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# 2006 IPCC Guidelines for National Greenhouse Gas Inventories

## Volume 3

# Industrial Processes and Product Use

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# VOLUME 3

# INDUSTRIAL PROCESSES AND PRODUCT USE

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# CHAPTER 1

# INTRODUCTION

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# 1 INTRODUCTION

## 1.1 INTRODUCTION

This volume, Industrial Processes and Product Use (IPPU), covers greenhouse gas emissions occurring from industrial processes, from the use of greenhouse gases in products, and from non-energy uses of fossil fuel carbon. The former section 'Solvent and Other Product Use' in the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* has been incorporated in this volume.

Greenhouse gas emissions are produced from a wide variety of industrial activities. The main emission sources are releases from industrial processes that chemically or physically transform materials (for example, the blast furnace in the iron and steel industry, ammonia and other chemical products manufactured from fossil fuels used as chemical feedstock and the cement industry are notable examples of industrial processes that release a significant amount of $CO_2$). During these processes, many different greenhouse gases, including carbon dioxide ($CO_2$), methane ($CH_4$), nitrous oxide ($N_2O$), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), can be produced.

In addition, greenhouse gases often are used in products such as refrigerators, foams or aerosol cans. For example, HFCs are used as alternatives to ozone depleting substances (ODS) in various types of product applications. Similarly, sulphur hexafluoride ($SF_6$) and $N_2O$ are used in a number of products used in industry (e.g., $SF_6$ used in electrical equipment, $N_2O$ used as a propellant in aerosol products primarily in food industry) or by end-consumers (e.g., $SF_6$ used in running-shoes, $N_2O$ used during anaesthesia). A notable feature of these product uses is that, in almost all cases, significant time can elapse between the manufacture of the product and the release of the greenhouse gas. The delay can vary from a few weeks (e.g., for aerosol cans) to several decades as in the case of rigid foams. In some applications (e.g., refrigeration) a fraction of the greenhouse gases used in the products can be recovered at the end of product's life and either recycled or destroyed. In addition, several other fluorinated greenhouse gases may be used in special processes, for example in semiconductor manufacture:

- nitrogen trifluoride ($NF_3$)
- trifluoromethyl sulphur pentafluoride ($SF_5CF_3$)
- halogenated ethers (e.g., $C_4F_9OC_2H_5$, $CHF_2OCF_2OC_2F_4OCHF_2$, $CHF_2OCF_2OCHF_2$)

and other halocarbons not covered by the Montreal Protocol including $CF_3I$, $CH_2Br_2$, $CHCl_3$, $CH_3Cl$, $CH_2Cl_2$.

This volume of the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (*2006 IPCC Guidelines*) also provides estimation methods for halogenated greenhouse gases which are not covered by the Montreal Protocol and for which GWP values are not available from the IPCC Third Assessment Report (TAR), inter alia:

- $C_3F_7C(O)C_2F_5$[1]
- $C_7F_{16}$
- $C_4F_6$
- $C_5F_8$
- c-$C_4F_8O$.

Some of the methods can be used for other halocarbons not controlled by the Montreal Protocol (inlcuding several fluids and blends e.g., traded under the commercial lables of the Fluorinert™ and Galden® product families)[2]

Product use is combined with the industrial process guidance because in many cases production and import/export data are needed to estimate emissions in products and because product use may also occur as part of industrial activities, apart from the non-industrial sectors (retail, services, households.) It is therefore desirable to link estimation of emissions associated with production and product use. The non-energy uses of fossil fuels

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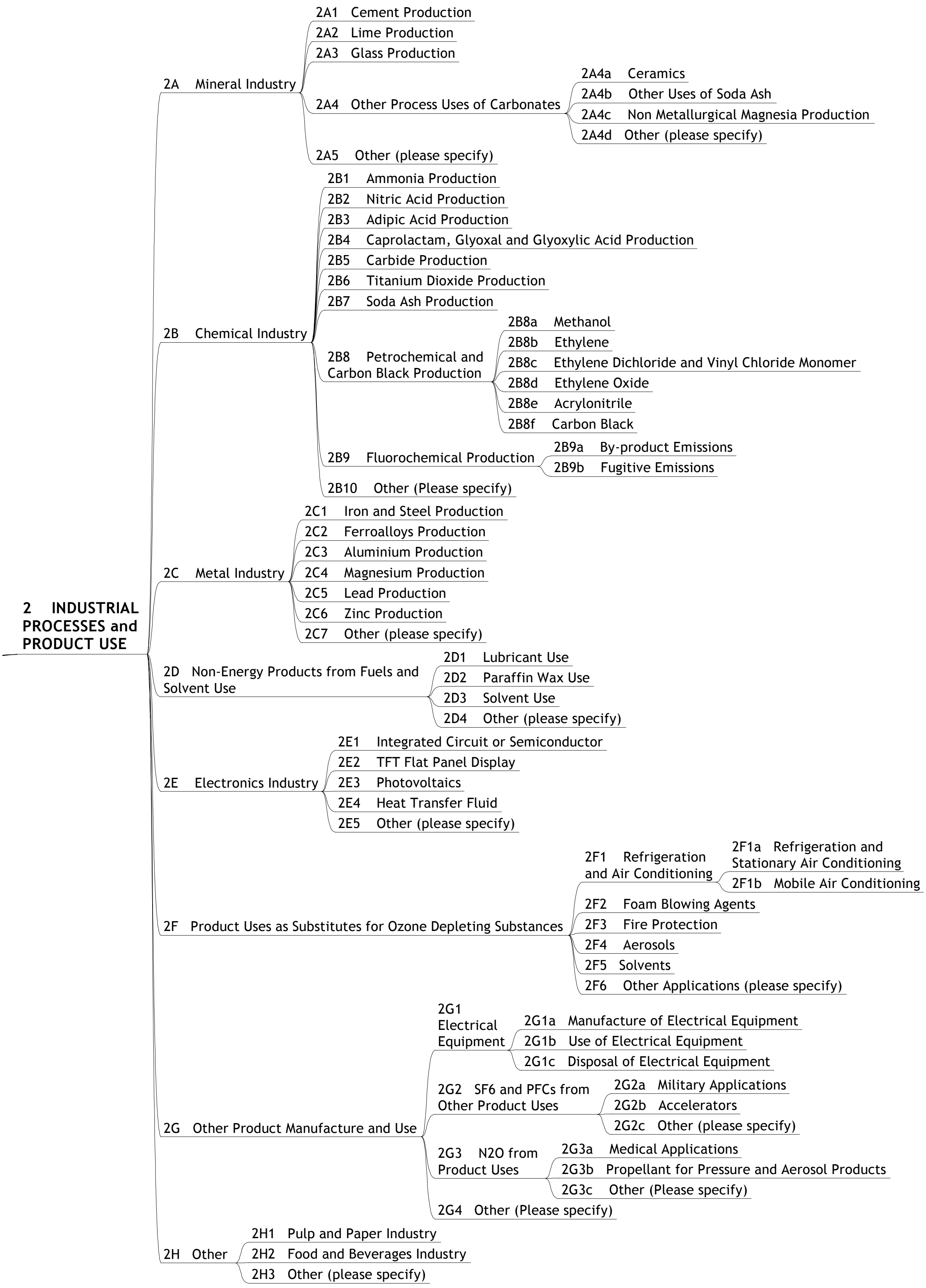
[1] This gas is traded as Novec™612 which is a fluorinated ketone produced by 3M (Milbrath, 2002).

[2] The Fluorinert™ materials are selected from fully fluorinated alkanes, ethers, tertiary amines and aminoethers and mixtures thereof to obtain the desired properties. The Galden® fluids span a range of fully fluorinated polyethers, called perfluoropolyethers (PFPEs).

encompass their uses as feedstock, reductants and as non-energy products in which their physical properties are used directly rather than combusted for energy purposes.

