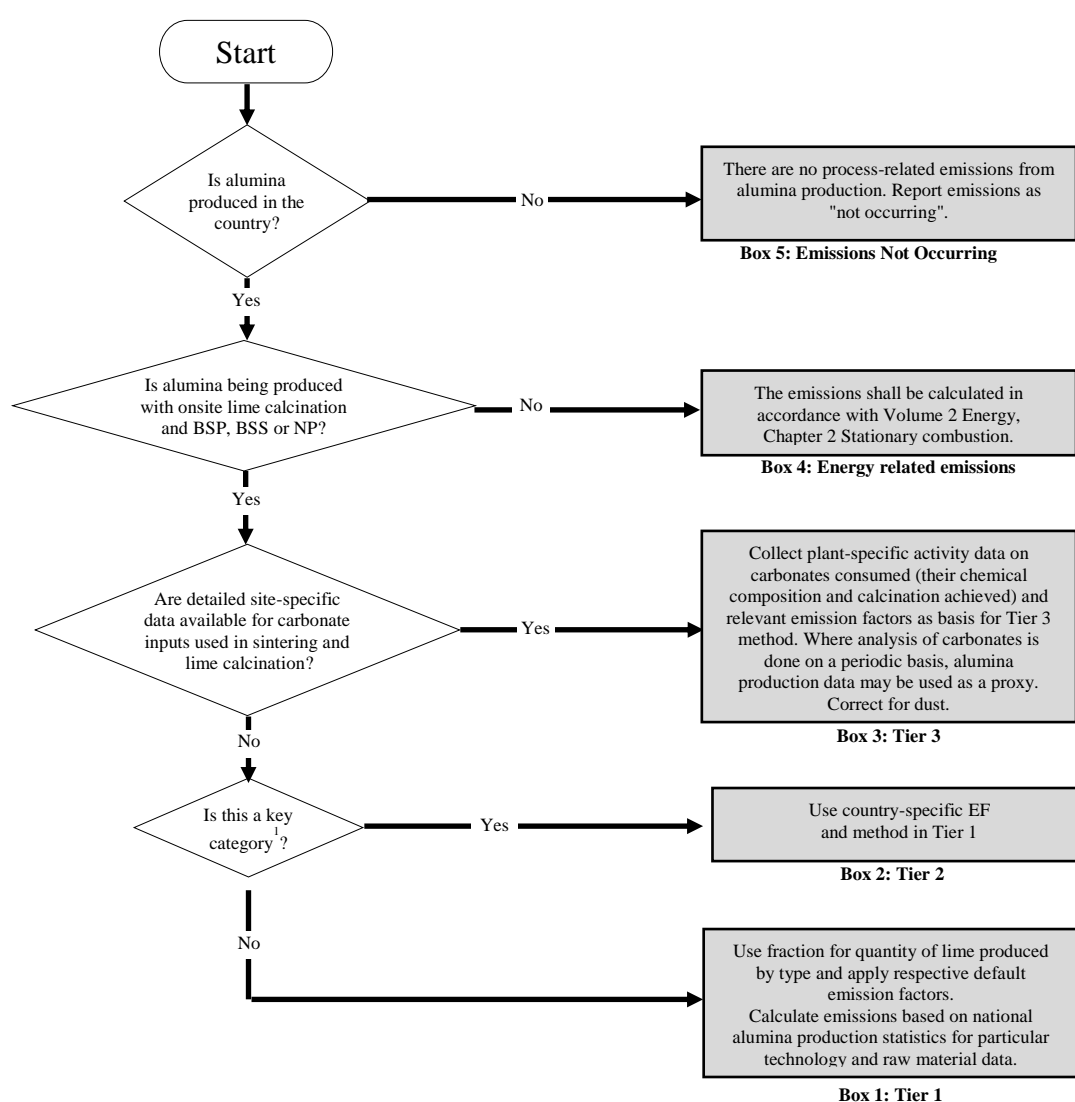
EF_{Lime} = default emission factor for lime production, tonnes CO₂/tonne lime (Volume 3, Section 2.3.1.2)

The Tier 1 approach is based on the following assumptions about the alumina production and sintering process:

Final Draft

- The mass fraction of alumina produced by sintering process (rather than the leaching process) is stable over time;
- In case of alumina production from the nepheline ore, 100% of alumina is produced with the sintering process;
- Plants are generally able to control the CaCO_3 content of the raw material inputs and output of sintering process within close tolerances;
- The CaCO_3 content of the raw materials inputs from a given plant tends not to change significantly over time;
- The main source of the CaO for most plants is CaCO_3 and, at least at the plant-specific level, any major non-carbonated sources of CaO are readily quantified (see Section 4.4.5.3 below);
- A 100 percent (or very close to it) calcination factor is achieved for the carbonate inputs for sintering output, including (commonly to a lesser degree) material lost to the system as non-recycled dust; and
- Dust collectors at plants capture essentially all of the dust;
- The capture of CO_2 cannot be quantified and assumed to be zero.

Figure 4.12b (new) Decision tree for estimation of CO_2 emissions from alumina production



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

TIER 2 METHOD FOR SINTERING

The Tier 2 method is a country specific method. This uses the same approach to Tier 1 in accordance with Equation 4.27g, but with regional or country specific emissions factors for calculation of CO₂ from sintering, instead of default emission factors.

TIER 3 METHOD FOR SINTERING: USE OF CARBONATE INPUT DATA

Where national level data for lime production at alumina refineries are available on the types of lime produced, it is *good practice* to estimate emissions using a Tier 3 approach described in of Chapter 2, Section 2.

For sintering processes, CO₂ emissions are calculated using a mass balance approach that considers the carbonates and carbon content of input and output materials. Carbonates of input materials are destroyed due to high temperatures in sintering kilns. The Tier 3 method uses actual concentrations of impurities.

Tier 3 is based on the collection of disaggregated data on the types (compositions) and quantities of carbonates consumed in the sintering process at a particular plant, as well as the respective emission factors of the carbonates consumed. Emissions are then calculated using Equation 4.27h. The Tier 3 approach includes an adjustment to subtract any uncalcined carbonate within sintering kiln dust (SKD) that is not returned to the kiln. If the SKD is fully calcined, or all of it is returned to the kiln, this SKD correction factor becomes zero. Tier 3 is still considered to be *good practice* in instances where inventory compilers do not have access to data on uncalcined SKD. However, excluding uncalcined SKD may result in slightly overestimated emissions.

Limestones and shales (raw materials) may also contain a proportion of organic carbon (kerogen), and other raw materials (e.g., fly ash) may contain carbon residues, which would yield additional CO₂ when burned. These emissions typically are not accounted for in the Energy Sector, but if carbon-containing raw materials are used extensively, inventory compilers should endeavour to see if they are included in the Energy Sector. Currently however, there is insufficient data on the kerogen or carbon contents of non-fuel raw materials for mineral processes to allow a meaningful default value related to the average kerogen content of raw materials to be provided in this chapter. For plant-level raw material-based calculations (Tier 3) where the kerogen content is high (i.e., contributes more than 5% of total heat), it is *good practice* to include the kerogen contribution to emissions.

The Tier 3 approach will likely only be practical for individual plants and countries that have access to detailed plant-level data on the carbonate raw materials. Emissions data collected at the plant level should then be aggregated for purposes of reporting national emissions estimates. It is recognized that frequent calculations of emissions based on direct analysis of carbonates could be burdensome for some plants. As long as detailed chemical analyses of the carbonate inputs are carried out with sufficient frequency to establish a good correlation between the carbonates consumed at the plant level and the resulting alumina production, the sinter output may then be used as a proxy for carbonates for emissions calculations in the intervening periods. That is, a plant may derive a rigorously-constrained emission factor for the plant's alumina, based on periodic calibration to the carbonate inputs and outputs.

EQUATION 4.27H (NEW)**TIER 3: EMISSIONS BASED ON CARBONATE RAW MATERIAL INPUTS TO THE SINTERING KILN**

$$CO_2 \text{ Emissions} = \sum_i (M_{oi} \cdot C_{iCO_2}) + E_{LC} + EF_s \cdot M_s + (0.71 C_{Na_2O} \cdot V_s) / 1000 - E_{sp} - E_{rm} - E_{SKD} - E_{nf} \cdot E_{cc}$$

Where:

$CO_2 \text{ Emissions}$ = total emissions of CO₂ from sintering kiln, tonnes

$\sum_i (M_{oi} \cdot C_{iCO_2})$ = CO₂ emissions from carbonates in bauxite or nepheline ore decomposed in kiln, tonnes

M_{oi} = mass of i ore recalculated per dry conditions consumed in the kiln, tonnes

C_{iCO_2} = the weighted average content of CO₂ in i bauxites (nephelines) according to chemical analysis and assumption that 100% calcination will be achieved (in the absence of chemical analysis results, the content of CO₂ in nephelines is determined as the difference in loss on ignition and SO₃), as given by Equation 4.27k), fraction

E_{LC} = CO₂ emissions released from lime calcination, tonnes CO₂. The calculation shall be done in accordance to Tier 3 approach described in Volume 3 IPPU, Chapter 2, Section 2.3. To avoid double counting before applying this method it is necessary to check if limestone usage data from alumina plant is already considered at national level and CO₂ emissions from lime calcination are already considered in lime production data. If limestone usage for sintering process at alumina plants has not

Final Draft

2172 been considered at national level, this process shall be considered as source related to alumina
 2173 production emission. If the emissions are considered as lime calcination emissions they shall be
 2174 removed from calculations by this formula.

2175 $EF_s \bullet M_s$ = CO₂ emissions from soda carbonate decomposition, tonnes. To avoid double counting before
 2176 applying this method it is necessary to check if this source is already considered at national level. If
 2177 soda decomposition in sintering process at alumina plants has not been considered at national level,
 2178 this process shall be considered as source related to alumina production emission. If the emissions
 2179 accounted for in Volume 3 (under Industrial Processes and Product Use), Chapter 2 (Mineral Industry
 2180 Emissions), Section 2.5 (Other Process Uses of Carbonates) they shall be removed from calculations
 2181 by this formula.

2182 EF_s = emission factor for soda carbonate forwarded to the kiln with ore, tonnes CO₂ / tonnes soda carbonate
 2183 (see Table 2.1 Chapter 2 Mineral Industry emissions)

2184 M_s = mass of soda forwarded to the kiln with ore, tonnes

2185 $(0.71 C_{Na2O} \bullet V_s) / 1000$ = CO₂ emissions from the decomposition of soda contained in a soda solution,
 2186 tonnes

2187 0.71 = stoichiometric conversion factor of CO₂ from Na₂O. Na₂O is measure in the soda solution.

2188 C_{Na2O} = concentration of sodium oxide (carbonate) in the soda solution, forwarded to the kiln, g/L

2189 V_s = volume of soda solution, m³

2190 E_{sp} = CO₂ emissions captured during carbonization process and contained in produced sodium carbonate,
 2191 tonnes CO₂ (as given by Equation 4.27i)

2192 E_{rm} = CO₂ emissions based on the mass of carbon in bauxite or nepheline residue, tonnes (refer to Equation
 2193 4.27l)

2194 E_{SKD} = CO₂ emissions from un-calcined SKD not recycled to the kiln, tonnes (refer to Equation 4.27j)

2195 E_{nf} = CO₂ emissions from carbon-bearing non-fuel materials (as given by Equation 4.27m), tonnes.

2196 E_{cc} = CO₂ absorption through use of circulating water collected from bauxite/nepheline storage residue area
 2197 and/or absorption through bauxite residue neutralization (as given by Equation 4.27n), tonnes

2198

<p>2199 EQUATION 4.27I (NEW)</p> <p>2200 EMISSIONS CAPTURED DURING CARBONIZATION PROCESS AND CONTAINED IN PRODUCED</p> <p>2201 SODIUM CARBONATE</p> <p>2202 $E_{sp} = EF_s \bullet M_{sout}$</p>

2203 Where:

2204 E_{sp} = CO₂ emissions captured during carbonization process and contained in produced sodium carbonate,
 2205 tonnes

2206 EF_s = emission factor for soda carbonate forwarded to the kiln with ore tonnes CO₂ / tonnes soda carbonate
 2207 (see Table 2.1 Chapter 2 Mineral Industry emissions).