**Figure 1.1 Industrial Processes and Product Use categories**



This chapter presents:

- the definition and structure of the treatment of industrial processes and product use (1.1);
- a number of general or cross-cutting issues (1.2), among which are the definition of industrial process and fuel combustion emissions (1.2.1) and sources of international data (1.2.5);
- the nature of non-energy uses of fossil fuels (1.3);
- the completeness and allocation of $CO_2$ from non-energy use of fuels (1.4); and
- the choice between the mass-balance and emission-factor approaches (1.5) with specific relevance to the fluorinated gases covered in Chapters 7 and 8 of this volume.

#### SECTOR CLASSIFICATION AND STRUCTURE

Figure 1.1 sets out the structure and classification codes for each category and subcategory for the IPPU Sector.

# 1.2 GENERAL AND CROSS-CUTTING ISSUES

## 1.2.1 Definition of industrial process and fuel combustion emissions

Allocating emissions from the use of fossil fuel between the Energy and IPPU Sectors can be complex. The feedstock and reductant uses of fuels frequently produce gases that may be combusted to provide energy for the process. Equally part of the feedstock may be combusted directly for heat. This can lead to uncertainty and ambiguity in reporting. To help to overcome this problem, these *Guidelines* introduce practical guidance on when to allocate $CO_2$ emissions released from combustion of fuel to the subcategory fuel combustion within the energy source category or to the industrial process source category. The rule is given in Box 1.1.

The problems encountered when allocating $CO_2$ emissions to fuel combustion or industrial processes are particularly prominent when by-product fuels or waste gases are transferred from the manufacturing site and combusted elsewhere in quite different activities. This fact has formed the principle for the guidance given in Box 1.1, which provides a definition for fuel combustion and a criterion for deciding whether emissions from by-product fuels should be reported in the IPPU Sector or in an Energy Sector source category. Section 1.3 provides background information on the nature of non-energy uses of fossil fuels, accounting for feedstock and reductant uses of fossil fuels and on the links with the fossil fuel use in the Energy Sector.

## 1.2.2 Capture and abatement

In certain IPPU categories, particularly large point sources of emissions, there could be capture of emissions for recovery and use, or destruction. It is *good practice* to account for capture of emissions using detailed country-specific or more suitably plant-level data. Consequently, Tier 1 methods provided in this volume are not appropriate for tracking this type of abatement. Capture should be incorporated into equations by means of an additional term that represents either a measured quantity of capture, or the efficiency of an abatement system in combination with that system's utilisation throughout the year. It is recommended not to account for capture by using a modified emission factor, as this reduces transparency and risks inconsistency in time series.[3]

Should $CO_2$ capture technology be installed and used at a plant, it is *good practice* to deduct the $CO_2$ captured in a higher tier emissions calculation. Quantities of $CO_2$ for later use and short-term storage should not be deducted from $CO_2$ emissions except when the $CO_2$ emissions are accounted for elsewhere in the inventory[4]. The default

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[3] In industries such as nitric acid and adipic acid production, it is standard engineering practice to design modern plants with built-in destruction technology, often in response to the need to address NOx emissions. In these special cases, it is possible to use emission factors that reflect this destruction technology, provided that the inventory compiler can document that the technology is in place and has been utilised.

[4] Examples include urea production (Section 3.2) and the use of $CO_2$ in methanol production (Section 3.9) where $CO_2$ due to the final products is accounted for.

assumption is that there is no carbon dioxide capture and storage (CCS) taking place.[5] Any methodology taking into account $CO_2$ capture should consider that $CO_2$ emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately inventory compilers should ensure that the same quantities of $CO_2$ are not double counted. In these cases the total amount of $CO_2$ captured should preferably be reported in the corresponding fuel combustion and IPPU source categories in proportion to the amounts of $CO_2$ generated in these source categories. For additional information on $CO_2$ capture and storage refer to Volume 2, Section 2.3.4.

For gases other than $CO_2$, it is *good practice* to ensure that later emissions of the captured gases are accounted for where they occur. An example of this is for HFC-23 produced as by-product from HCFC-22 production. Here the substance is extracted from the off gas and used in products or processes. Methods to appropriately address these capture efficiencies can be found within this volume where sufficient information currently exist.

Often a partly or full abatement of greenhouse gas emissions from a process will occur by means of off-gas treatment e.g., the destruction of greenhouse gases by post-combustion. This approach is often applied for substances with high global warming potentials such as PFCs in the semiconductor industry or HFC-23 in the chemical industry. Destruction efficiencies depend equally on operating practices and technologies applied.

### BOX 1.1
### ALLOCATION OF $CO_2$ EMISSIONS TO FUEL COMBUSTION OR INDUSTRIAL PROCESS EMISSIONS

Fuel combustion is defined in a functional way as:

*the intentional oxidation of materials within an apparatus that is designed to provide heat or mechanical work to a process, or for use away from the apparatus.*

The aim of this definition is to separate the combustion of fuels for distinct and productive energy use from the heat released from the use of hydrocarbons in chemical reactions defining an industrial process.

Process fuels may be obtained directly from the feedstock as in the case of ammonia manufacture where natural gas provides both feedstock and fuel. Alternatively, process fuels may be obtained indirectly through the use of by-products of feedstock processing or reductant use. Examples are the off gases obtained from the steam cracking of naphtha feedstock for ethylene manufacture and blast furnace gas from blast furnaces.

During these activities emissions may occur from both the fuel combustion and industrial process stages. However, it is often impractical or impossible to report separately the two types of emissions. (See Section 1.3.2 below.) Accordingly the following rule has been formulated to simplify reporting:

*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. These source categories are normally 2B and 2C. However, if the derived fuels are transferred for combustion in another source category, the emissions should be reported in the appropriate part of Energy Sector source categories* (*normally 1A1 or 1A2*).

Two examples may help illustrate the definition.

1. If blast furnace gas is combusted entirely within the Iron and Steel industry (whether for heating blast air, site power needs or for metal finishing operations) the associated emissions are reported in the IPPU source subcategory 2C1. If part of the gas is delivered to a nearby brick works for heat production or a main electricity producer then the emissions are reported in source subcategories (1A2f or 1A1a).

2. If surplus methane or hydrogen from the steam cracking of naphtha is combusted within the petrochemical site for another process then the emissions are reported as emissions in IPPU, 2B8. On the other hand, if the gases are passed to a nearby refinery for fuel use then the associated emissions would be reported under 1A1b, Petroleum Refining.

---

[5] If a country reports capture of $CO_2$, it is *good practice* to ensure that $CO_2$ is stored in long-term geological storage sites that are monitored according to the guidance in Chapter 5, $CO_2$ Transport, Injection and Geological Storage, of Volume 2: Energy.

## 1.2.3 Precursors

Methodologies for the estimation of emissions of precursors ($NO_x$, NMVOC, CO, $SO_2$ and $NH_3$) are not given in these *Guidelines*. Emissions of these gases can be estimated using the other well-established guidance. One example is the EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005)[6]. This guidebook has been developed for emission inventories of substances regulated under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) (see Box 7.1, Chapter 7, Precursors and Indirect Emissions, of Volume 1: General Guidance and Reporting) and covers all source sectors and should therefore be considered as the primary source of information for estimation of these emissions.

Volume 1, Table 7.1 provides a link between the IPCC source categories and the corresponding methodology chapters in the EMEP/CORINAIR Emission Inventory Guidebook. This table provides information on the specific EMEP/CORINAIR chapter in which methodological guidance can be found on $NO_x$, CO, NMVOC, $SO_2$ and $NH_3$. It also includes information on the availability of methods and the significance of precursor emissions from particular source categories.

Some of the methodologies and emission factors in the EMEP/CORINAIR Emission Inventory Guidebook are relevant to conditions and source categories in both developed and developing countries. However, for some sectors, such as solvents, differences between the developed and developing countries may be larger and the EMEP/CORINAIR Emission Inventory Guidebook should be used with great care.

## 1.2.4 Indirect $N_2O$

Deposition of nitrogen containing compounds onto soils gives rise to emissions of $N_2O$. This occurs through both nitrification and denitrification processes (see Volume 4: Agriculture, Forestry and Other Land Use). These are called 'indirect $N_2O$' emissions. To ensure consistency across the inventory it is important to estimate indirect $N_2O$ emissions from deposition of nitrogen containing compounds emitted in the IPPU Sector. The methodology is simple and attributes all indirect emissions of $N_2O$ to the original source of the nitrogen.

The nitrogen sources are $NO_x$ (NO and $NO_2$) and $NH_3$. $NO_x$ is primarily emitted form fuel combustion while $NH_3$ is mainly emitted from agriculture, though there can be significant industrial process emissions of both these gases. Information for estimating emissions of $NO_x$ and $NH_3$ can be found elsewhere. One example is the EMEP/CORINAIR Emission Inventory Guidebook. (EEA, 2005)

Comprehensive guidance is provided in Chapter 7, Precursors and Indirect Emissions, of Volume 1: General Guidance and Reporting, on estimating indirect $N_2O$ emissions resulting from $NO_x$ and/or $NH_3$ emissions. Where countries have an existing $NO_x$ and/or $NH_3$ inventory it is *good practice* to estimate indirect $N_2O$.

## 1.2.5 International data sources

Good national data are to be preferred and used wherever available. In cases where data availability is a problem inventory compilers may consult international data sources for proxy data for IPPU estimates. Sources include:

- United Nations (UN) industrial production statistics which are available in hard copy in the 'Industrial Commodity Statistics Yearbook' (UN, 2004) from 1991 onwards and as CD-ROM with statistics from 1950 onwards; data (in physical units) are given by commodity and country for all years and almost all commodities relevant for emission inventories.
- OECD publishes production data in monetary units (value of production) for the OECD countries (http://www.oecd.org/statsportal/0,2639,en_2825_293564_1_1_1_1_1,00.html) but data for the most recent years are not available. OECD also sells a publication with additional data (http://www.oecd.org/document/63/0,2340,en_2825_499554_1935935_1_1_1_1,00.html), but according to the web site the most recent data are for 2001. National account data can be also accessed, for a charge, for the years up to 2002. Most useful is perhaps the STAN (Industry Structural Analysis) database of the OECD (again only available via subscription at http://hermia.sourceoecd.org/vl=4126925/cl=58/nw=1/rpsv/cw/vhosts/oecdstats/16081307/v265n1/contp1-1.htm), this contains monetary production data, for years up to 2002, for major industries. Note, however, that the monetary value reflects not only the production quantity but also the price of the product - which may fluctuate from one year to another - so the data should be used with care.

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[6] The EMEP/CORINAIR Nomenclature for Reporting (NFR) source categories have been developed to be compatible to the IPCC reporting categories (EEA, 2005).

- Eurostat publishes PRODCOM data (Eurostat, 2005) for many European countries.
- Statistics on production of a large number of commodities and capacity of individual plants are provided by the commodity and country by the U.S. Geological Survey as part of the International Minerals Statistics and Information (USGS, 2005).

**TABLE 1.1**
**INDUSTRIAL PROCESSES AND PRODUCT USE CATEGORIES AND THEIR POSSIBLE EMISSIONS**

| **2 Industrial Processes and Product Use** (Note 1, 2) | $CO_2$ | $CH_4$ | $N_2O$ | HFCs | PFCs | $SF_6$ | Other halo-genated Gases (Note3) |
|---|---|---|---|---|---|---|---|
| **2A Mineral Industry** | | | | | | | |
| 2A1: Cement Production | X | * | | | | | |
| 2A2: Lime Production | X | * | | | | | |
| 2A3: Glass Production | X | * | | | | | |
| 2A4: Other Process Uses of Carbonates | | | | | | | |
| 2A4a: Ceramics | X | * | | | | | |
| 2A4b: Other Uses of Soda Ash | X | * | | | | | |
| 2A4c: Non Metallurgical Magnesia Production | X | * | | | | | |
| 2A4d: Other | X | * | | | | | |
| 2A5: Other | X | * | * | | | | |
| **2B Chemical Industry** | | | | | | | |
| 2B1: Ammonia Production | X | * | * | | | | |
| 2B2: Nitric Acid Production | * | * | X | | | | |
| 2B3: Adipic Acid Production | * | * | X | | | | |
| 2B4: Caprolactam, Glyoxal and Glyoxylic Acid Production | * | * | X | | | | |
| 2B5: Carbide Production | X | X | * | | | | |
| 2B6: Titanium Dioxide Production | X | * | * | | | | |
| 2B7: Soda Ash Production | X | * | * | | | | |
| 2B8: Petrochemical and Carbon Black Production | | | | | | | |
| 2B8a: Methanol | X | X | * | | | | |
| 2B8b: Ethylene | X | X | * | | | | |
| 2B8c: Ethylene Dichloride and Vinyl Chloride Monomer | X | X | * | | | | |
| 2B8d: Ethylene Oxide | X | X | * | | | | |
| 2B8e: Acrylonitrile | X | X | * | | | | |
| 2B8f: Carbon Black | X | X | * | | | | |
| 2B9: Fluorochemical Production (Note 4) | | | | | | | |
| 2B9a: By-product Emissions (Note 5) | | | | X | X | X | X |
| 2B9b: Fugitive Emissions (Note 5) | | | | X | X | X | X |
| 2B10: Other | * | * | * | * | * | * | * |
| **2C Metal Industry** | | | | | | | |
| 2C1: Iron and Steel Production | X | X | * | | | | |
| 2C2: Ferroalloys Production | X | X | * | | | | |
| 2C3: Aluminium Production | X | * | | | X | | |
| 2C4: Magnesium Production (Note 6) | X | | | X | X | X | X |
| 2C5: Lead Production | X | | | | | | |
| 2C6: Zinc Production | X | | | | | | |
| 2C7: Other | * | * | * | * | * | * | * |
| **2D Non-Energy Products from Fuels and Solvent Use** (Note 7) | | | | | | | |
| 2D1: Lubricant Use | X | | | | | | |
| 2D2: Paraffin Wax Use | X | * | * | | | | |
| 2D3: Solvent Use (Note 8) | | | | | | | |
| 2D4: Other (Note 9) | * | * | * | | | | |
| **2E Electronics Industry** | | | | | | | |
| 2E1: Integrated Circuit or Semiconductor (Note 10) | * | | * | X | X | X | X |
| 2E2: TFT Flat Panel Display (Note 10) | | | | X | X | X | X |
| 2E3: Photovoltaics (Note 10) | | | | X | X | X | X |
| 2E4: Heat Transfer Fluid (Note 11) | | | | | | | X |
| 2E5: Other | * | * | * | * | * | * | * |

### TABLE 1.1 (CONTINUED)
### INDUSTRIAL PROCESSES AND PRODUCT USE CATEGORIES AND THEIR POSSIBLE EMISSIONS

| **2 Industrial Processes and Product Use** (Note 1, 2) | $CO_2$ | $CH_4$ | $N_2O$ | HFCs | PFCs | $SF_6$ | Other halo-genated Gases (Note3) |
|---|---|---|---|---|---|---|---|
| **2F Product Uses as Substitutes for Ozone Depleting Substances** | | | | | | | |
| 2F1: Refrigeration and Air Conditioning | | | | | | | |
| 2F1a: Refrigeration and Stationary Air Conditioning | * | | | X | X | | * |
| 2F1b: Mobile Air Conditioning | * | | | X | X | | * |
| 2F2: Foam Blowing Agents | * | | | X | * | | * |
| 2F3: Fire Protection | * | | | X | X | | * |
| 2F4: Aerosols | | | | X | X | | * |
| 2F5: Solvents (Note 12) | | | | X | X | | * |
| 2F6: Other Applications | * | * | * | X | X | | * |
| **2G Other Product Manufacture and Use** | | | | | | | |
| 2G1: Electrical Equipment | | | | | | | |
| 2G1a: Manufacture of Electrical Equipment (Note 13) | | | | | X | X | * |
| 2G1b: Use of Electrical Equipment (Note 13) | | | | | X | X | * |
| 2G1c: Disposal of Electrical Equipment (Note 13) | | | | | X | X | * |
| 2G2: $SF_6$ and PFCs from Other Product Uses | | | | | | | |
| 2G2a: Military Applications | | | | | * | X | * |
| 2G2b: Accelerators (Note 14) | | | | | * | X | * |
| 2G2c: Other | | | | | X | X | * |
| 2G3: $N_2O$ from Product Uses | | | | | | | |
| 2G3a: Medical Applications | | | X | | | | |
| 2G3b: Propellant for Pressure and Aerosol Products | | | X | | | | |
| 2G3c: Other | | | X | | | | |
| 2G4: Other | * | * | | * | | | * |
| **2H Other** | | | | | | | |
| 2H1: Pulp and Paper Industry (Note 15) | * | * | | | | | |
| 2H2: Food and Beverages Industry (Note 15) | * | * | | | | | |
| 2H3: Other | * | * | * | | | | |