2208 M_{sout} = mass of soda produced for using out of plant, tonnes.

2209

<p>2210 EQUATION 4.27J (NEW)</p> <p>2211 EMISSIONS FROM UN-CALCINED SKD NOT RECYCLED TO THE KILN</p> <p>2212 $E_{SKD} = ((M_{dr} + M_{dnr}) \bullet E_{ac} / 100 \% - M_{dr}) \bullet C_{CO2}$</p> <p>2213 OR</p> <p>2214 $E_{SKD} = (M_d \bullet E_{ac} / 100 \% - M_{dr}) \bullet C_{CO2}$</p>

2215 Where:

2216 E_{SKD} = CO₂ emissions from un-calcined SKD not recycled to the kiln, tonnes.

2217 M_{dr} = mass of SKD recycled to the kiln, tonnes.

2218 M_{dnr} = mass of SKD not recycled to the kiln (= 'lost' SKD), tonnes.

2219 M_d = mass of SKD forwarding to exhausted gases cleaning facilities at sintering kilns, tonnes.

2220 E_{ac} = efficiency of exhausted gases cleaning facilities at sintering kilns, percentage.

2221 C_{CO_2} = carbon content in dust recalculated in CO₂, fraction.

2222

2223 **EQUATION 4.27K (NEW)**

2224 **WEIGHTED AVERAGE CONTENT CO₂ IN 'I' BAUXITES (NEPHELINES)**

2225 $C_{iCO_2} = \sum_j (EF_j \cdot M_j \cdot F_j)$

2226 Where:

2227 C_{iCO_2} = the weighted average content of CO₂ in i bauxites (nephelines) according to chemical analysis,
2228 assuming 100% calcination of the carbonate, fraction

2229 EF_j = emission factor for the particular carbonate j , tonnes CO₂ / tonnes carbonate (see Table 2.1 Chapter
2230 2 Mineral Industry emissions)

2231 M_j = mass fraction of carbonate j consumed in the kiln, fraction

2232 F_j = fraction calcination achieved for carbonate j , fraction¹

2233

2234 **EQUATION 4.27L (NEW)**

2235 **EMISSIONS FROM BAUXITES (NEPHELINES) RESIDUE**

2236 $E_{rm} = 44/12 \cdot M_{br} \cdot C_c$

2237 Where:

2238 E_{rm} = CO₂ emissions based on the mass of carbon in bauxite or nepheline residue, tonnes

2239 M_{br} = mass of dry bauxite or nepheline residue disposed, tonnes

2240 C_c = mass fraction of C in dry bauxite or nepheline residue, fraction

2241

2242 **EQUATION 4.27M (NEW)**

2243 **EMISSIONS FROM CARBON-BEARING NON-FUEL MATERIALS**

2244 $E_{nf} = \sum_k (M_k \cdot X_k \cdot EF_k)$

2245 Where²:

2246 E_{nf} = CO₂ emissions from carbon-bearing nonfuel materials, tonnes

2247 M_k = mass of organic or other carbon-bearing non-fuel raw material k , tonnes

2248 X_k = fraction of total organic or other carbon in specific non-fuel raw material k , fraction

2249 EF_k = emission factor for kerogen or other carbon-bearing nonfuel raw material k , tonnes CO₂/tonne
2250 carbonate

2251

¹ For F_i , calcination fraction (Equation 4.27k): In the absence of actual data, it may be assumed that, at the temperatures and residence times achieved in sintering kilns, the degree of calcination achieved for all material incorporated in the sintering feed is 100 percent (i.e., $F_i = 1.00$) or very close to it. For SKD, a F_i of <1.00 is more likely but the data may show high variability and relatively low reliability. In the absence of reliable data for SKD, an assumption of $F_i = 1.00$ will result in the correction for SKD to equal zero.

² The ignored CO₂ emissions from non-carbonate carbon (e.g., carbon in kerogen, carbon in fly ash) in the non-fuel raw materials can be considered negligible if the heat contribution from kerogen or other carbon is < 5% of total heat (from fuels).

Final Draft

EQUATION 4.27N (NEW)
CO₂ ABSORPTION THROUGH USE OF CIRCULATING WATER COLLECTED FROM
BAUXITE/NEPHELINE STORAGE RESIDUE AREA AND/OR ABSORPTION THROUGH BAUXITE
RESIDUE NEUTRALIZATION

$$E_{cc} = V_{gas} \cdot C_{co_2} \cdot D_{co_2} \cdot GTE_{co_2} / 100$$

Where:

E_{cc} = CO₂ absorption through use of circulating water collected from bauxite/nepheline storage residue area and/or absorption through bauxite residue neutralization, tonnes

V_{gas} = exhaust gas volume forwarded to exhaust gas treatment facility, cubic meters

C_{co_2} = CO₂ concentration in exhaust gas (instrumental measures), fraction of volume

D_{co_2} = CO₂ destiny under normal conditions, tonn/cubic meters

GTE_{co_2} = exhaust gas treatment facility efficiency (instrumental measures), percentage

4.4.5.3 CHOICE OF EMISSION FACTORS FOR ALUMINA PRODUCTION

Emissions factors for Sintering can be chosen based on available data. In the case that site-specific data is not available, Tier 1 default emission factors can be used. Emissions factors for lime production are provided in Volume 3, Section 3.3.1.2.

TIER 1 METHOD FOR SINTERING

The implementation of sintering processes is determined by bauxite quality (alumina content), carbonates and silica content in the ore which can vary significantly. Based on existing process data from operating plants, Tier 1 emissions factors were derived for Bayer-sintering processes and the nepheline-sintering process (NP), to be applied in Equation 4.27g (see Table 4.17a). For Bayer-sintering process Tier 1 emissions factors can be applied for both parallel (BSP) and sequential (BSS) processes.

TABLE 4.17A (NEW)
TECHNOLOGY SPECIFIC DEFAULT EMISSION FACTORS FOR THE CALCULATION OF CO₂ EMISSIONS FROM ALTERNATIVE SINTERING PROCESSES (TIER 1 METHOD)

Technology	EF _{SintAl₂O₃} (tonne CO ₂ /tonne Al) ^a	Uncertainty Range (%) ^b
Bayer-sintering (BSP and BSS)	0.81	-8/+4
Nepheline-sintering process (NP)	2.46	-2/+4

^a The defaults based on the following process data – alumina content (Al₂O₃) is 45.8% in bauxites and 26.2% in nepheline ore. Bauxite and nepheline consumption in sintering is very depend on Al₂O₃ content and in case of poor ore where Al₂O₃ content is out of range EF shall be higher and uncertainty level will increase.

^b Uncertainty range is based on calculations from alumina plants that operate sintering kilns for several years based on alumina content as described above.

TIER 2 METHOD FOR SINTERING

Country-specific emission factors should be collected based on knowledge of technologies (technological routes) implemented at a country's facilities and also based on data for lime (country-specific carbon content). Tier 1 method then should be applied.

If alumina plants have sintering processes, site specific data should be obtained relating to the volume of alumina production, % of alumina produced with sintering. Plant specific volume of alumina production, percentage of alumina produced with sintering and information about the bauxite sources or technology and country specific emissions factors shall be calculated and should be provided for each national-level GHG emissions calculation campaign.

TIER 3 METHOD FOR SINTERING

The Tier 3 emission factors are based on the actual CO₂ content of the carbonates present (see Equation 4.27h in this chapter and Table 2.1 of Volume 3, Chapter 2 Mineral Industry Emissions). The Tier 3 approach requires the full accounting of carbonates (species and sources).

CO₂ emissions captured by other CO₂ capturing technologies can be calculated using site specific data only. Where such data is unavailable, CO₂ emissions captured do not considered in CO₂ emissions calculation.

If there is no site-specific data for mass of carbon in bauxite or nepheline residue, the following data can be used as worldwide figures:

- CO₂ in bauxite and nepheline residue 1% of dry content with a $\pm 50\%$ uncertainty range¹.

Emissions correction factor for sintering kiln dust (SKD)

Dust may be generated at various points in the kiln line apparatus used for sintering. The composition of this dust can vary depending on where it is generated but all may be included under the term 'sintering kiln dust' (SKD). SKD includes particulates derived from the raw materials, and the original carbonate component of the dust may be incompletely calcined. SKD can be efficiently captured by dust control technology and then recycled to the kiln (the preferred practice), or it may be directly returned to the kiln in the combustion air, or it may be disposed of after capture. The degree to which SKD can be recycled to the kiln depends on various considerations and usually 100% of collected dust are returned to the kiln. Any SKD not recycled to the kiln is considered to be 'lost' to the process and emissions associated with it will not be accounted by sintering process. To the degree that the lost SKD represents calcined carbonate raw materials, the emissions from these calcined raw materials represent a subtraction in the Tier 3 calculation. The kiln dust may consist of dust from raw materials as well as dust from burning of liquid or solid fuels. In that case where combustion and process emissions are to be reported separately, e.g. for alumina production, inventory compilers good practice ensure that the carbon in dust related to fuel combustion are not double counted. In these cases, the total amount of C in dust from fuel burning should preferably be extracted from IPPU source categories in proportion to the amounts of CO₂ generated in these source categories.

4.4.5.4 CHOICE OF ACTIVITY DATA

TIER 1 METHOD

In Tier 1, national-level data should be collected only for those plants where lime calcination processes are part of alumina production process. However, calcined lime purchased from other producers should not be considered to avoid double counting.

If a proportion of calcined lime is produced for uses other than alumina production, to avoid double counting CO₂ emissions from carbonates decomposition at the lime calcination kiln shall be related to alumina production in the proportion of lime used for alumina production only. CO₂ emissions related to other uses of calcined lime shall be reported as emissions related to lime calcination described at Chapter 2 Section 2.3. The detailed information about choice of activity data for lime production please refer to Section 2.3.1.3 in Volume 3, Chapter 2.

If alumina plants have sintering processes, site specific data should be obtained relating to the volume of alumina production, % of alumina produced with sintering. Plant specific volume of alumina production, percentage of alumina produced with sintering and information about the bauxite sources or technology should be provided for each national-level GHG emissions calculation campaign.

TIER 2 METHOD

In Tier 2, national-level data should be collected only for those plants where sintering/lime calcination processes are part of alumina production process. However, calcined lime purchased from other producers should not be considered to avoid double counting.

¹ The uncertainty range is based on expert judgment.

Final Draft

TIER 3 METHODS

For lime production process refer to Section 2.3.1.3 Choice of Activity Data in Volume 3, Chapter 2.

The type of activity data required for Tier 3 is likely available only at individual plants. Any reporting entity using Tier 3 should ensure that all carbonate inputs (i.e., types, amounts, all sources) to the kiln are fully investigated as part of the initial implementation of the Tier 3 method, and the full investigation repeated whenever there is any significant change in materials or processes. After a full analysis of the carbonate inputs is completed, and assuming that no significant change in the composition of materials or production process takes place, it is consistent with *good practice* to develop a rigorous plant-specific emission factor based on the carbonate input analysis and apply that emission factor to sintering process. Subsequently, the sintering production data may then be used for the carbonate calculations to estimate emissions. To be consistent with *good practice*, this linkage should be periodically recalibrated.

In general, data related to carbonated input materials should be collected annually. However, it is likely that there could be a carbonate component within the mass of carbon in bauxite or nepheline residue, emissions from uncalcined SKD not recycled to the kiln, and perhaps some other fuels (emissions from carbon-bearing nonfuel materials). If, during the full investigation, it is determined that the amount of carbonates from non-major sources is small (e.g., less than 5% of total carbonate) the plant can apply a constant value for the minor source(s) in intervening years before the next full investigation. Recognizing that estimating activity data for these smaller sources may lead to analytical (and other) errors, it may be assumed for emission calculation purposes that the minor source of carbonate is CaCO_3 , but this assumption should be transparently documented.

Activity data should exclude any carbonates that are not fed into the kiln.

4.4.5.5 COMPLETENESS

Alumina production data may be available in national statistical databases, or could be collected, if such data have not been published in national statistics.

Completeness is a particularly important issue to consider where plant specific data are used to estimate national emissions using Tier 3. Under Tier 3, it is important that all alumina plants with lime production and sintering processes are considered, and that all carbonates consumed in the sintering process are included in the emission calculation. Plants with bauxites/nephelines sintering processes are well identified in each country, but data on the fraction weight of carbonates consumed may not be readily available. In order for the Tier 3 method to be considered ‘complete’, all carbonates consumed must be recorded.

In countries where only a subset of plants with lime production and bauxites/nephelines sintering processes report data for the Tier 3 method, it may not be possible to report emissions using a Tier 3 for all facilities during the transition. Where data on the carbonate inputs are not available for all plants to report using Tier 3, it may be possible to determine the share of production represented by non-reporting plants and use this information to estimate the remaining emissions using Tier 1 in order to ensure completeness during the transition period.

The potential for double counting also should be considered. For example, it is good practice for inventory compilers to review statistics used to estimate emissions from the source category ‘Other Process Uses of Carbonates’ and ‘Lime production’ to ensure that emissions reported in that source category do not result from the use of these carbonates in alumina production. Where carbonates are used for alumina production, it is *good practice* to report the emissions under Alumina Production. Finally, inventory compilers should include only process-related emissions from alumina production in this source category. To avoid double-counting, it is *good practice* to account for combustion-related emissions in the Energy volume.

There is one additional issue that, while not included in the current methodology, may become relevant for consideration in the future. Sodium alkaline contained in bauxite/nepheline residue area can re-absorb atmospheric CO_2 . However, the rate of carbonation is very slow (years to centuries).

4.4.5.6 DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to collect site specific data where possible for all inventory years. However, often it can be difficult to collate historic data for closures, closed operations or if significant changes in changes in technology or sourcing of bauxites/nephelines has taken place. In such cases, inventory compilers can consult industry experts to assist with extrapolation of CO_2 emission figures (e.g. normalization by volume of alumina production or based on applying of data from similar plants in the reporting country or average worldwide figures for similar technology). See also Chapters 2 and 5 of Volume 1 of 2006 IPCC Guidelines.

For lime production, refer to Section 2.3.1.5 in Chapter 2.

4.4.6 Uncertainty assessment for alumina production

Uncertainty estimates for bauxite/nepheline sintering processes result predominantly from uncertainties associated with activity data, and to a lesser extent, from uncertainty related to the emission factor.

Uncertainty estimates for lime production is described at Section 2.3.2 Uncertainty assessment in Chapter 2 Volume 3 of 2006 *IPCC Guidelines*.

4.4.6.1 EMISSION FACTOR UNCERTAINTIES

For Tier 1, the major uncertainty component is associated with the emission factor for sintering.

For Tier 2 and 3, there is relatively little uncertainty associated with the emission factors of the source carbonates because they are based on plant specific data, stoichiometric ratios and mass balance approaches.

4.4.6.2 ACTIVITY DATA UNCERTAINTIES

The uncertainty for percentage of bauxite/nepheline processing at sintering process is moderate. The level of uncertainty is indicated in the Table. 4.17b. The uncertainty in data on alumina production tonnages is about 1 percent.

For Tier 3, the uncertainty in data on weight or mass of *i* ore recalculated per dry conditions consumed in the kiln tonnages, is about 1-2 percent. Collecting data from individual producers (if complete) rather than using national totals will reduce the uncertainty of the estimate because these data will account for variations in conditions at the plant level. Except for SKD the greatest sources of uncertainty associated with Tier 3 are the uncertainties associated with identification of carbonate species (1-5%) and the weight of raw materials.

Although emissions are much smaller than from carbonates, there may be considerable uncertainty associated with estimating emissions from SKD in Tier 3 if plants do not weigh the SKD that is not recycled to the kiln or if the plants lack SKD scrubbers. Where the weight and composition of SKD are unknown for a plant, the uncertainty will be higher. As an example, an estimate of the uncertainties for different factors is presented in equations 4.27h-4.27n. The uncertainties are presented in Table 4.17b and are approximate component uncertainties – that is, they are those associated with a particular operation or activity in the bauxite/nepheline processing at sintering process. In order to quantify uncertainty for bauxite/nepheline processing at sintering process, the default uncertainties provided in Table 4.17b should be combined.

Final Draft

TABLE 4.17B (NEW) DEFAULT UNCERTAINTY VALUES FOR BAUXITE/NEPHELINE SINTERING PROCESSES		
Uncertainty ^a	Comment	Tier
Chemical Analysis / Composition		
1-3%	Percentage of bauxite processing at sintering process	1
10%	Estimation of percentage of bauxite processing at sintering process	1
-2/+4%	Emission factor for sintering (NP)	1
-8/+4%	Emission factor for sintering (BSP and BSS)	1
10%	Assumption that emission factor for sintering is permanent over the years	1
5%	The content of sodium oxide (carbonate) in the soda solution, forwarded to the kiln	3
15%	Estimation of content of sodium oxide (carbonate) in the soda solution, forwarded to the kiln	3
5%	The weighted average content of C in dry bauxite/nepheline residue	3
50%	Estimation of weighted average content of C in dry bauxite/nepheline residue	3
1%	Weight or mass share of particular carbonate consumed in the kiln	3
2%	Fraction calcination achieved for carbonates	3
10-20%	Assumption 100% of fraction calcination achieved for carbonate	3
3%	Weight or mass of organic or other carbon-bearing nonfuel raw material	3
3%	Fraction of total organic or other carbon in specific nonfuel raw material	3
50%	Estimation of weight or mass of organic or other carbon-bearing nonfuel raw material	3
50%	Estimation of fraction of total organic or other carbon in specific nonfuel raw material	3
1-3%	Kerogen (or other non-carbonate carbon) determination	3
10%	CO ₂ concentration in exhaust gas	3
5%	Exhaust gas treatment facility efficiency	3
1%	CO ₂ destiny under normal conditions	3
Production Data		
1-2%	Reported (plant-level) alumina production data	1, 3
10%	Use of estimated country (or aggregated plant) production data (national statistics).	1
1-2%	Weight or mass of ore recalculated per dry conditions consumed in the kiln	3
10%	Estimation of weight or mass of ore recalculated per dry conditions consumed in the kiln	3
1-2%	Weight or mass of soda forwarded to the kiln with ore	3
10%	Estimation of weight or mass of soda forwarded to the kiln with ore	3
2%	Volume of soda solution	3
35%	Estimation of volume of soda solution	3
1-2%	Weight or mass of soda produced for using out of plant	3
5%	CO ₂ emissions captured by other CO ₂ capturing technologies	3
15%	Estimation of CO ₂ emissions captured by other CO ₂ capturing technologies	3
5%	Mass of bauxite/nepheline residue disposed	3
10%	Estimation of bauxite/nepheline residue disposed	3
2%	Exhaust gas volume forwarded to exhaust gas treatment facility	3

2418

TABLE 4.17B (NEW) (CONT.) DEFAULT UNCERTAINTY VALUES FOR BAUXITE/NEPHELINE SINTERING PROCESS		
SKD		
1-2%	Weight or mass of SKD recycled to the kiln	3
10%	Estimation of weight or mass of SKD recycled to the kiln	3
1-2%	Weight or mass of SKD not recycled to the kiln	3
10%	Estimation of weight or mass of SKD not recycled to the kiln	3
1-2%	Efficiency of exhausted gases cleaning facilities at sintering kilns	3
10%	Estimation of efficiency of exhausted gases cleaning facilities at sintering kilns	3
1-2%	Carbon content in dust recalculated in CO ₂	3
10%	Estimation of carbon content in dust recalculated in CO ₂	3
^a Uncertainty estimates are based on expert judgement.		

4.4.7 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation for alumina production

4.4.7.1 QUALITY ASSURANCE / QUALITY CONTROL (QA/QC)

In addition to the general guidance on QA/QC, specific procedures of relevance to this source category are outlined below.

COMPARISON OF EMISSIONS ESTIMATES USING DIFFERENT APPROACHES

Comparisons could be made between estimated emissions using different tiers. For example, if a bottom-up approach is used to collect activity data (i.e., collection of plant-specific data), then inventory compilers should compare the emissions estimates to the estimates calculated using national production data alumina production (top-down approach). In cases where a hybrid Tier 1 or Tier 3 approach is used during a transition period, it is considered *good practice* also to estimate emissions for all facilities using the lower Tier in order to compare the results of the analysis to the results derived using the hybrid approach. The results of such comparisons should be recorded for internal documentation, including explanations for any discrepancies.

REVIEW OF EMISSION FACTORS

Inventory compilers should compare aggregated national emission factors with the IPCC default factors in order to determine if the national factor is reasonable relative to the IPCC default. Differences between national factors and default factors should be explained and documented, particularly if they are representative of different circumstances.

If the aggregated top-down approach is used, but some limited plant-specific data are available, inventory compilers should compare the site or plant level factors with the aggregated factor used for the national estimate. This will provide an indication of the reasonableness and the representability of the data.

SITE-SPECIFIC ACTIVITY DATA CHECK

For site-specific data, inventory compilers should review inconsistencies between sites to establish whether they reflect errors, different measurement techniques, or result from real differences in emissions, operational

Final Draft

2450 conditions or technology. For alumina production, inventory compilers should compare plant data with other plants
2451 in the country.

2452 Inventory compilers should ensure that emission factors and activity data are developed in accordance with
2453 internationally recognised and proven measurement methods. If the measurement practices fail this criterion, then
2454 the use of these emissions or activity data should be carefully evaluated, uncertainty estimates reconsidered, and
2455 qualifications documented. If there is a high standard of measurement and QA/QC in place at most sites, then the
2456 uncertainty of the emissions estimates may be revised downwards.

2457 4.4.7.2 REPORTING AND DOCUMENTATION

2458 It is *good practice* to document and archive all information required to produce the national emissions inventory
2459 estimates. Specific documentation and reporting relevant to this source category follow.

2460 TIER 1 METHOD

2461 Any information regarding the carbonates content of sintering feed should be documented, including use of default
2462 values different from those discussed in section 4.4.5.3.

2463 TIER 2 METHOD

2464 Any county-specific information should be documented (technologies, amount of alumina produced by each
2465 technology type, amount and quality of lime used, etc.)

2466 TIER 3 METHOD

2467 When documenting the Tier 3 method it is important to document all the procedures undertaken and methodologies
2468 used to identify the weight fraction and identities of all carbonates, including carbonates incorporated in any raw
2469 materials along with the corresponding emission factors.

2470 Estimating total emissions from carbonate inputs can overestimate emissions if the carbonates are not fully
2471 calcined. Any corrections should be documented. This includes documenting the fraction calcination of the raw
2472 materials and the quantity and fraction calcination of the SKD.

2473 It is likely that plants will find it impractical to undertake chemical analyses of all raw material inputs on a daily
2474 basis for the purpose of CO₂ calculations. Instead, it is *good practice* for a full analysis to take place at each facility
2475 on a number of occasions throughout the year to fully characterise the carbonate inputs. Facilities will likely
2476 develop a relationship between carbonate input and alumina production that will be applied to the plant's routine
2477 calculation alumina production with sintering for intervening periods. In addition to identifying all procedures
2478 used to calculate emissions from the carbonate inputs, all steps necessary to identify the relationship between
2479 carbonate input and alumina production should be documented.

2480 All underlying information should be documented and reported, it is not considered *good practice* to report just
2481 final emissions estimates.

2482

2483

2484

2485

2486

2487

2488

2489

2490

2491 **4.5 MAGNESIUM PRODUCTION**

2492 No Refinement

2493

2494 **4.6 LEAD PRODUCTION**

2495 No Refinement

2496

2497 **4.7 ZINC PRODUCTION**

2498 No Refinement

2499

4.8 RARE EARTHS PRODUCTION

This sub-chapter 4.8 “Rare Earths Production” provides new guidance for greenhouse gas (GHG) emissions from the primary production of rare earth (RE) metals and alloys¹, specifically CO₂ and perfluorocarbon (PFC) emissions. Since the *2006 IPCC Guidelines* do not have existing guidance on emissions from the rare earths industry, this is an entirely new sub-chapter, and follows on sub-chapter 4.7 Chapter 4 Volume 3 of the *2006 IPCC Guidelines*.

4.8.1 Introduction

‘Rare earths’ is used to refer to the group of 17 chemically similar metallic elements of scandium (Sc), yttrium (Y) and the lanthanides, i.e.: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). The raw materials and trading goods are often in the form of rare earth oxides (REO).

Worldwide, primary production of many rare earth (RE) metals and alloys is carried out using a molten fluoride-salt electrolytic reduction process that is similar to primary aluminium’s Hall-Heroult process² (refer to sub-chapter 4.4). According to (Vogel & Friedrich 2015; Vogel & Friedrich 2018; Zhang *et al.* 2018), this process consists of:

- Dissolving and electrolytically reducing REOs (e.g. Nd₂O₃) in a molten salt of rare earth fluorides (REF₃) and lithium fluoride (LiF) – an example composition is 85% wt NdF₃, 10% LiF and 5% Nd₂O₃ for Nd metal production;
- Carbon anodes (e.g. graphite), which are consumed in the process;
- Cathodes, which are either inert (e.g. tungsten cathodes for Nd metal production) or are consumed in the process (e.g. Fe cathodes for Dy-Fe alloy production);
- A process that is carried out at high temperature (~1050-1100°C) and depending on the technology, may be periodically interrupted or disturbed by anode replacements, cathode removal/replacement and removal of liquid RE metal/alloy, etc.

Neodymium (Nd) is one of the most commonly produced RE metals by this process. Other RE metals and alloys produced via this route include: Pr, Pr-Nd, La, Dy-Fe, Gd-Fe, Ho-Fe, Ce, La-Ce, Y-Mg and mischmetal (Vogel & Friedrich 2018).

Alternative routes for RE metal and alloy production are outside the scope of these guidelines, since they are either not employed on an industrial scale or do not generate GHGs (Vogel & Friedrich 2018). These include chloride-salt electrolytic reduction (now largely replaced by the fluoride-based process) and calciothermic reduction (e.g. for production of samarium for Sm-Co magnets).

Industrial fluoride-based rare earth smelters vary in terms of electrical current (and hence size), the number and configuration of anodes and cathodes, and the level of automation in the process. Currently, the most widely used technologies are those at lower amperage (~5-6 kA) – these typically employ small round-shaped cells, with only single (or several) vertical anodes and cathodes and typically have very low levels of automation. Higher amperage technologies typically are larger, oval or rectangular shaped cells and are equipped with multiple vertical anodes and/or cathodes (Wen *et al.* 2004; Wen *et al.* 2012; Vogel & Friedrich 2015).

In general, the level of automation in rare earth production is considerably lower than that found in primary aluminium production (sub-section 4.4). However, some newer production technologies may be equipped with automatic process control features, including automatic feeding of REOs and automatic detection of anode effects, in order to reduce perfluorocarbon GHG emissions (refer to section 4.8.2.3).

¹ Carbon dioxide (CO₂) emissions associated with the production of electricity from fossil fuel combustion to produce rare earth metals and alloys are covered in Volume 2: Energy.

² Due to similarities between the primary aluminium and rare earth metal smelting processes (both produce metal from electrolysis of metal oxides in molten fluoride-salts, using consumable carbon anodes), the guidelines here for the rare earths industry have been adapted using existing guidelines for primary aluminium production (*2006 IPCC Guidelines*, Volume 3, Chapter 4, sub-chapter 4.4) as a basis. Although both processes generate CO₂ and PFC emissions through similar fundamental mechanisms, there are clear differences in technology and cell design, production scale, cathode and raw materials, operating conditions (amperage, voltage, temperature) and particularly levels of automation. Therefore, the guidance provided here is specific to current understanding of rare earth metals production.