1) ‘X’ denotes gases for which methodological guidance is provided in this volume.
2) ‘*’ denotes gases for which emissions may occur but for which no methodological guidance is provided in this volume.
3) For precursors (NOx, CO, NMVOC, $SO_2$ and $NH_3$) see Table 7.1 in Chapter 7 of Volume 1.
4) The Tiers 2 and 3 methodologies are applicable to any of the fluorinated greenhouse gases listed in Tables 6.7 and 6.8 of the Contribution of Working Group I to the Third Assessment Report of the IPCC (IPCC, 2001), comprising HFCs, PFCs, $SF_6$, fluorinated alcohols, fluorinated ethers, $NF_3$, $SF_5CF_3$. In these tiers all estimates are based on measurements, either measured losses from the process or measured emissions, and accommodate process-specific releases. For the Tier 1 methodology, default values are provided for HFC-23 emissions from HCFC-22 manufacture and for process emissions of HFCs, PFCs and $SF_6$. For the other materials there are too few manufacturers, each with individual technology, to permit the use of general default values.
5) The ‘Other halogenated gases’ are fluorinated alcohols, fluorinated ethers, $NF_3$, $SF_5CF_3$.
6) Small amounts of $CO_2$ used as a diluent for $SF_6$ and emitted during magnesium processing is considered insignificant and is usually counted elsewhere. The ‘other halogenated gases’ here mainly comprise fluorinated ketones.
7) Emissions from feedstock uses in petrochemical industry should be addressed in 2B8 (Petrochemical and Carbon Black Production). Emissions from some product uses should be allocated to each industry source category (e.g., $CO_2$ from carbon anodes and electrodes → 2C (Metal Industry)).
8) Only NMVOC emissions and no direct greenhouse gases are relevant to this category. Therefore no methodological guidance is provided in this volume. For guidance on NMVOC, see Chapter 7, Volume 1.
9) Emissions from Asphalt Production, Paving of Roads and Roofing are included here. For details, see Section 5.4 of this volume.
10) The ‘Other halogenated gases’ are $NF_3$, $c\text{-}C_4F_8O$, etc.
11) The ‘Other halogenated gases’ here include $C_4F_9OC_2H_5$ (HFE-7200), $CHF_2OCF_2OC_2F_4OCHF_2$ (H-Galden 1040x), $CHF_2OCF_2OCHF_2$ (HG-10), etc.
12) Emissions from use of fluorinated gases as solvent should be reported here. Emissions from aerosols containing solvents should be reported under Category 2F4 rather than under this category. Emissions from other solvent use should be reported under 2D3.
13) At the time of writing of these *Guidelines*, no emissions of ‘Other halogenated gases’ are identified, but it is possible that these gases may be used and emitted in the future.
14) At the time of writing of these *Guidelines*, no emissions of PFCs or ‘Other halogenated gases’ are identified, but it is possible that these gases may be used and emitted in the future.
15) No specific section on these categories is provided in this volume, but methodological guidance on $CO_2$ emissions from use of carbonates from these industries is provided in Chapter 2, Section 2.5 of this volume.

# 1.3 NATURE OF NON-ENERGY USES OF FOSSIL FUELS

As explained in Section 1.1 some $CO_2$ emissions from fossil fuels arise from uses that are not primarily for energy purposes and, in this section, the principles are described which have guided their estimation and reporting. The methods used to estimate emissions are described in the specific IPPU source category chapters (Chapters 3, 4 and 5). This section provides important and additional background information for the use of data relating to non-energy use and the links between these data and the fossil fuel use.

Non-energy use is widespread, diverse and the correct reporting of its emissions is conceptually difficult. It is *good practice* to ensure that all fossil fuels supplied for non-energy purposes can be linked to uses covered by the inventory and the reported emissions are consistent with the carbon supplied. Accordingly, Section 1.4 provides guidance for assessing consistency and completeness of carbon emissions from feedstock use of fuels by (a) checking that feedstock requirements of processes included in the inventory are in balance with the feedstock supply as recorded in national energy statistics, (b) checking that total reported bottom-up calculated $CO_2$ emissions from feedstock sources at different subcategory levels are complete and consistent, (c) documenting and reporting how these emissions are allocated in the inventory.

## 1.3.1 Types of uses

Some primary fuels (coal, natural gas) and secondary fuels derived from coal and crude oil may be used for non-fuel purposes. These are commonly referred to as non-energy use of fuels although their use may involve combustion of part of the hydrocarbon content for heat-raising.

Three categories of non-energy use can be distinguished depending on its use:

1. *Feedstock*: Feedstocks are fossil fuels that are used as raw materials in chemical conversion processes in order to produce primarily organic chemicals and, to a lesser extent, inorganic chemicals (especially ammonia) and their derivatives (OECD/IEA/Eurostat, 2004). In most cases, part of the carbon remains embodied in the product manufactured. The use of hydrocarbon feedstocks in chemical conversion processes is almost entirely confined to the chemical and petrochemical industries.
2. *Reductant*: Carbon is used as reducing agent for the production of various metals (Chapter 4) and inorganic products (Sections 3.6 – 3.8). It is either used directly as reducing agent or indirectly via the intermediate production of electrodes used for electrolysis. In most cases, only very small amounts of carbon are embodied in the product manufactured, while the major part is oxidised during the reduction process.
3. *Non-energy product*: Apart from fuels, refineries and also coke ovens produce some non-energy products which are used directly (i.e., without chemical conversion) for their physical or diluent properties or which are sold to the chemical industry as chemical intermediate. Lubricants and greases are used in engines for their lubricating properties; paraffin waxes are used as candles, for paper coating etc.; bitumen on roofs and roads for its waterproofing and wear qualities. Refineries also produce white spirits, which are used for their solvent properties.

This chapter discusses emissions that result from the first use of the hydrocarbons belonging to these three categories. Table 1.2 shows the types of hydrocarbons used in the three categories and the main applications. The list of fuel types and processes is illustrative and not exhaustive as some lesser uses of refinery or coke oven products are omitted. For example, refinery olefins are not shown because only a minor portion of the olefins used for the manufacture of intermediate products is produced in refineries.

This section focuses on the issues surrounding the reporting of industrial process and fuel combustion emissions from the use of fossil fuels as feedstocks and reductants (the first and second categories in Table 1.2). The relatively simpler issues affecting estimation of emissions from the first uses of non-energy products (the third category in Table 1.2) are presented with the methods in Chapter 5.

In addition to the emissions from the first use of hydrocarbons, products made from feedstocks (methanol, ethylene, carbon black) and their derivatives may lead to additional emissions after manufacture and sale. For example, the conversion of ethylene to ethylene oxide leads to substantial industrial process $CO_2$ emissions (Section 3.9).