In the fluoride-based rare earths smelting process, the most significant GHG process emissions are (Liu *et al.* 2001; Vogel *et al.* 2017; Cai *et al.* 2018):

1. Carbon dioxide (CO₂) emissions from the consumption of carbon anodes in the electrolytic reaction converting rare earth oxides to rare earth metals;
2. Perfluorocarbons (PFCs) emissions of CF₄ and C₂F₆ during anode effects. While not commonly observed, very low levels of C₃F₈ and trace levels of other PFCs (e.g. c-C₄F₈ and C₄F₁₀) have also been reported (Cai *et al.* 2018).

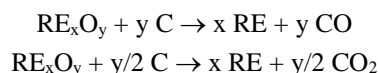
Carbon monoxide (CO) is another major process emission; SO₂ might also be emitted in very small amounts.

The decision trees in Figure 4.17 and Figure 4.18 provide guidance for selecting a methodology to estimate CO₂ and PFC emissions, respectively, from rare earth metal production. Since default emission factors have been provided, all inventory compilers in countries with rare earth metal production should be able to implement at a minimum level the Tier 1 method and thereby ensure completeness of reporting.

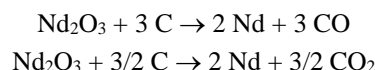
4.8.2 Methodological Issues

4.8.2.1 CHOICE OF METHOD FOR CO₂ EMISSIONS FROM PRIMARY RARE EARTH METAL PRODUCTION

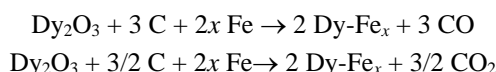
During normal operations, rare earth metals are produced at the cathode and carbon is consumed at the anode, forming carbon monoxide (CO) and carbon dioxide (CO₂) gases by electrolysis, as per the generic electrolytic reduction reactions below for production of any rare earth metal (RE) from its oxide (REO) (Liu *et al.* 2001; Vogel *et al.* 2017) :



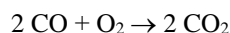
An example reaction for Nd metal production from its oxide is as follows:



For rare earth alloys that are formed by alloying with a consumable iron cathode during production, an example is the production of Dy-Fe alloy from its rare earth oxide; the reaction is as follows (Martinez *et al.* 2018):



While CO is the most dominant gas produced in these reactions (Liu *et al.* 2001; Vogel *et al.* 2017), it is assumed that all CO gas oxidises in the process and is ultimately emitted to the atmosphere as CO₂ gas (Vogel & Friedrich 2018), as follows:



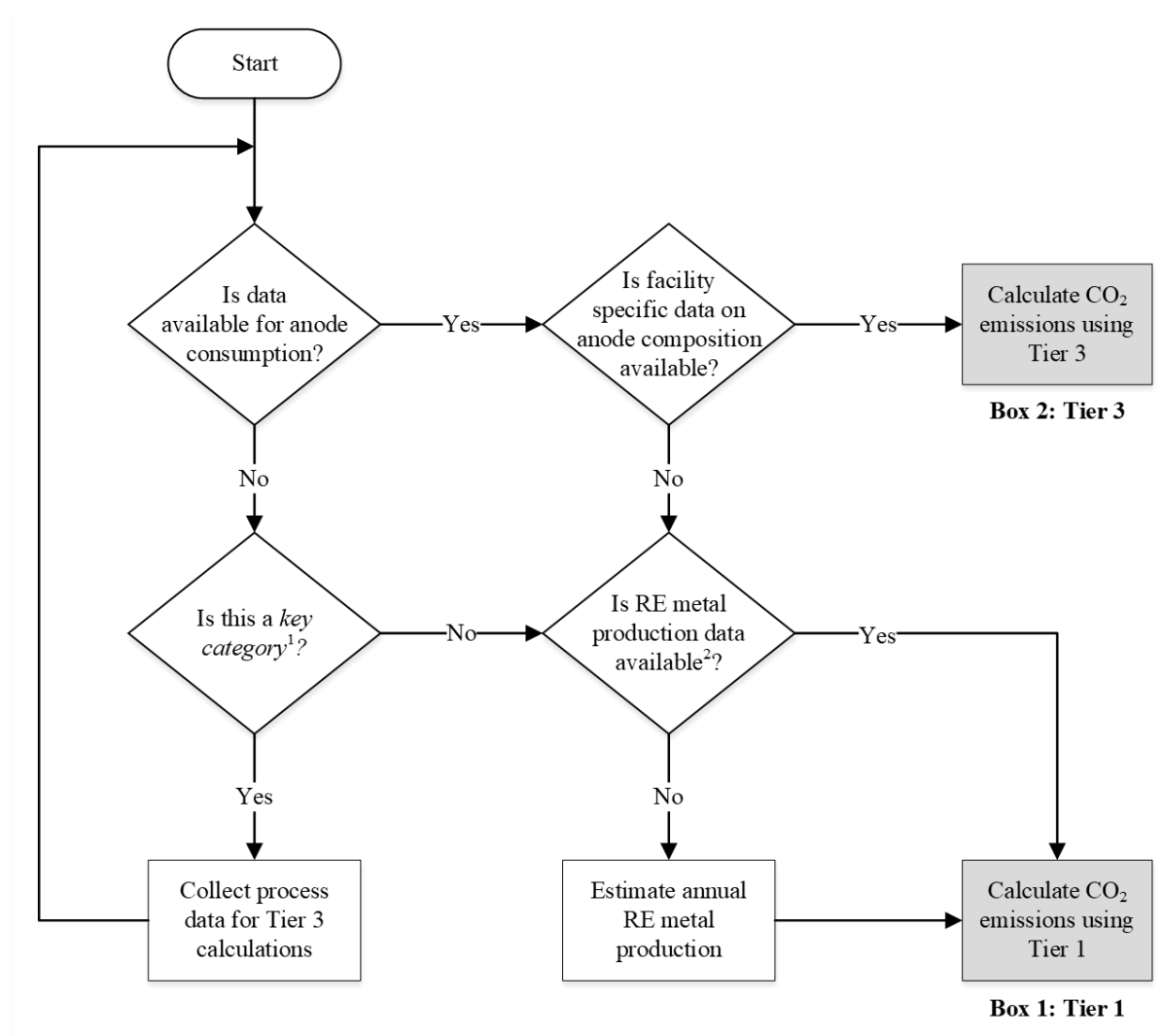
Most CO₂ emissions therefore result from the electrolysis reaction of the carbon anode with rare earth oxides (REO). The consumption of carbon anodes is the principal source of process related CO₂ emissions from primary rare earth production. The reactions leading to CO₂ emissions are relatively well understood and the emissions are directly connected to the tonnes of RE metal or alloy produced, through the fundamental electrochemical equations for RE oxide reduction at a carbon anode and oxidation from thermal processes. Both of these fundamental processes producing carbon dioxide should be included in process parameters routinely monitored at production facilities, i.e. the net anode carbon consumed.

Final Draft

Due to a lack of published information, no other sources of process-related CO₂ emissions have been considered in these guidelines. For example, it is assumed that industrial rare earth facilities currently do not manufacture or ‘pre-bake’ their own graphite anodes (vs. prebaked carbon anodes in the primary aluminium industry, perhaps due to much lower process volumes, refer to sub-chapter 4.4.2.1) and hence GHGs from anode baking (and associated energy use) are not considered here.

The decision tree shown in Figure 4.17 describes good practice in choosing the CO₂ inventory methodology appropriate for national circumstances.

Figure 4.17 (new) Decision tree for calculation of CO₂ emissions from primary rare earth (RE) metal production



Notes:

1. For discussion of *key categories* and use of decision trees, see Volume 1, Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources).

2. For Tier 1 CO₂ emissions calculation, the production data does not require differentiation of specific rare earth metals and alloys produced (Nd, Pr, Ce, La metals and/or Nd-Pr, Dy-Fe alloys, etc). There is also no need for further differentiation as to the type of rare earth cell technology used at each facility.

3. The decision tree only provides a two-tiered methodology: Tier 1 using default emission factors, and Tier 3 using facility-specific anode consumption + anode composition data. An additional Tier 2 method using default factors for anode composition data (corresponding to Tier 2 in the CO₂ decision tree for aluminium production, sub-chapter 4.4.2.1) has not been provided, since there is no default anode composition data for rare earths publicly available.

Tier 1 method for CO₂ emissions – default emission factors

The Tier 1 method for calculating CO₂ emissions uses a lower order estimate based only on rare earth metal production. Given the uncertainty associated with the Tier 1 method, it is *good practice* to use higher tier methods if CO₂ from primary rare earths is a key category. Total CO₂ emissions from all rare earth (RE) metals and alloys produced are calculated according to Equation 4.35.

EQUATION 4.35 (NEW)
PROCESS CO₂ EMISSIONS FROM ANODE CONSUMPTION (TIER 1)

$$E_{CO_2} = \sum_i [EF_{CO_2} \cdot (AW_{base} / AW_i) \cdot MP_i]$$

Where:

E_{CO_2} = Total CO₂ emissions from carbon anode consumption (tonnes CO₂)

EF_{CO_2} = CO₂ default emission factor for RE metal/alloys (tonnes CO₂/tonne RE metal)

AW_{base} = Atomic weight of base case rare earth metal, i.e. neodymium = 144.24 (g/mol)

AW_i = Atomic weight of rare earth metal/alloy type i (g/mol)

MP_i = Total metal production for RE metal/alloy type i (tonnes RE metal)

Only one default CO₂ emission factor has been provided in these guidelines, taking neodymium (Nd) metal as the base case – refer to Table 4.26. The scarcity of published data means that default emission factors are not available for other RE metals and alloys. However, Equation 4.35 includes a factor to correct the default to account for differences in atomic weight among the RE metals. This factor is the atomic weight for Nd divided by the atomic weight of the metal or alloy actually produced. Taking Dy-Fe alloy as an example (assuming 80% Dy, 20% Fe by weight)¹, the atomic weight is 117.59 g/mol and the atomic weight ratio (AW_{base} / AW_i) is 1.23. Note that Equation 4.35 could be used for more precise estimates of total CO₂ emissions from RE metals production if more Tier 1 default factors for specific RE metals/alloys become available in the future. In that case, where an emission factor for a particular RE metal was applied to that RE metal, the atomic weight ratio (AW_{base} / AW_i) would simply be set to 1.

Tier 3 method for CO₂ emissions – by facility-specific carbon mass balance

In the Tier 3 method, CO₂ emissions are calculated using a mass balance approach that assumes that the carbon content of net anode consumption² is all ultimately emitted to the atmosphere as CO₂ gas³. The Tier 3 method uses actual concentrations of anode impurities from each facility. The choice of method between the Tier 1 and Tier 3 method will depend on whether process data for (i) net carbon anode consumption and (ii) baked anode composition are both available from individual facilities. Unfortunately, a more generic Tier 2 method (similar to that for aluminium production, in sub-section 4.4.2.1) using default factors for net anode consumption and anode composition (including impurity levels) is not available due to the scarcity of published information.

CO₂ emissions for the Tier 3 method are calculated according to Equation 4.36. This requires facility-specific operating data for all the components in Equation 4.36 (note this assumes the same anode composition is used for production of all RE metals and alloys).

EQUATION 4.36 (NEW)
PROCESS CO₂ EMISSIONS FROM ANODE CONSUMPTION (TIER 3)

$$E_{CO_2} = \sum_i (NAC_i \cdot MP_i) \cdot [(100 - Imp_a) / 100] \cdot (44 / 12)$$

¹ Taking 100g basis for a Dy-Fe alloy with 80:20 wt fraction of Dy to Fe, the molar composition is 0.492 mol Dy, 0.358 mol Fe, or 58% mol Dy, 42% mol Fe. The atomic weight is therefore = 100 g / (0.492 + 0.358) mol = 117.59 g/mol.

² ‘Net anode consumption’ (NAC) refers to the total anode consumption per tonne of metal, minus any unused or ‘spent’ anode material when old anodes are exchanged for new anodes. This unused or ‘spent’ anode material is not consumed in the electrolysis process but might be recycled to make new anodes.

³ While CO is the most dominant gas product from the rare earths electrolytic reduction reaction (Liu *et al.* 2001), it is assumed that any CO formed eventually is converted to CO₂ gas. The same carbon mass-balance approach is assumed for the primary aluminium industry, in sub-chapter 4.4.2.1.

Final Draft

Where:

 E_{CO_2} = Total CO₂ emissions from carbon anode consumption (tonnes CO₂) NAC_i = Net anode consumption per tonne of RE metal/alloy type i (tonnes anode/tonne RE metal) MP_i = Total metal production for RE metal/alloy type i (tonnes RE metal) Imp_a = Total content of non-carbon impurities (e.g. sulfur, ash, etc) in baked carbon anodes (wt %)44/12 = CO₂ molecular mass: carbon atomic mass ratio (dimensionless)

Equation 4.36 can be applied to each rare earth smelter in the country and the results summed to arrive at total national emissions.

It is possible to use a hybrid Tier 1 and 3 approach if facility specific net anode consumption and composition data (impurity content, e.g. ash, sulfur, etc) are not available for each smelter.