Emissions from subsequent uses of ‘used’ non-energy products (post-consumer waste) are not included in this volume on IPPU Sector but are covered under the Energy and Waste Sectors depending on whether the treatment occurs with or without energy recovery or in the form of wastewater treatment.

TABLE 1.2
TYPES OF USE AND EXAMPLES OF FUELS USED FOR NON-ENERGY APPLICATIONS

| Type of use | Example of fuel types | Product/process | Chapter |
|---|---|---|---|
| Feedstock | natural gas, oils, coal | ammonia | 3.2 |
| | naphtha, natural gas, ethane, propane, butane, gas oil, fuel oils | methanol, olefins (ethylene, propylene), carbon black | 3.9 |
| Reductant | petroleum coke | carbides | 3.6 |
| | coal, petroleum coke | titanium dioxide | 3.7 |
| | metallurgical cokes, pulverised coal, natural gas | iron and steel (primary) | 4.2 |
| | metallurgical cokes | ferroalloys | 4.3 |
| | petroleum coke, pitch (anodes) | aluminium [1] | 4.4 |
| | metallurgical coke, coal | lead | 4.6 |
| | metallurgical coke, coal | zinc | 4.7 |
| Non-energy product | lubricants | lubricating properties | 5.2 |
| | paraffin waxes | misc. (e.g., candles, coating) | 5.3 |
| | bitumen (asphalt) | road paving and roofing | 5.4 |
| | white spirit[2], some aromatics | as solvent (paint, dry cleaning) | 5.5 |

[1] Also used in secondary steel production (in electric arc furnaces) (see Chapter 4.2).

[2] Also known as mineral turpentine, petroleum spirits, industrial spirit ('SBP').

## 1.3.2 Accounting for feedstock and reductant uses of fossil fuels and their $CO_2$ emissions

Ideally the estimation of emissions from the uses of fuels as feedstocks and reductants would proceed from knowledge of the specific plant data relevant for the processes considered. However, it is rare that all necessary data are available and for some, at least, of the estimations national data on the non-energy use of fuels may be needed. To identify the appropriate data for the estimation of $CO_2$ emissions from processes using fuel hydrocarbons as feedstock or as reductant, it is necessary to understand the relationships between the hydrocarbon flows and national energy data.

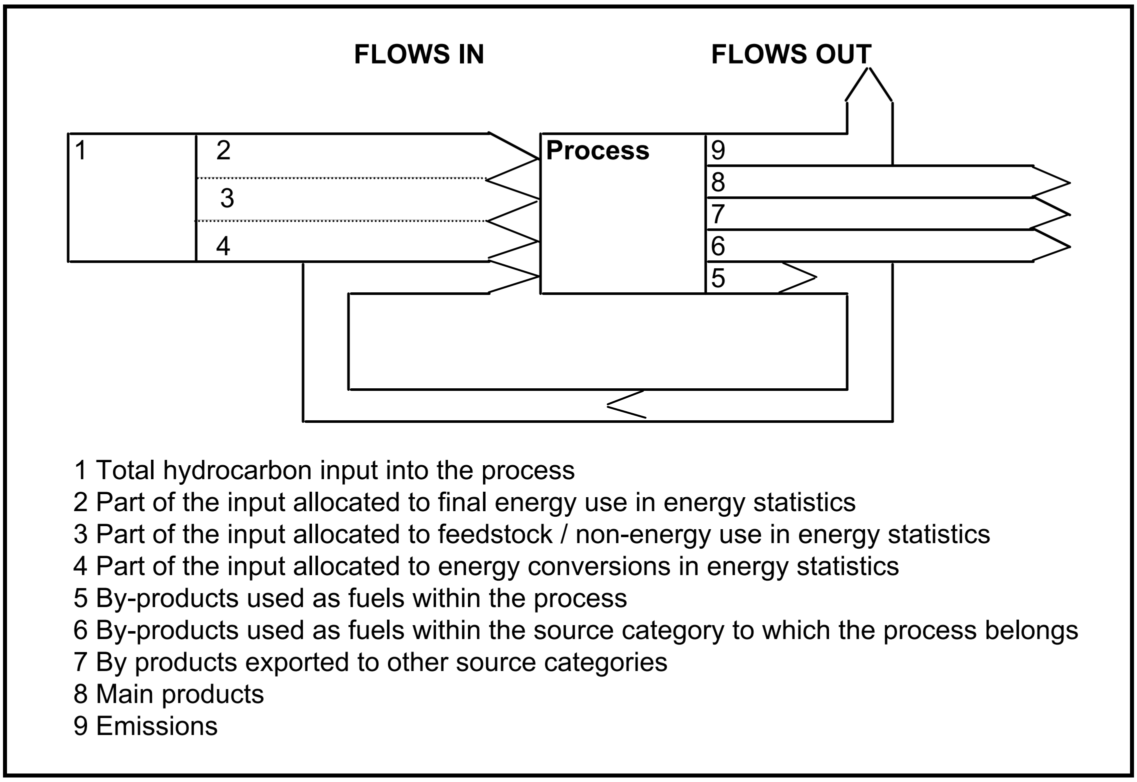
The use of the term non-energy use differs between countries and sources of energy statistics (Patel, 1999). For example, the three categories given above are often not grouped together as non-energy use in energy statistics. In most energy statistics, fuel inputs of *reductants* to blast furnaces are not included but accounted for as inputs to a fuel conversion activity transforming coke and other inputs to blast furnace gas (see below). The International Energy Agency (IEA) follows this approach. It also reports the *feedstock* category as a memo item under energy use within the chemicals branch of industry whereas supplies of *non-energy products* as defined above are reported under 'non-energy use'. In contrast, in many national energy statistics, the total of the three categories (usually without blast furnaces) is reported as one single category called non-energy use.

The accounting practice for the feedstock and reductant use of fuels differs significantly between countries and between processes. A general *hydrocarbon balance* for processes where hydrocarbon inputs are used for feedstock /reductant purposes is illustrated in Figure 1.2 and can help to understand the differences in system boundaries for non-energy use in energy statistics across countries.

In some processes using hydrocarbons as raw materials, fuel by-products are produced next to the main products. The by-products are combusted to supply energy to either the same process (Flow 5), to other processes in the same industrial sector (Flow 6) or elsewhere in other industrial sectors (Flow 7).

In primary iron production in blast furnaces, coke is used together with coal and other supplemental inputs to reduce iron ore. Coke is made from coal in coke ovens, which also yields coal tar and coke oven gas. In the blast furnace, blast furnace gas is produced. The pig iron formed in the blast furnace is mostly transformed into steel in the basic oxygen furnace, thereby producing oxygen furnace gas containing most of the carbon embodied in the pig iron. Some pig iron may also be supplied to iron foundries and other applications. In national and international energy statistics, in order to maintain an energy balance, inputs to coke ovens and blast furnaces are normally not reported as non-energy use (reductant) but identified as energy flows in the energy conversion sector. All products of these processes (coke, coke oven gas, coal tars, blast furnace gas and oxygen furnace gas) are reported as output from the conversion sector unless parts are consumed in the process itself or in other processes of the conversion sector. The output of the conversion sector is reported as final energy use (in the sector where the fuel is used) or as final non-energy use (coal tars).

**Figure 1.2 General material balance of industrial processes where products are made using hydrocarbon feedstock (size of flows arbitrarily chosen). (Adapted from Neelis *et al.*, 2005)**



In the steam cracking process to produce ethylene and other basic chemicals, besides the main products (Flow 8), fuel by-products are produced. The fuel by-products are partly used to sustain the endothermic steam cracking reaction (Flow 5) partly used as fuel for other chemical purposes (Flow 6) and partly they are used in other sectors (Flow 7, e.g., backflows to the refineries for incorporation in refinery production). In contrast to the primary iron and steel industry, the conversion of the input hydrocarbons to the fuel by-products is often not covered as an energy conversion process in national energy statistics, usually because the data on production of fuel by-products are not available. Instead, the total hydrocarbon input (including the hydrocarbons that will appear in the fuel by-products) is allocated to feedstock use. In countries, where the production of by-products is known, the combustion of fuel by-products may be included as final energy consumption in the national energy statistics and may be excluded from non-energy use.