4.8.2.2 CHOICE OF EMISSION FACTORS FOR CO₂ EMISSIONS FROM PRIMARY RARE EARTH METAL PRODUCTION

Tier 1 method for CO₂ emissions

Table 4.26 lists the default emission factors for CO₂ per tonne of RE metal, for use in Equation 4.35. Given the scarcity of published data and since only minor differences in emission factors are expected across different RE metals and alloy types¹, only one default emission factor is provided for all RE metals. This uses Nd metal production as the basis, since it is the most common RE metal produced via fluoride-salt electrolysis. It is *good practice* to check the Emissions Factor Database (EFDB) as a source for future CO₂ emission factors for rare earth metals production.

TABLE 4.26 (NEW) TIER 1 DEFAULT EMISSION FACTORS FOR CALCULATING CO ₂ EMISSIONS FROM ANODE CONSUMPTION		
Rare Earth Metal / Alloy i	Emission Factor, EF_{CO_2} (tonnes CO ₂ /tonne RE metal)	Uncertainty Range (%)
Nd metal, and all other Rare Earth metals/alloys	0.56 ^a	-22/+24% ^b
Source: ^a CO ₂ default emission factor is based on a net anode carbon consumption of 152 kg C/tonne RE metal (average anode consumption reported from 4 industrial production lines in China - (Cai <i>et al.</i> 2018)) and converting this to CO ₂ by mass balance, assuming 100% conversion of anode carbon to CO ₂ . ^b Assuming the default CO ₂ emissions factor represents a current efficiency of 75%, an uncertainty range of -22%/+24% from the default CO ₂ factor might be expected if individual facilities operate at a different current efficiency level (e.g. 60 to 95%), based on first principle calculations described in footnote 1. However, actual variations in CO ₂ emissions may be as low as ±10%, based on highest and lowest industrial net carbon anode consumption values reported in (Cai <i>et al.</i> 2018), converted by mass balance to CO ₂ . Therefore, where possible, development and use of Tier 3 emission factors is encouraged.		

¹ A difference of only -4% / +8% in CO₂ emission factors was estimated across different rare earth metals (from La to Gd metal, using Nd metal as a base case), when evaluating CO₂ emissions by first principles. This is due to the similarities in atomic mass for these rare earth metals. A first principles calculation for CO₂ was done by taking electrolysis of Nd₂O₃ to Nd metal as a basis (see Section 4.8.2.1 for stoichiometric reactions), assuming a gas production ratio of ~75% CO, 25% CO₂ by direct electrolysis at 1050°C and anode current density of 1.0 A/cm² (Liu *et al.* 2001); Vogel and Friedrich (2015). CO₂ emitted is then calculated assuming: (i) all CO is ultimately oxidised to CO₂, (ii) process has a 75% faradaic current efficiency (% anode carbon that is electrolytically consumed to produce metal), and (iii) an additional 10% anode carbon consumed via non-electrolytic processes (oxidation of carbon due to exposure with air). The obtained net anode carbon consumption (150 kg carbon / tonne RE metal) is similar to figures obtained from industrial rare earth surveys (Cai *et al.* 2018).

Tier 3 method for CO₂ emissions

Table 4.27 lists the facility-specific activity data (and uncertainties) at individual facilities, for use in Equation 4.36. The most significant factors in Equation 4.36 are metal production and net anode consumption for each RE metal or alloy type *i*. Both these parameters should be collected from individual operating facilities for use with Tier 3. The other compositional terms in the equation make minor adjustments for non-carbon components of the anodes (e.g. sulphur and ash, expected to be <3% wt) and thus are not as critical. Tier 3 is based on the use of specific operating facility data for these minor components. Carbon consumed per tonne of metal produced is typically recorded by rare earth production facilities given its economic significance; facilities refer to this as ‘net anode consumption’ or ‘net carbon consumption’.

TABLE 4.27 (NEW) DATA SOURCES AND UNCERTAINTIES FOR PARAMETERS USED IN TIER 3 METHOD FOR CO ₂ EMISSIONS FROM ANODE CONSUMPTION		
Parameter	Data Source	Uncertainty (±%)
<i>MP_i</i> : total metal production for RE metal type <i>i</i> (tonnes metal per year)	Individual facility records	±10% ^a
<i>NAC_i</i> : net anode consumption per tonne of RE metal type <i>i</i> (tonnes per tonne metal)	Individual facility records	±10% ^b
<i>Imp_a</i> : total non-carbon impurity content in baked anodes (wt %) ^c	Individual facility records	±10% ^b
Source: ^a Uncertainties in facility specific metal production records are expected to be low (i.e. ±10%, based on expert judgement). However note (Vogel & Friedrich 2018) estimates an uncertainty of up to ±40% (±15,000 tonnes) for the 35,000 tonnes estimated global RE metal production by fluoride electrolysis in 2015, due to unreported / illegal production of RE metals (Kingsnorth 2015). ^b Uncertainties for CO ₂ based on facility specific information (apart from metal production) have been estimated based on expert judgement, using uncertainty factors similar to those applied in the primary aluminium sector (sub-chapter 4.4, Table 4.11: uncertainties for Tier 3 method for CO ₂ emissions from prebake cells). ^c Non-carbon impurities can include sulfur, ash, etc.		

4.8.2.3 CHOICE OF METHOD FOR PFCs

During electrolysis of a RE metal, rare earth oxides (REOs) are dissolved in a fluoride melt comprising of rare earth fluorides (RE_xF_y) and lithium fluoride (LiF). An example melt composition for Nd metal production is 85% wt NdF₃, 10% LiF and 5% Nd₂O₃.

Perfluorocarbons (mainly CF₄ and C₂F₆ – collectively referred to as PFCs) are formed from the reaction of the carbon anode with the fluoride melt (e.g. NdF₃ or DyF₃) during a process upset condition known as an ‘anode effect’. This occurs when the concentration of dissolved REO in the electrolyte is too low to completely support the standard anode reaction (normally producing RE metal and CO/CO₂ gases), enabling additional anode reactions that form PFC gases (Vogel *et al.* 2017; Cai *et al.* 2018; Kjos *et al.* 2018; Zhang *et al.* 2018). In addition to CF₄ and C₂F₆, other PFCs reported by Cai *et al.* (2018) during RE metal production included: very low levels of C₃F₈ (<1% total PFCs) and trace levels of c-C₄F₈ and C₄F₁₀ (<0.05% total PFCs). However, quantification of these PFCs (other than CF₄ and C₂F₆) in industrial measurements is extremely challenging and often impractical, given the extremely low detection limits required.

Final Draft

Box 4.4 (NEW)**ANODE EFFECT DESCRIPTION (FOR RARE EARTH METAL PRODUCTION BY FLUORIDE ELECTROLYSIS)**

An ‘anode effect’ is a process upset condition where an insufficient amount of rare earth oxide is dissolved in the electrolyte, resulting in the emission of PFC-containing gases and causing voltage to be elevated above normal operating range. However, PFC generation might also occur in the absence of detectable changes in voltage (Vogel *et al.* 2017; Kjos *et al.* 2018).

Unlike the analogous primary aluminium industry (refer to Box 4.2), many rare earth technologies currently do not use automated computer control systems to detect anode effects, for example using an elevated voltage threshold. As such, facility-specific activity data (e.g. anode effect performance data) is often not available to estimate PFC emissions.

Due to reported differences in emissions profile (Cai *et al.* 2018; Zhang *et al.* 2018), PFC emissions can be estimated separately for two groups of rare earth metals and alloys:

- *Rare earth-iron (RE-Fe) alloys*¹ with high melting-point (>1300°C) rare earth elements, e.g. Dy-Fe, Gd-Fe and Ho-Fe;
- *All other rare earth (Other-RE) metals/alloys* including single and mixed rare earth metals, e.g. Nd, La, Pr-Nd, etc.

In choosing a method for PFC emissions, it should be noted that the uncertainty associated with the Tier 3 methodology is significantly lower than for Tier 1; therefore it is *good practice* to use Tier 3 methodologies if this is a *key category*. However, a pre-requisite for the Tier 3 method is the availability of facility-specific emission factors, obtained through individual facility measurements. While no good practice guidance currently exists on the measurement of PFCs and obtaining Tier 3 emission factors for the rare earth industry, the US EPA and IAI protocols for measurement of PFCs in the aluminium smelting industry provide good analogous references (International Aluminium Institute 2006; US Environmental Protection Agency & International Aluminium Institute 2008).

The decision tree in Figure 4.18 describes *good practice* in choosing the PFC inventory methodology appropriate for national circumstances. The Tier 3 approach is preferred because plant-specific emission factors will lead to estimates that are more accurate. If no PFC measurements have been made to establish Tier 3 plant-specific emission factors, the Tier 1 method can be used until measurements have been made. Countries can use a combination of Tier 1 and Tier 3 depending on whether plant-specific emission factors are available from individual facilities.

Note that while the fundamental mechanisms that generate PFCs and anode effects in the rare earths industry are similar to those in primary aluminium production (refer to sub-chapter 4.4), the lack of automation currently found in the rare earths industry prevents the use of facility-specific activity data (e.g. using anode effect performance data as per Tier 2 and 3 methods for PFC accounting in primary aluminium production) as a more accurate methodology for estimating PFCs. Therefore, higher Tier 2 and 3 methods using process performance statistics or activity data have not been included in these guidelines².

While rare earths production currently has a lower level of automation and process control compared to primary aluminium production (see sub-chapter 4.4), the industry is still very much under development. There is ongoing research to develop industrial technologies that can minimise PFC emissions (e.g. employing automation to ensure control of REO concentrations) (Vogel & Friedrich 2017; Martinez *et al.* 2018). However, due to the scarcity of published information on industrial emissions, separate PFC emission factors have not been provided for these technologies.

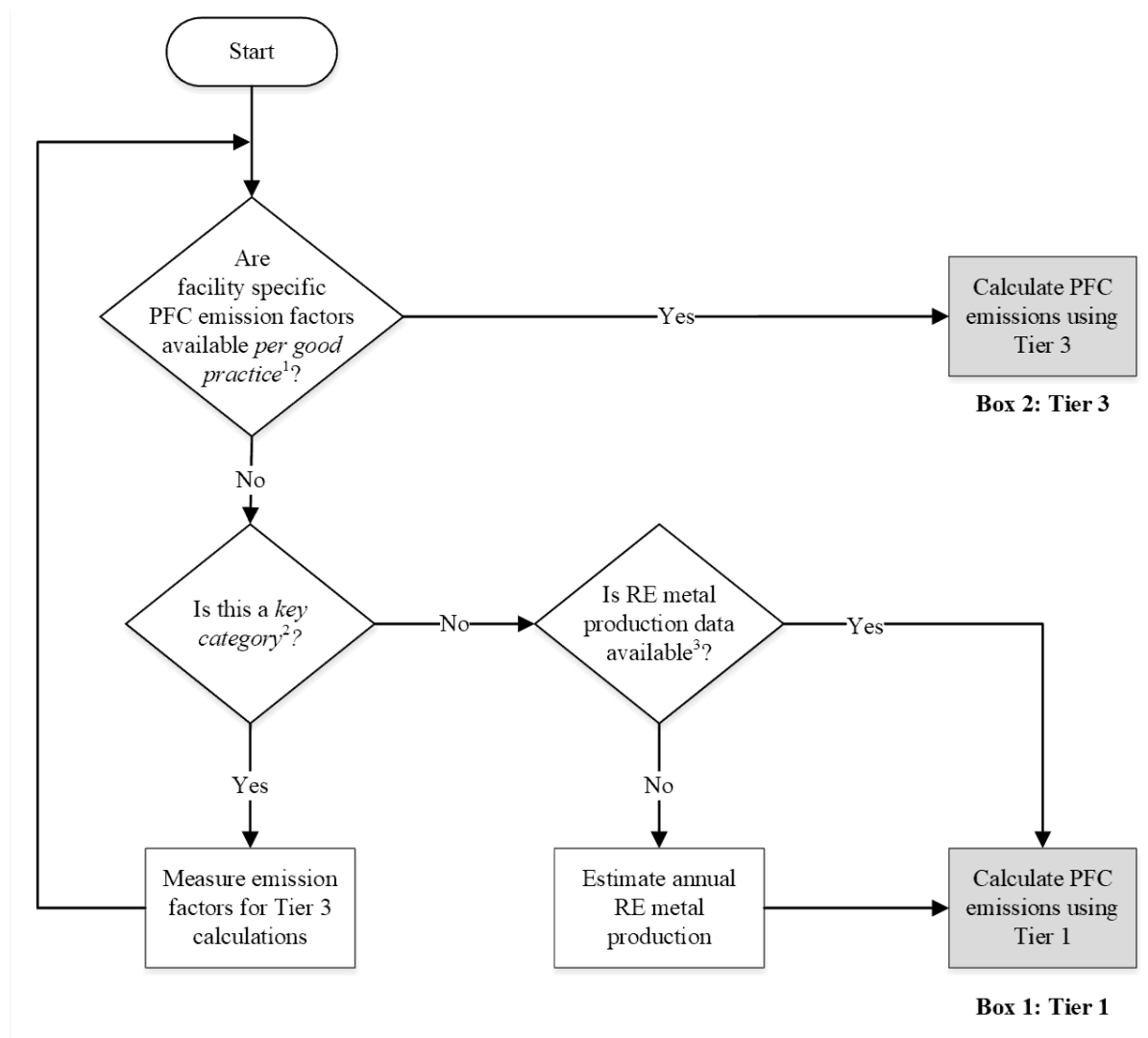
Given the potential for further development within the industry, it is *good practice* to establish Tier 3 plant-specific emission factors for individual facilities where significant technology development and/or adoption of automated

¹ This category of RE-Fe alloys represented <5% of total rare earth metals/alloys produced by electrolysis in 2016 (expert opinion). Due to their high melting point, these RE elements are typically produced using an alloying cathode (e.g. Fe) and high operating cell voltage (compared to cells for all other RE metals/alloys in similar conditions); the higher operating temperature and cell voltage is thought to be one of the reasons behind higher PFC emissions (expert opinion; Cai *et al.* 2018; Zhang *et al.* 2018).