In the production of synthesis gas to produce ammonia, methanol and other chemicals, the hydrocarbon input is used to produce synthesis gas via the steam reforming or partial oxidation processes. Since steam reforming is an endothermic process, part of hydrocarbon input is burned in a furnace to sustain the reaction. Therefore, part of the hydrocarbon input results in $CO_2$ emissions from fuel combustion, whereas another part results in industrial process emissions. In conventional steam reforming, combustion and reforming take place in separate reactors and separate data for the hydrocarbon requirements of each may exist. In more advanced process concepts and in partial oxidation, it is much more difficult to distinguish clearly between combustion and process emissions. According to the allocation principle given in Box 1.1, all emissions from the production of synthesis gas should be reported in the IPPU Sector.

Uses of *other hydrocarbon inputs* in processes other than those discussed here may also be reported as non-energy use in national energy statistics. The model figure above and the processes already described should therefore be seen as examples.

In national energy statistics a gross definition of non-energy use for these processes may be applied in which the *total* hydrocarbon input is allocated to non-energy use. Statisticians may also apply a net definition by subtracting from the total input the part allocated to final energy use in the process. In the case of a 'gross' definition, Flow 1 equals Flow 3 in Figure 1.2 and Flow 2 and 4 are absent. In the case of a 'net' definition, the input (Flow 1) is divided between non-energy use (Flow 3) and final energy use (Flow 2). Apart from pure gross and pure net definitions mixed approaches are sometimes applied, depending on the data availability for certain processes and certain fuels. It is necessary to understand well the definition of non-energy use when preparing the inventory in the given country in order to prevent double counting and ensure that $CO_2$ emissions are not overlooked (see Section 1.4). Ideally, available data would cover all flows identified in Figure 1.2. Alternatively the consumption of fuels in the process (Flow 5) will permit an estimate of IPPU Sector emissions. However, it is unusual that either data set is available so the above description of processes and data should provide sufficient understanding to guide the search for the key data elements required for reporting IPPU Sector emissions. These are the fuel carbon supplied to the process (Flow 1), the carbon contained in products (Flow 8) and by-product fuels *used in another source category* (Flow 7; also see Box 1.1). An estimate of emissions may be made by subtracting the last two items from the first.

### 1.3.3 Emissions from refinery processes

Refineries manufacture petroleum products for fuel and for non-energy uses, and in doing so produce hydrogen and other gases, intermediate products and basic chemicals. The $CO_2$ emissions from fuel consumed by the refinery for this activity are reported as Energy Sector emissions. This principle is maintained in the *Guidelines* even when some fuel use in the refinery is to support manufacture of chemicals for sale (for example, propylene or aromatics). The manufacture of basic chemicals in refineries is a normal occurrence usually through the treatment of by-products of mainstream manufacture and they may be used in other refinery processes or transferred to adjoining petrochemical works. However, in some circumstances the demand for basic chemicals may cause the refinery to adjust production processes to increase supply of the chemical and sell directly into the market. Despite this activity the fuel use to support all processes is still considered as refinery fuel and the emissions as Energy Sector emissions. It is important to recognise that the production for sale of basic chemicals in refineries is considered a secondary activity distinct from the manufacture of chemicals in adjoining or co-located petrochemical works. This is consistent with the separate statistical classification of the two economic activities.

## 1.4 QC OF COMPLETENESS AND ALLOCATION OF $CO_2$ FROM NON-ENERGY USES

### 1.4.1 Introduction

The inventory compiler has the task of minimizing omissions and avoiding double counting of emissions from fossil carbon bearing products. It is also important to ensure that all sources have been identified and correctly allocated to a source category.

Two Quality Control (QC) approaches are described below to facilitate the organisation and completion of this task. Inventory compilers are not expected to obtain data for non-energy use which are not normally available except where the balance checks below reveal a significant shortfall requiring explanation.

Before using the QC checks it is necessary to understand the definition of non-energy use (including use as feedstock and as reductant) and the principles of its categorisation as described in Section 1.3. Emissions from the uses of the carbon in the materials in each of the categories may occur at first or subsequent uses as derivative products as well as in their final destruction. In order to avoid double counting it is essential to be aware that some of the carbon emissions from the products derived from fossil fuels will be reported in the Waste or Energy Sectors.

In summary, it is *good practice* to check the completeness of all fuels and sources discussed here and to document where and how they are reported in the inventory. The inventory compiler should ensure that all fossil fuels used for non-energy purposes can be linked to uses covered by the inventory and check that reported emissions are consistent with the carbon used. The two QC methods proposed for checking completeness are:

(a) Check that total reported bottom-up calculated $CO_2$ emissions from the non-energy uses of fossil fuels at different subcategory levels are complete and consistent. (Section 1.4.3.1)

(b) Check that feedstock requirements of processes included in the inventory are in balance with the feedstock supply as recorded in national energy statistics. (Section 1.4.3.2)

In practice, QC activities are only part of the inventory development process and inventory compilers need to balance quality control requirements, improved accuracy and reduced uncertainty against requirements for timeliness and cost effectiveness. A *good practice* system seeks to achieve that balance and to enable continuous improvement of inventory estimates. Section 6.2 of Volume 1 provides more information on practical considerations on the prioritization of QA/QC and verification efforts. Taking this into account, it is considered *good practice* to perform at least the first completeness check on $CO_2$ emissions, in particular if the total reported $CO_2$ emissions from non-energy use of fuels are larger than the smallest level *key category*. In addition, the inventory compiler is encouraged to check on the balance of feedstock supply and requirements if he/she has sufficient capacity to do so.

In addition to these QC methods, this section also provides guidance on documenting and reporting how these emissions are allocated in the inventory and how the completeness was checked (Section 1.4.4). $CO_2$ emissions from non-energy use are included together with emissions from the Energy Sector (1A) where waste gases from IPPU processes have been used and reported in the Energy Sector. Irrespective of any QC on completeness, for reasons of transparency and comparability between countries it is *good practice* to report where these sources are allocated in the inventory. (See example format in Section 1.4.4.)

## 1.4.2 Scope of methods

QC of completeness (covered in Section 1.4.3) can be distinguished from the QC of documenting allocation, which is covered in Section 1.4.4. Checking the completeness of accounting uses two top-down methods, each of which is limited in its scope to emissions from first uses of fuels for non-energy purposes. QC of allocation checks where all emissions arising from non-energy uses of fuels, the destruction of non-energy products and fugitive emissions from fuels manufacture are reported.

In addition to the $CO_2$ completeness check the inventory compiler is encouraged to check on the balance of feedstock supply and requirements if he/she has sufficient capacity to do so. It uses the same data for feedstock and other non-energy uses from energy statistics and carbon contents as in the calculation of excluded carbon in the Reference Approach for $CO_2$ from fuel combustion in the Energy Sector (see Chapter 6, Volume 2).

## 1.4.3 Quality control of completeness

The *$CO_2$ completeness check* (Section 1.4.3.1) starts from energy balance data and is designed to check that all significant emissions of $CO_2$ from the first non-energy uses of fossil fuels are reported somewhere in the inventory, without double counting. The emissions are the sum of $CO_2$ emissions from (a) fuels used as feedstock in the chemical industry, (b) fuels used as reductant in the metal industry, (c) fuel products oxidised during use (partly or fully; direct emissions or emissions of carbon containing non-$CO_2$ gases (NMVOC, CO and $CH_4$) oxidised in the atmosphere).

Subsequent $CO_2$ emissions may occur in the waste phase if the waste oils or waste products are incinerated. However, the amount of fossil-carbon containing products disposed of annually as waste is not equal to the amount used annually for first uses because fossil-carbon containing products may be imported or exported or they may be used for several years before they are discarded. The complications which arise from external trade hold equally for emissions resulting from the use of products made from feedstocks and their derivatives. Since derivative products may also be imported or exported the emissions from their use (e.g., from ethylene oxide or acrylonitrile production) cannot be linked directly to the first non-energy use of fossil fuels. For these reasons the *$CO_2$ completeness check* is limited to the first non-energy uses of fossil carbon which lead to emissions and does not include $CO_2$ emissions from waste incineration. Other non-energy sources of fossil $CO_2$ are flaring, venting and other fugitive emissions in the Category 1B and are also excluded from this completeness checking method.

The *feedstock balance check* (Section 1.4.3.2) is simpler in concept and starts from non-energy statistics for feedstock/reductant supplies and compares them with the reported (or implied) requirements for feedstock by the various IPPU processes. This check identifies discrepancies between the two sets of data that may indicate omitted processes or feedstock use classified as fuel combustion.

### 1.4.3.1 $CO_2$ COMPLETENESS CHECK

The principle of this method is based on comparisons of reported $CO_2$ emissions with potential $CO_2$ emissions from the fuel for non-energy uses and consists of three steps:

1. $CO_2$-equivalent carbon contents are calculated for the non-energy use of fossil fuels as reported in national energy statistics (including the coke and other solid fuel inputs into blast furnaces).
2. Total $CO_2$ emissions reported per IPPU subcategory are related to (main) fuels used for non-energy purposes. This should include emissions from by-product fuels transferred from the IPPU Sector and reported elsewhere in the Energy Sector.

3. Total reported fossil IPPU $CO_2$ emissions are compared with a top-down estimate of potential $CO_2$ of the carbon content of the feedstocks used. The comparison is made by calculating the actual $CO_2$ released as a fraction of the total potential $CO_2$ in the input fuels. The fractions may then be compared with values observed for different industries (see below, 'Step 3: Actions arising from the comparison'). In case of significant discrepancies, likely causes of differences should be listed, taking into account the accuracy of the allocation of sources to individual fuels.

### Step 1: Feedstock amount and $CO_2$-equivalent carbon content

The amount of feedstock and non-energy use entered in Table 1.3 is the final consumption of each fuel for 'non-energy' purposes as reported in the national energy statistics. The quantities should be expressed in, or converted to, Terajoules (TJ) using the net calorific (lower heating) values (see Chapter 1 of Volume 2 for IPCC default values). Next the potential $CO_2$-eq. emissions associated with the carbon contents can be calculated using country-specific or IPCC default carbon content values (see Chapter 1 of Volume 2 for IPCC default values).

If a country accounts separately for the production of by-product gases from chemical production processes in their energy statistics, these should also be added in the top row of fuel amounts associated with feedstock emissions of $CO_2$ and the corresponding amount of $CO_2$-eq. calculated using country-specific carbon content values.

### Step 2: Allocating source category $CO_2$ emissions to one or more feedstock fuels

The $CO_2$ emissions reported in the IPPU Sector that arise mainly from the metal and chemical industries, should be allocated to the corresponding fuel types used as input for the process. Emissions resulting from the non-energy use of fossil fuels reported elsewhere should be included here too. Guidance for this allocation is provided in Table 1.3, where for each subcategory the most common feedstock fuel is marked as a bolded box. Other fuels that are known to be used as feedstock for these sources are indicated with a regular box. In most cases these boxes are the only allocations to be checked for the country-specific application. If no specific information is available, all $CO_2$ emissions may be assigned to the bold box. Where country-specific information shows that several fuels are used as feedstock, either the specific fractions for each fuel can be used or each may be given an equal share of the source total.

### Step 3: Actions arising from the comparison

The fraction of potential $CO_2$ actually released may be calculated per fuel type or per group of fuels, and can be assessed for their level, trend and interannual variation. The values of the fractions may be compared with values inferred from the information provided for the methodological tiers for the source categories or from literature (e.g., Neelis *et al.,* 2005).

Small differences or changes may be expected due to process-specific technological or operational differences. Major differences can arise from large differences in technologies or, when comparing with other countries' data or literature, from the use of a different definition of feedstocks (for details see Section 1.3). A third explanation of discrepancies may be due to errors in the presumed allocation of source category emissions to specific fuel types used as feedstock in the process.

### TABLE 1.3 VERIFICATION OF COMPLETENESS OF REPORTED $CO_2$ FROM NON-ENERGY USE OF FOSSIL FUELS

| NOTES | | | | | | | Solids | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Year:__________ | | | | | Unit | Coal | Coke | Coal tars | Coal oils | BF/OF gas | (CO gas) b) | Total solids |
| 2 | A: Declared NEU (from commodity balance) | | | | | TJ | | | | | | | |
| 3 | B: Carbon Content | | | | | kg C/GJ | | | | | | | |
| | C: Total supplied for feedstock/non-energy | [C = A * B / 1000] | | | | Gg C | | | | | | | |
| 4 | **D: Total supplied for feedstock/non-energy** | **[D = C * 44/12]** | | | | Gg $CO_2$-eq. | | | | | | | |
| 5 | **E: Implied carbon fraction oxidised** | **[E = F / D * 100]** | | | | % | | | | | | | |
| | | | Activity a) | $CO_2$ Emissions a) | IEF $CO_2$ | | | | | | | | |
| 6 | **F: Total fossil IPPU $CO_2$ reported** | | | | | Gg $CO_2$ | | | | | | | |
| | **2 INDUSTRIAL PROCESSES** | | | | | Gg $CO_2$ | | | | | | | |
| 7 | **2A: Mineral Industry** | | | | | Gg $CO_2$ | | | | | | | |
| | (Please specify the subcategory.) | | | | | Gg $CO_2$ | | | | | | | |
| 7 | **2B: Chemical Industry** | | | | | Gg $CO_2$ | | | | | | | |
| | 2B1: Ammonia Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2B5: Carbide Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2B6: Titanium Dioxide Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2B8: Petrochemical and Carbon Black Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2B8a: Methanol | | | | | Gg $CO_2$ | | | | | | | |
| | 2B8b: Ethylene | | | | | Gg $CO_2$ | | | | | | | |
| | 2B8f: Carbon Black | | | | | Gg $CO_2$ | | | | | | | |
| | 2B10: Other | | | | | Gg $CO_2$ | | | | | | | |
| 7 | **2C: Metal Industry** | | | | | Gg $CO_2$ | | | | | | | |
| | 2C1: Iron and Steel Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2C2: Ferroalloys Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2C3: Aluminium Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2C5: Lead Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2C6: Zinc Production | | | | | Gg $CO_2$ | | | | | | | |
| | 2C7: Other | | | | | Gg $CO_2$ | | | | | | | |
| 7 | **2D: Non-Energy Products from Fuels and Solvent Use** | | | | | Gg $CO_2$ | | | | | | | |
| | 2D1: Lubricant Use | | | | | Gg $CO_2$ | | | | | | | |
| | 2D2: Paraffin Wax Use | | | | | Gg $CO_2$ | | | | | | | |
| | 2D3: Solvent Use | | | | | Gg $CO_2$ | | | | | | | |
| | 2D4: Other | | | | | Gg $CO_2$ | | | | | | | |
| 7 | **2H: Other** | | | | | Gg $CO_2$ | | | | | | | |
| | 2H1: Pulp and Paper Industry | | | | | Gg $CO_2$ | | | | | | | |
| | 2H2: Food and Beverage Industry | | | | | Gg $CO_2$ | | | | | | | |
| | 2F3: Other | | | | | Gg $CO_2$ | | | | | | | |
| | **EXCEPTIONS REPORTED ELSEWHERE** | | | | | Gg $CO_2$ | | | | | | | |
| 7 | **1A FUEL COMBUSTION ACTIVITIES** | | | | | Gg $CO_2$ | | | | | | | |
| | 1A1a: Main Activity Electricity and Heat Production | | | | | Gg $CO_2$ | | | | | | | |
| | 1A1b: Petroleum Refining | | | | | Gg $CO_2$ | | | | | | | |
| | 1A1c: Manufacture of Solid Fuels and Other Energy Industries | | | | | Gg $CO_2$ | | | | | | | |
| | 1A2: Manufacturing Industries and Construction | | | | | Gg $CO_2$ | | | | | | | |