² Accounting of PFCs using activity data - such as anode effect performance statistics - in the rare earths industry is possible. However this requires the industry to first have consistent definitions of anode effect performance, i.e. how to define the start/end of an anode effect to determine the frequency and the duration of anode effects. Secondly, the level of automation in rare earth facilities must be sufficiently high to ensure accurate and consistent records these anode effect performance statistics, a condition that does not currently reflect the majority of the rare earths industry.

control systems have taken place. Finally, it is *good practice* to check the Emissions Factor Database (EFDB) as a source for future PFC emission factors for rare earths production.

Figure 4.18 (new) Decision tree for calculation of PFC emissions from primary rare earth (RE) metal production



Notes:

1. While *good practice* guidelines for obtaining facility specific PFC emission factors from rare earth production facilities are currently not available, the IAI and US EPA/IAI greenhouse gas protocols for aluminium smelters are useful references due to the many similarities between primary aluminium and rare earth smelting using fluoride-salts (International Aluminium Institute 2006; US Environmental Protection Agency & International Aluminium Institute 2008).

2. For discussion of *key categories* and use of decision trees, see Volume 1, Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources).

3. For Tier 1 PFC emissions calculation, the production data requires differentiation of (a) *rare-earth iron (RE-Fe) alloys*, e.g. Dy-Fe and (b) *all other rare earth (Other-RE) metals/alloys*, e.g. Nd, Pr-Nd and La. However, there is no need for further differentiation as to the specific rare earth metal/alloy produced, or type of rare earth cell technology used at each facility.

4. This decision tree only provides a two-tiered methodology: Tier 1 using default emission factors, Tier 3 using facility-specific emission factors. Additional Tier 2-3 methods using anode effect activity data to estimate PFC emissions (similar to the Tier 2-3 methods in the PFC decision tree for aluminium production, sub-chapter 4.4.2.3) has not been provided, due to the lack of available activity data.

Final Draft

Tier 1 and Tier 3 method for PFCs – by production

Both Tier 1 and Tier 3 methods for calculating PFCs employ emission factors that are based on metal production. Methods are provided for CF₄ and C₂F₆ gases since these are the major PFCs generated. C₃F₈ is also included for sake of completeness, however it is a very minor component of PFCs generated in rare earths (<1% total PFCs) and it can be challenging or impractical to quantify from industrial facilities (if obtaining Tier 3 facility-specific emission factors), given the extremely low detection limits required. Estimation of all other PFCs are beyond the scope of this method as they are not significant (Cai *et al.* 2018).

The Tier 1 method uses default emission factors based on industrial measurements. PFC emissions can be calculated according to Equation 4.37, where emission factors for CF₄, C₂F₆ and C₃F₈ gases are default emission factors (refer to Table 4.28). The level of uncertainty in the Tier 1 methodology is greater because individual facility emissions performance¹ is not taken into account. Note that some researchers (Vogel & Friedrich 2018) have estimated PFC emission factors two to three-orders of magnitude greater than the default values given in Table 4.28. These higher values were not used here because they were not measured, but modelled based on a mass balance of NdF₃ inputs to replace consumed fluorides, with the unlikely assumption that all consumed fluorides are due to PFC generation. Nevertheless, they do indicate that the PFC emission factors from some facilities may be higher than the Tier 1 factors presented here. Therefore, where possible, development and use of Tier 3 facility-specific PFC emission factors is encouraged.

Note that Equation 4.37 enables calculation of PFC emissions by individual RE metal/alloy produced. However default emission factors are only available for two generic types of metals/alloys: (i) *rare earth-iron alloys* (e.g. Dy-Fe) and (ii) *all other rare earth metals/alloys* (e.g. Nd, Pr-Nd), rather than all possible combinations of RE metals / alloys due to the scarcity of published industrial emissions data². Therefore, two default Tier 1 emission factors for RE metals have been provided in these guidelines (Table 4.28). Hence, Equation 4.37 can be used with differentiation of RE metal production into these two metal/alloy types; further differentiation into specific RE metals/alloys is not required.

EQUATION 4.37 (NEW)
PFC EMISSIONS FROM RARE EARTH METALS PRODUCTION (TIER 1 AND TIER 3)

$$E_{CF4} = \sum_i [(EF_{CF4, i} / 1000) \cdot MP_i]$$

and

$$E_{C2F6} = \sum_i [(EF_{C2F6, i} / 1000) \cdot MP_i]$$

and

$$E_{C3F8} = \sum_i [(EF_{C3F8, i} / 1000) \cdot MP_i]$$

Where:

E_{CF4} = Emissions of CF₄ from RE metal production, kg CF₄

E_{C2F6} = Emissions of C₂F₆ from RE metal production, kg C₂F₆

E_{C3F8} = Emissions of C₃F₈ from RE metal production, kg C₃F₈

$EF_{CF4, i}$ = Emission factor by RE metal *i* for CF₄, g CF₄/tonne RE metal

$EF_{C2F6, i}$ = Emission factor by RE metal *i* for C₂F₆, g C₂F₆/tonne RE metal

$EF_{C3F8, i}$ = Emission factor by RE metal *i* for C₃F₈, g C₃F₈/tonne RE metal

MP_i = Metal production by RE metal *i*, tonnes RE metal

¹ PFC emissions performance is impacted by technology, operating conditions and the anode effect performance of individual facilities. While anode effect performance data from facilities are used to directly estimate PFCs in the analogous aluminium smelting industry (refer to section 4.4.2.3), a similar method for rare earths has not been provided due to a lack of supporting data that characterises emissions according to process statistics, such as anode effect performance.

² While Tier 1 default emission factors are not available for all individual RE metal/alloy types, Equation 4.37 provides a template for the future (when such factors might become available) and for potential use in Tier 3 calculations.

The Tier 3 method uses facility-specific emission factors in place of Tier 1 default emission factors. Facility-specific emission factors are calculated from direct PFC measurement data at the individual facility (either continuous or periodic measurements) and are obtained using established measurement practices and protocols – refer to analogues guidelines for the aluminium industry (International Aluminium Institute 2006; US Environmental Protection Agency & International Aluminium Institute 2008)). It is *good practice* to use the Tier 3 method to estimate PFCs from rare earths when that is a *key category*.

For Tier 3, if facility-specific emission factors and production data are available for individual RE metals and alloys, then Equation 4.37 can be employed to calculate differentiated PFC emissions for each RE metal/alloy; total PFC emissions can be obtained via the summation of these differentiated emissions. However, if differentiated emission factors and production data by RE metal/alloy are unavailable, it is acceptable to use Equation 4.37 without differentiation of RE metals/alloys produced.

Given the practical challenges in quantifying very low levels of C₃F₈, if a Tier-3 facility-specific emission factor cannot be determined, it is possible to use a hybrid Tier 1-Tier 3 approach (i.e. Tier 1 emission factor for C₃F₈; Tier 3 emission factors for CF₄ and C₂F₆).

4.8.2.4 CHOICE OF EMISSION FACTORS FOR PFCs

Tier 1: Default emission factors for PFCs

Default emission factors for the Tier 1 method of estimating PFC emissions from rare earth metal production are provided in Table 4.28, for use in Equation 4.37.

TABLE 4.28 (NEW) TIER 1 DEFAULT EMISSION FACTORS AND UNCERTAINTY RANGES FOR THE CALCULATION OF PFC EMISSIONS FROM RARE EARTH PRODUCTION						
	CF ₄		C ₂ F ₆		C ₃ F ₈	
Rare Earth Metal, <i>i</i>	<i>EF</i> _{CF₄} (g/tonne RE metal)	Uncertainty Range ^c (+/- %)	<i>EF</i> _{C₂F₆} (g/tonne RE metal)	Uncertainty Range ^c (+/- %)	<i>EF</i> _{C₃F₈} (g/tonne RE metal)	Uncertainty Range ^c (+/- %)
RE-iron alloys (Dy-Fe, etc) ^a	146.1	+/- 99%	14.6	+/- 99%	0.05	+/- 99%
Other-RE metals/alloys (Nd, Pr-Nd, La, etc) ^b	35.8	-54% / +30%	5.2	-95% / +108%	0.21	-52% / +30%
Sources:						
^a For <i>rare earth-iron (RE-Fe) alloys</i> , CF ₄ default emission factors is based on the average of two industrial measurements from production of Dy-Fe alloy (1 cell) in China (Cai <i>et al.</i> 2018; Zhang <i>et al.</i> 2018). C ₂ F ₆ and C ₃ F ₈ default emission factors were calculated using the CF ₄ default factor, multiplied by the respective C ₂ F ₆ /CF ₄ and C ₃ F ₈ /CF ₄ ratio measured by (Cai <i>et al.</i> 2018) for Dy-Fe production. Given that default factors are based on only two data points, a higher uncertainty bound +/-99% has been estimated (expert opinion) rather than using the lowest/highest reported emission values.						
^b For <i>all other rare earth (Other-RE) metals/alloys</i> , CF ₄ default emission factors is based on the average of industrial measurements from production of: (i) Nd metal (16 cells) (Zhang <i>et al.</i> 2018) and (ii) Pr-Nd alloy (15 cells, 6 cells) and La metal (6 cells) in China (Cai <i>et al.</i> 2018). C ₂ F ₆ and C ₃ F ₈ default emission factors were calculated using the CF ₄ default factor, multiplied by the average C ₂ F ₆ /CF ₄ and C ₃ F ₈ /CF ₄ ratio, respectively, measured by (Cai <i>et al.</i> 2018) from Pr-Nd alloy (15 cells, 6 cells) and La metal (6 cells) production. The uncertainty range is estimated from the lowest/highest emission values from both industrial studies.						
^c Note that the default factors and uncertainty ranges here have been estimated with very limited sources of measured industrial data. Some researchers (Vogel & Friedrich 2018) have estimated PFC emission factors two to three-orders of magnitude greater than the default values in this table (modelled 'medium-emissions' scenario for Nd production, based on mass balance of NdF ₃ inputs to replace consumed fluorides, but with the unlikely assumption that all consumed fluorides are due to PFC generation). Therefore where possible, development and use of Tier 3 facility-specific PFC emission factors is encouraged.						

Final Draft

Tier 3: Facility-specific emission factors for PFCs

The Tier 3 facility-specific emission factors (and uncertainties), determined through direct PFC measurements at individual facilities is listed in Table 4.29, for use in Equation 4.37.

TABLE 4.29 (NEW) DATA SOURCES AND UNCERTAINTIES FOR PARAMETERS USED IN TIER 3 METHOD FOR PFC EMISSIONS		
Parameter	Data Source	Uncertainty (+/- %)
EF_{CF_4} : CF ₄ emission factor for metal type i (kg CF ₄ /tonne RE metal)	Individual facility records	±10% ^a
$EF_{C_2F_6}$: C ₂ F ₆ emission factor for metal type i (kg C ₂ F ₆ /tonne RE metal)	Individual facility records	±10% ^a
$EF_{C_3F_8}$: C ₃ F ₈ emission factor for metal type i (kg C ₃ F ₈ /tonne RE metal)	Individual facility records	±35% ^a
MP_i : metal production for RE metal type i (tonnes metal per year)	Individual facility records	±10% ^b
Source: ^a Uncertainties for facility-specific emission factors have been derived from estimated sampling and gas analysis uncertainties during direct industrial measurement of PFCs in rare earth facilities (Cai <i>et al.</i> 2018). Uncertainties for C ₂ F ₆ and especially C ₃ F ₈ can be higher, particularly when concentrations are close to detection limits of gas measurement systems. Determination of Tier 3 facility-specific emission factors for C ₃ F ₈ can be challenging and impractical, given the very low detection limits required to quantify these low-level emissions. It is possible therefore to use a hybrid Tier 1-Tier 3, where C ₃ F ₈ emissions are estimated using Tier 1 default factors, and CF ₄ and C ₂ F ₆ using Tier 3, respectively. ^b Uncertainties in facility specific metal production records are expected to be low (i.e. ±10%, based on expert opinion). However (Vogel & Friedrich 2018) estimates an uncertainty of up to +40% (+15,000 tonnes) for the 35,000 tonnes estimated global RE metal production by fluoride electrolysis in 2015, due to unreported / illegal production of RE metals (Kingsnorth 2015).		

4.8.2.5 CHOICE OF ACTIVITY DATA AND EMISSION FACTORS

Production statistics should be available from every facility to enable use of the Tier 1 methods for both CO₂ and PFC emissions. Therefore, uncertainty in the tonnes of rare earth metals and alloys produced is likely to be low in most countries that have good reporting systems (±10% uncertainty, based on expert judgement); other sources (Vogel & Friedrich 2018) estimate up to +40% uncertainty in global RE metal production (in 2015) due to the presence of unreported or illegal RE metal production in some parts of the world.

For PFC emissions, it is *good practice* to use Tier 3 facility-specific emission factors for individual facilities, where reliable measurements have been taken to establish facility-specific emission factors (i.e. using a method similar to that in the USEPA/IAI Protocol for Measurement of CF₄ and C₂F₆ emissions from Primary Aluminium Production, 2008).

For CO₂ emissions, it is also *good practice* to collect data to support Tier 3 methods, which requires facility specific information on anode consumption and anode composition to calculate CO₂ emissions.

4.8.2.6 COMPLETENESS

Completeness for this source category requires accounting for both CO₂ and PFC emissions during the production of rare earth metals. Primary RE metal production facilities (by fluoride-electrolysis of REOs) are expected to have the information required for these estimates, including records of the tonnes of RE metals produced (both total and by individual RE metal/alloy types) throughout the entire time series covered by the inventory. In addition, anode consumption data are expected to be available over the same period. Primary RE production (by fluoride-electrolysis of REOs) also utilizes a high intensity of electricity (per tonne of RE metal); however carbon dioxide emissions associated with electricity input are covered separately under Volume 2: Energy.

Completeness also requires that all rare earth metals production and/or all rare earth metal producers in the country be identified. As noted above, some sources have estimated that global RE metal production may have been

underestimated by 40% in 2015 due to unreported or illegal RE metal production in some parts of the world (Vogel & Friedrich 2018).

4.8.2.7 DEVELOPING A CONSISTENT TIME SERIES

Rare earth metal/alloy production statistics should be available for the entire history of the facility.

Developing a consistent time series for CO₂ emissions should not be a problem since it is expected that most facilities have measured and recorded activity data for anode consumption and composition. Where historic anode consumption and compositional data are missing, carbon dioxide emissions can be estimated from RE metal production utilizing the Tier 1 method.

Developing a consistent time series for PFC emissions should also be reasonably straightforward as both Tier 1 and 3 methods utilise metal production statistics to estimate emissions. Backcasting of Tier 3 methods is preferred over the use of Tier 1 emission factors. Because PFC emissions have only recently become a focus area of the rare earths industry, the majority of facilities do not have further activity data to support any other methodologies (e.g. process-data on anode effect performance as per the primary aluminium industry, sub-chapter 4.4.2.3).

It is *good practice* to consult with representatives from the operating facilities, either directly or through regional, national or international organizations representing the rare earths industry to develop the best strategy for the specific group of operating locations included in the national inventory.

4.8.3 Uncertainty assessment

There are major differences in the uncertainty for PFC emissions depending on the choice of Tier 1 or Tier 3 methods. The differences in uncertainty resulting from the choice of Tier 1 or Tier 3 methods for CO₂ emissions is smaller, but still significant.

4.8.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties in CO₂ emission factors

For CO₂ emissions, there are major differences in the uncertainty of emissions depending on the choice of Tier 1 or 3 methods. The overall uncertainty in calculating CO₂ emissions from carbon anode consumption for Tier 3 should be less than $\pm 20\%$, and less than $\pm 30\%$ for Tier 1. While Tier 1 default emission factors are calculated using the same first principles as Tier 3 (mass-balance assuming all carbon content in the net anode consumed is emitted as CO₂), there are assumptions for Tier 1 which increases the level of uncertainty. These include: (i) an assumed net anode consumption and (ii) assuming zero non-carbon impurities, i.e. 100% of net anode consumed is in the form of carbon. The use of facility-specific net anode consumption and anode compositional data in the Tier 3 method removes the need for these assumptions, leading to lower uncertainty in calculating CO₂ using Tier 3. This is because the reactions leading to carbon dioxide emissions is reasonably well understood and the emissions are very directly connected to the tonnes of RE metal produced through fundamental electrochemical equations for REO reduction at the carbon anode and oxidation from thermal processes. Both these processes are taken into account when calculating CO₂ using net anode consumption and anode compositional data.

Uncertainties in PFC emission factors

For PFC emissions, there are major reductions in uncertainty when choosing the Tier 3 over the Tier 1 method. The high level of uncertainty in the Tier 1 method results from the default emission factors being based on only two sets of industrial PFC measurements from rare earth facilities (Cai *et al.* 2018; Zhang *et al.* 2018). Due to the limited number of industrial measurements, there is no differentiation of Tier 1 default emission factors for different rare earth metals and production technologies, apart from the two generic metal/alloy types: (i) rare earth-iron (RE-Fe) alloys and (ii) all other rare earth (Other-RE) metals/alloys. In order to achieve lower uncertainty using Tier 3 PFC calculations, it is important to use *good practices* in making facility specific PFC measurements. Measurement *good practices* have been established for the aluminium industry in a protocol available globally (International Aluminium Institute 2006; US Environmental Protection Agency & International Aluminium Institute 2008); due to the similarities between the industries, these are recommended as a guiding reference for measurements in the rare earths industry, until a RE industry-specific protocol or guideline is established. When properly obtained, the Tier 3 coefficients will have an uncertainty of $\pm 10\%$ for CF₄ and C₂F₆ and $\pm 35\%$ for C₃F₈ at the time coefficients are measured (Cai *et al.* 2018).

2903 4.8.3.2 ACTIVITY DATA UNCERTAINTIES

2904 While uncertainties in annual production data for RE metals should be minor (less than $\pm 10\%$), there are some
 2905 reports of unreported/illegal production in parts of the world that amount to $\pm 40\%$ of estimated global metal
 2906 production in 2015 (Kingsnorth 2015; Vogel & Friedrich 2018). The uncertainty in recorded carbon anode
 2907 consumption is estimated to be low (less than $\pm 10\%$).

2908

2909 4.8.4 Quality Assurance/Quality Control (QA/QC), 2910 Reporting and Documentation

2911 4.8.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

2912 It is *good practice* at all primary rare earth metal production facilities to maintain records of all the necessary
 2913 activity data to support calculations of emission factors as suggested in these guidelines. These records will include
 2914 production of rare earth metals (ideally by RE metal/alloy type and by RE technology type) and consumption of
 2915 carbon materials used. It is *good practice* to aggregate emission estimates from each smelter to estimate total
 2916 national emissions. However, if smelter-level production data is unavailable, smelter capacity data may be used
 2917 along with aggregate national production to estimate smelter production.

2918 It is *good practice* to verify facility CO₂ emission factors per tonne of RE metal by comparison with the expected
 2919 range of variation that would be predicted from the variation noted in Table 4.26 for CO₂ specific emissions.
 2920 Similarly, facility-specific PFC emission factors per tonne RE metal should be compared with the expected range
 2921 of variation noted in Table 4.28. It is suggested that any inventory value outside the expected range of variation
 2922 be confirmed with the data source.

2923 Use of standard measurement methods improves the consistency of the resulting data and knowledge of the
 2924 statistical properties of the data. Until a rare earths industry-specific guideline or protocol has been established,
 2925 the US EPA 'Protocol for Measurement of Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions
 2926 from Primary Aluminum Production' (US Environmental Protection Agency & International Aluminium Institute
 2927 2008) is an internationally recognized standard and can be used as a guidance document for obtaining PFC
 2928 emission factors for a rare earths facility, given the similarities between aluminium and rare earths fluoride-
 2929 electrolysis processes¹. It is *good practice* to encourage plants to use this method for developing Tier 3 PFC
 2930 emission factors. Significant differences between calculated coefficients based on PFC measurements and the
 2931 industry average Tier 1 emission factors should elicit further review and checks on calculations. Large differences
 2932 should be explained and documented.

2933 Inter-annual changes in emissions of carbon dioxide per tonne RE metal are not likely to exceed $\pm 20\%$ ² based on
 2934 the consistency of the underlying processes that produce carbon dioxide. In contrast, inter-annual changes in
 2935 emissions of PFCs per tonne of RE metal may change by values as much as $\pm 100\%$ ³. Increases in PFC specific
 2936 emissions can result from process instability or major changes in process conditions, such as unforeseen power
 2937 interruptions, changes in sources of REO feed materials, cell operational problems, and changes in amperage to
 2938 increase RE metal production. Decreases in PFC specific emissions can result from upgrades in cell technology
 2939 such as increasing automation, installation of equipment to continuously feed REO, improved work practices and
 2940 better control of raw materials.

¹ Note that unlike the aluminium industry, the Tier 3 methodology for rare earths estimates PFCs using production-based emission factors only. The method does not consider more detailed process data, such as anode effect coefficients and performance data (as per the Tier 2-3 methodology for accounting PFCs from aluminium in sub-chapter 4.4), due to a lack of published data to support it.

² Inter-annual variations in CO₂ emissions in the analogous aluminium industry (sub-chapter 4.4) typically do not vary more than $\pm 10\%$; however, given the scarcity of published data, greater variations (i.e. $\pm 20\%$) might be allowed for in the rare earth industry.

³ Inter-annual variations in PFC emissions in the analogous aluminium industry (sub-chapter 4.4) typically do not vary more than $\pm 100\%$; a similar level of variations might be expected in the rare earth industry, as supported by reductions in measured emissions over time in one facility (Cai *et al.* 2018).

4.8.4.2 REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Chapter 6, Quality Assurance and Quality Control, Internal Documentation and Archiving. Some examples of specific documentation and reporting relevant to this source category are provided below.

It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced. To improve transparency, it is *good practice* to report emissions for PFCs from rare earths production separately from other source categories. Additionally, it is *good practice* that CF₄, C₂F₆ and C₃F₈ emissions are reported separately on a *mass basis*.

The supporting information necessary to ensure transparency in reported emissions estimates is shown in Table 4.30 below.

Much of the production and process data are considered proprietary by operators, especially where there is only one smelter in a country. It is *good practice* to exercise appropriate techniques, including aggregation of data, to ensure protection of confidential data.

TABLE 4.30 (NEW) GOOD PRACTICE REPORTING INFORMATION FOR CALCULATING CO ₂ AND PFC EMISSIONS FROM RARE EARTH METAL PRODUCTION BY TIER		
Data	Tier 1	Tier 3
CO₂ emissions		
Annual national production (by metal and alloy type)	X	
Annual production by facility (by metal and alloy type)		X
Net anode consumption		X
Anode composition / impurity		X
PFC emissions (CF₄, C₂F₆ and C₃F₈ reported separately on mass basis)		
Annual national production (by metal/alloy type)	X	
Annual production by facility (by metal/alloy type)		X
Default technology emission coefficients	X	
Facility-specific emission coefficients		X
Supporting documentation	X	X

4.9 REFERENCES

SECTION 4.2

References newly cited in the 2019 Refinement

EU IPPC BREF (2013). Best Available Techniques (BAT) Reference Document for Iron and Steel Production, Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), Rainer Remus, Miguel A. Aguado-Monsonet. Serge Roudier, Luis Delgado Sancho, JRC Reference Report, 2013, available at http://eippcb.jrc.ec.europa.eu/reference/BREF/IS_Adopted_03_2012.pdf.

Fruehan, R.J., Fortini, O., Paxton, H.W., & Brindle, R. (2000) Theoretical Minimum Energies To Produce Steel for Selected Conditions. Prepared under contract to Energetics, Inc. Columbia, MD For the U.S. Department of Energy Office of Industrial Technologies Washington., DC Carnegie Mellon University Pittsburgh, PA, March 2000, available at https://www.energy.gov/sites/prod/files/2013/11/f4/theoretical_minimum_energies.pdf

International Organization for Standardization (ISO). (2013a) ISO 14404-1:2013 - Calculation method of carbon dioxide emission intensity from iron and steel production - Part 1: Steel plant with blast furnace. Available at <https://www.iso.org/standard/57298.html>.

International Organization for Standardization (ISO). (2013b) ISO 14404-2:2013 - Calculation method of carbon dioxide emission intensity from iron and steel production - Part 2: Steel plant with electric arc furnace (EAF). Available at <https://www.iso.org/standard/57299.html>

Japan NIR 2018: National Greenhouse Gas Inventory Report of Japan (2018), Greenhouse Gas Inventory Office of Japan (GIO), Center for Global Environmental Research (CGER) & National Institute for Environmental Studies (NIES). (2018) Available at: http://www-gio.nies.go.jp/aboutghg/nir/2018/NIR-JPN-2018-v4.1_web.pdf

Official Journal of the European Union. (2011a) Commission Decision of 27 April 2011 determining transitional Union-wide rules for harmonised free allocation of emission allowances pursuant to Article 10a of Directive 2003/87/EC of the European Parliament and of the Council.

Official Journal of European Union. (2011b) Average performance of 10% most efficient installation in EU for the year of 2007-2008, "Benchmark value for steel industry under the EU-ETS" (May 2011).

ThyssenKrupp Industrial Solutions AG. (2014) Coke plant technologies, available at https://www.thyssenkrupp-industrial-solutions.com/media/products_services/coke_plants/tkis_coke_plant_technologies.pdf

U.S. Environmental Protection Agency (2008). Technical Support Document for the Iron and Steel Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases, Office of Air and Radiation U.S. Environmental Protection Agency September 9, 2008, available at: <http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockkey=P1009F3X.TXT>

U.S. Environmental Protection Agency (2012). Available and Emerging Technologies for Reducing Greenhouse Gas Emissions from the Iron and Steel Industry Prepared by the Sector Policies and Programs Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, September 2012, available at: <https://www.epa.gov/sites/production/files/2015-12/documents/ironsteel.pdf>.

U.S. Code of Federal Regulations (CFR). (2018) Title 40: Protection of Environment, Part 98 - Mandatory greenhouse gas reporting, Subpart C - General Stationary Fuel Combustion Sources, §98.33 Calculating GHG emissions, U.S. Environmental Protection Agency, available at: https://www.ecfr.gov/cgi-bin/text-idx?SID=921a214b1daec4eb768bb5caead0dbaa&mc=true&node=se40.23.98_133&rgn=div8

Zhang, X., Wu, G., Wu, S. & Xiang, X. (2012) Determination of carbon dioxide emission factors in typical processes for large iron-steel companies. *Acta Scientiae Circumstantiae* **42**(8): 2024-2027, available at http://www.actasc.cn/hjkxxb/ch/reader/create_pdf.aspx?file_no=20111012001.

References copied from the 2006 Guidelines

EEA (2005). EMEP/CORINAIR. Emission Inventory Guidebook – 2005, European Environment Agency, Technical report No 30. Copenhagen, Denmark, (December 2005). Available from web site see: <http://reports.eea.eu.int/EMEP/CORINAIR4/en>

IPPC (2001). Integrated Pollution Prevention and Control (IPPC), Best Available Techniques Reference Document on the Production of Iron and Steel, December 2001, available at http://eippcb.jrc.ec.europa.eu/reference/BREF/isp_bref_1201.pdf.

- 3013 International Iron and Steel Institute (2004). Steel Statistical Yearbook 2004: International Iron and Steel Institute,
3014 COMMITTEE ON ECONOMIC STUDIES, Brussels.
- 3015 Schoenberger, H. (2000). European Conference on “The Sevilla Process: A Driver for Environmental Performance
3016 in Industry” Stuttgart, 6 and 7 April 2000, BREF on the Production of Iron and Steel - conclusion on BAT,
3017 Dr. Harald Schoenberger, Regional State Governmental Office Freiburg, April 2000.

3019 SECTION 4.4

3020 References newly cited in the 2019 Refinement

- 3021 Aarhaug, T. A., Ferber, A., Gaertner, H., Kolas, S., Ryman, S. O. & P., G. (2018) Validation of Online Monitoring
3022 of PFC by QCL with FTIR Spectroscopy. In: *TMS Light Metals*, pp. 1487-1493. Phoenix.
- 3023 Asheim, H., Aarhaug, T. A., Ferber, A., Kjos, O. S. & Haarberg, G. M. (2014) Monitoring of Low Cell Voltage
3024 PFC Formation in 200 to 300 kA Aluminium Electrolysis Cells. In: *7th KIFEE*, Kyoto.
- 3025 Bardai, A., Aga, B. E., Berveling, A., Droste, C., Fechner, M., Haugland, E., Karlsen, M., Liane, M., Ryman, S.
3026 O., Vee, T. H., Wedershoven, E. & Ovstetun, F. (2009) HAL 4e - Hydro's new generation cell technology. In:
3027 *TMS Light Metals*, pp. 301-305.
- 3028 Burkat, V. S., et al. (2018). Study of perfluorocarbon (PFC) emissions from vertical stud (VSS) self-baking anode
3029 cells during production of aluminium outside anode effects. *Metallurgist*.
- 3030 Chen, X., Li, W., Zhang, Y., Qiu, S. & Bayliss, C. (2013) Investigation on formation mechanism of non-anode
3031 effect related PFC emissions from aluminum reduction cells. In: *TMS Light Metals*, pp. 877-881.
- 3032 Dando, N., Xu, W. & Marks, J. (2009) Comparison of PFC Emissions for Operation and Newly Started Pots at the
3033 ALCOA Fjardaal Point Fed Prebake Smelter. In: *TMS Light Metals*, ed. G. P. Bearne, pp. 269-273.
- 3034 Dando, N. R., Menegazzo, N., Espinoza-Nava, L., Westendorf, N. & Batista, E. (2015) Non anode effects PFC :
3035 Measurement consideration and potential impact. In: *Light Metals*, pp. 551-555. Orlando.
- 3036 Dando, N. R., Xu, W., Nichols, R., Rusche, S. & Nemie, M. (2008) Comparison of PFC Emission Rates for
3037 Operation and Newly Started Pots at a Horizontal Stud Soderberg Smelter. In: *TMS Light Metals*, ed. D.
3038 DeYoung, pp. 233-237.
- 3039 Dion, L., Gaboury, S., Picard, F., Kiss, L. I., Poncsak, S. & Morais, N. (2018a) Universal Approach to Estimate
3040 Perfluorocarbons Emissions During Individual High-Voltage Anode Effect for Prebaked Cell Technologies.
3041 *JOM* **70**(9): 1887-1892.
- 3042 Dion, L., Kiss, L. I., Poncsák, S. & Lagacé, C. L. (2016) Prediction of low voltage tetrafluoromethane emissions
3043 based on the operating conditions of an aluminium electrolysis cell. *JOM* **68**(9): 2472-2482.
- 3044 Dion, L., Wong, D. S., Nunez, P., Gaboury, S. & Spirin, A. V. (2018b) Evaluation of time consistency when
3045 quantifying emissions of perfluorocarbons resulting from low voltage anode effects. In: *TMS Light Metals*, pp.
3046 1457-1462. Phoenix, AZ, USA.
- 3047 Emirates Global Aluminium. (2017) Reduction Cell Technologies. URL
3048 <https://www.ega.ae/en/technology/reduction-cell-technologies/>.
- 3049 Fraser, P., Steel, P. & Cooksey, M. (2013) PFC and Carbon Dioxide Emissions from an Australian Aluminium
3050 Smelter using Time-Integrated Stack Sampling and GC-MS, GC-FID Analysis. In: *TMS Light Metals*, pp. 871-
3051 876. San Antonio.
- 3052 International Aluminium Institute. (2006) The Aluminium Sector Greenhouse Gas Protocol. 65 pages.
- 3053 International Aluminium Institute. (2018) Current IAI statistics - Perfluorocarbons emissions.
- 3054 Kristensen, W., Hoskuldsson, G. & Welch, B. J. (2007) Potline startup with low anode effect frequency. In: *Light*
3055 *Metals*, pp. 712-717.
- 3056 Maltais, J.-N., Ross, J., Marcoux, A. & Gaudreault, G. (2010) Application of a Method for the Determination of
3057 PFC Emissions During Aluminium Pot Start-up. In: *TMS Light Metals*, pp. 271-276.
- 3058 Marks, J. & Nunez, P. (2018a) New Algorithm for Calculating CF₄ Emissions from High Voltage Anode Effects.
3059 In: *Light Metals*, Phoenix.
- 3060 Marks, J. & Nunez, P. (2018b) Updated Factors for Calculating PFC Emissions from Primary Aluminum
3061 Production. In: *TMS Light Metals*, pp. 1519-1525. Phoenix, AZ.

Final Draft

- Reny, P., Segatz, M., Leder, F.-M., Midtun, O. J., Hop, J. G. & Gikling, H. (2016) Low Energy Start-Up for Low Energy Cells. In: *International Committee for Study of Bauxite, Alumina & Aluminium*, Quebec city.
- Rio Tinto Alcan. (2013) AP Technology - Our products and services. URL <https://www.ap-technology.com/SitePages/products.aspx>.
- Tabereaux, A. (2004) Anode effects and PFC emissions rates. In: *8th australasian aluminium smelting technology conference*.
- US Environmental Protection Agency & International Aluminium Institute. (2008) Protocol for Measurement of Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions from Primary Aluminum Production. 42 pages.
- Wong, D. & Marks, J. (2013) Continuous PFC emissions measured on individual 400 kA cells. In: *Light Metals*, pp. 865-870. San Antonio.
- Wong, D., Nunez, P., Chen, X., Cai, B. & Bo, X. (2018) PFCs from the Chinese Aluminium Sector—Challenges in Emissions Accounting and Further Characteristics. In: *TMS Light Metals*, pp. 1527-1535. Phoenix.
- Wong, D. S., Fraser, P., Lavoie, P. & Kim, J. (2015) PFC emissions from detected versus nondetected anode effects in the aluminium industry. *JOM* **67**(2): 342-353.
- Xu, W., Dando, N. & Sedlacek, D. (2008) Comparison of PFC Emission Coefficients for Operating and Startup Pots at a Side Work Prebake Smelter. In: *TMS Light Metals*, ed. D. deYoung, pp. 245-248.
- Zarouni, A. A., Reverdy, M., Zarouni, A. & Vankatasubramaniam, K. G. (2013) A study of low voltage PFC emissions at DUBAL. In: *Light Metals*, pp. 859-863. San Antonio.

References copied from the 2006 Guidelines

- IAI (2000). International Aluminium Institute, International Aluminium Institute (2000) 'Life Cycle Assessment of Aluminium'
- IAI (2001). International Aluminium Institute, Perfluorocarbon Emissions Reduction Programme 1990 - 2000, 2001, available at <http://www.world-aluminium.org/iai/publications/documents/pfc2000.pdf>.
- IAI (2005a). International Aluminium Institute, The Aluminium Sector Greenhouse Gas Protocol, http://www.world-aluminium.org/environment/climate/ghg_protocol.pdf, 2005.
- IAI (2005b). International Aluminium Institute, survey on composition of production materials, 2005 (unpublished)
- IAI (2005c). International Aluminium Institute, Annual Anode Effect Survey 2003, www.world-aluminium.org, 2005.
- U.S. EPA and IAI (2003), U.S. Environmental Protection Agency and International Aluminium Institute, USEPA/IAI Protocol for Measurement of PFCs from Primary Aluminium Production, EPA 43-R-03-006, May 2003.

SECTION 4.8

References newly cited in the 2019 Refinement

- Cai, B., Liu, H., Kou, F., Yang, Y., Yao, B., Chen, X., Wong, D. S., Zhang, L., Li, J., Kuang, G., Chen, L., Zheng, J., Guan, D. & Shan, Y. (2018) Estimating perfluorocarbon emission factors for industrial rare earth metal electrolysis. *Resources, Conservation and Recycling* **136**: 315-323.
- International Aluminium Institute. (2006) The Aluminium Sector Greenhouse Gas Protocol. 65 pages.
- Kingsnorth, D. J. (2015) The Global Rare Earths Industry Today - Plagued by Illegal Production in China". In: *11th International Rare Earths Conference*, Singapore.
- Kjos, O. S., Solheim, A., Aarhaug, T., Osen, K. S., Martinez, A. M., Sommerseth, C., Gudbrandsen, H., Støre, A. & Gaertner, H. (2018) PFC Evolution Characteristics During Aluminium and Rare Earth Electrolysis. In: *Light Metals 2018*, pp. 1449-1455.
- Liu, K.-r., Chen, J.-s. & Wei, X.-j. (2001) Analysis of anodic gases in neodymium electrolysis. *The Chinese Journal of Nonferrous Metals* **11**(6): 1118-1120.

- 3111 Martinez, A. M., Osen, K. S., Store, A., Gudbrandsen, H., Kjos, O. S., Solheim, A., Wang, Z., Oury, A. & Namy,
 3112 P. (2018) Manufacturing of Dysprosium-Iron Alloys by Electrolysis in Fluoride-Based Electrolytes.
 3113 Electrolysis in a Laboratory-Scale Cell. *Metallurgical and Materials Transactions B: Process Metallurgy and*
 3114 *Materials Processing Science* **49**(4): 2063-2070.
- 3115 Vogel, H., Flerus, B., Stoffner, F. & Friedrich, B. (2017) Reducing Greenhouse Gas Emission from the
 3116 Neodymium Oxide Electrolysis. Part I: Analysis of the Anodic Gas Formation. *Journal of Sustainable*
 3117 *Metallurgy* **3**(1): 99-107.
- 3118 Vogel, H. & Friedrich, B. (2015) Development and Research Trends of the Neodymium Electrolysis – A Literature
 3119 Review. In: *8th European Metallurgical Conference (EMC)*, Dusseldorf, Germany.
- 3120 Vogel, H. & Friedrich, B. (2017) Reducing Greenhouse Gas Emission from the Neodymium Oxide Electrolysis.
 3121 Part II: Basics of a Process Control Avoiding PFC Emission. *International journal of nonferrous metallurgy*
 3122 **6**(3): 27-46.
- 3123 Vogel, H. & Friedrich, B. (2018) An estimation of PFC emissions by rare earth electrolysis. In: *TMS Light Metals*,
 3124 pp. 1507-1517. Phoenix.
- 3125 Wen, H., Kuang, G. & Mao, J. (2004) Circular 10 kA molten salt electrolyzer for preparing rare earth metal. In:
 3126 ed. China's State Intellectual Property Office, pp. 1-7. China: Ganzhou Keli Rare Earth New Materials Co.,
 3127 Ltd.
- 3128 Wen, H., Kuang, G. & Mao, J. (2012) 25 KA rare earth electrolytic cell for fluoride molten salt system. In: ed.
 3129 China's State Intellectual Property Office, pp. 1-6. China.
- 3130 Zhang, L., Wang, X. & Gong, B. (2018) Perfluorocarbon emissions from electrolytic reduction of rare earth metals
 3131 in fluoride/oxide system. *Atmospheric Pollution Research* **9**(1): 61-65.
- 3132
- 3133