a) Same Activity Data and emissions as in sectoral background table (also for Activity Data NE, NO, C, and for emissions NE, NO, IE, where applicable).
b) To be included only if coke production is reported as part of integrated iron and steel production.
1: To be specified per year
2: Cf. Auxiliary worksheet for CO2-Reference Approach to subtract the NEU from total apparent consumption
3: IPCC default or country-specific values
4: So-called potential emissions, i.e., carbon embodied in the feedstock/non-energy fuels expressed in $CO_2$-eq.
5: Ratio of $CO_2$ emissions (direct emissions reported as well as atmospheric inputs of $CO_2$ from other carbon (non-$CO_2$)) at some aggregation level (by detailed fuel type or by major fuel type) to total potential $CO_2$ in the feedstock NEU fuels consumed
6: Sum of subcategories below including IPPU sources allocated to Fuel Combustion Activities 1A (due to transfer of by-product fuels to another source category (and 1B, 4C when appropriate))
7: Sum of subcategories of that category

**TABLE 1.3 (CONTINUED) VERIFICATION OF COMPLETENESS OF REPORTED $CO_2$ FROM NON-ENERGY USE OF FOSSIL FUELS**

| NOTES | | | | | | | Liquids | | | | | | | | | | | | Gas | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Year:__________ | | | | | Unit | Naphtha | Gas oil | Fuel Oil | Ethane | LPG b) | Petcoke | Other | Chem. gas | Lubricants | Waxes | Bitumen | Total liquids | Nat Gas | Total gas |
| 2 | A: Declared NEU (from commodity balance) | | | | | TJ | | | | | | | | | | | | ■ | | ■ |
| 3 | B: Carbon Content | | | | | kg C/GJ | | | | | | | | | | | | ■ | | ■ |
| | C: Total supplied for feedstock/non-energy | [C = A * B / 1000] | | | | Gg C | | | | | | | | | | | | | | |
| 4 | **D: Total supplied for feedstock/non-energy** | **[D = C * 44/12]** | | | | Gg $CO_2$-eq. | | | | | | | | | | | | | | |
| 5 | **E: Implied carbon fraction oxidised** | **[E = F / D * 100]** | | | | % | | | | | | | | | | | | | | |
| | | | Activity a) | $CO_2$ Emissions a) | IEF $CO_2$ | | | | | | | | | | | | | | | |
| 6 | **F: Total fossil IPPU $CO_2$ reported** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | **2 INDUSTRIAL PROCESSES** | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| 7 | **2A: Mineral Industry** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | (Please specify the subcategory.) | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| 7 | **2B: Chemical Industry** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2B1: Ammonia Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | ▣ | |
| | 2B5: Carbide Production | | | | | Gg $CO_2$ | | | | | | ▣ | ☐ | | | | | | | |
| | 2B6: Titanium Dioxide Production | | | | | Gg $CO_2$ | | | | | | ☐ | | | | | | | | |
| | 2B8: Petrochemical and Carbon Black Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2B8a: Methanol | | | | | Gg $CO_2$ | | | | | | | ☐ | | | | | | ▣ | |
| | 2B8b: Ethylene | | | | | Gg $CO_2$ | ▣ | ☐ | ☐ | ☐ | ☐ | | ☐ | | | | | | | |
| | 2B8f: Carbon Black | | | | | Gg $CO_2$ | | | | | | | ☐ | | | | | | ▣ | |
| | 2B10: Other | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| 7 | **2C: Metal Industry** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2C1: Iron and Steel Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2C2: Ferroalloys Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2C3: Aluminium Production | | | | | Gg $CO_2$ | | | | | | ☐ | | | | | | | | |
| | 2C5: Lead Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2C6: Zinc Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2C7: Other | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| 7 | **2D: Non-Energy Products from Fuels and Solvent Use** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2D1: Lubricant Use | | | | | Gg $CO_2$ | | | | | | | | | ▣ | | | | | |
| | 2D2: Paraffin Wax Use | | | | | Gg $CO_2$ | | | | | | | | | | ▣ | | | | |
| | 2D3: Solvent Use | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2D4: Other | | | | | Gg $CO_2$ | | | | | | | ☐ | | | | ▣ | | | |
| 7 | **2H: Other** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2H1: Pulp and Paper Industry | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2H2: Food and Beverage Industry | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 2F3: Other | | | | | Gg $CO_2$ | | | | | | | ☐ | | | | | | | |
| | **EXCEPTIONS REPORTED ELSEWHERE** | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| 7 | **1A FUEL COMBUSTION ACTIVITIES** | | ■ | | ■ | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 1A1a: Main Activity Electricity and Heat Production | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 1A1b: Petroleum Refining | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 1A1c: Manufacture of Solid Fuels and Other Energy Industries | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |
| | 1A2: Manufacturing Industries and Construction | | | | | Gg $CO_2$ | | | | | | | | | | | | | | |

Note: In the tabular part, bolded boxes mark the main fuels as feedstock or reductant for the processes at the left hand side. Regular boxes mark other known feedstock/reductant for the processes at the left hand side.

### 1.4.3.2 FEEDSTOCK BALANCE CHECK

The principle of the *feedstock balance check* method is to compare the supply of feedstock/reductants as reported in national fuel statistics with the requirements for the feedstocks by each of the processes using them. A significant difference between the supply and the requirements of a feedstock leads to several suggested actions intended to identify omission of feedstock uses from the inventory or uses of fuel as feedstock that have been reported as fuel consumption or conversion.

Unlike the *$CO_2$ completeness check* the *feedstock balance check* is conducted at the level of fuel quantities and not $CO_2$ emissions. The method seeks confirmation that all feedstock carbon has been satisfactorily attributed to source categories identified in the inventory.

The workings of the method are explained below and readily set out in a worksheet (Table 1.5a). A list of feedstock fuels to be considered is presented in Table 1.4.

TABLE 1.4
LIST OF FOSSIL FUELS THAT CAN BE USED AS CHEMICAL FEEDSTOCK OR REDUCTANT

| **Solids** | **Liquids** | | **Gases** | **Other fuels** |
|---|---|---|---|---|
| coal | refinery gas | naphtha | natural gas | other fuel |
| metallurgical coke* | Ethane | kerosene | | waste (fossil carbon) |
| petroleum coke* | propane | gas oil | | |
| coal tars and oils* | butane | fuel oil | | |
| | LPG | waste oils | | |

* Includes uses as electrodes.

#### Step 1: Feedstock supply

Figures for supply of each feedstock/reductant are taken from national fuel statistics presented in commodity or energy balances. They will be shown as non-energy use or feedstock use according to the country's particular conventions and reductants as inputs to a transformation process. The quantities should be expressed in, or converted to, Terajoules (TJ) using net calorific (lower heating) values (see Chapter 1 of Volume 2 for IPCC default values).

The definitional basis for feedstock reporting differs between countries and this consideration is fully discussed in Sections 1.2.1 and 1.3.2. Some care is therefore needed to identify and use the correct hydrocarbon input figures that will correspond with a process's gross hydrocarbon requirements for the feedstock or reductant (including inputs not or only partly labelled as non-energy use in energy statistics). The total hydrocarbon process input attributed to feedstock/reductant use is required for the *feedstock balance check* described here, because the Specific Feedstock Consumption (SFC) figures of each process, as given in the table, include the fuel requirement. The SFC is the amount (expressed in TJ/Gg) of feedstock/reductant required per tonne of product produced.

#### Step 2: Feedstock requirements

The feedstock requirements of each process will include fuels taken directly or indirectly from the feedstock. Where the necessary data are available from industry sources they can then be entered into the 'requirements' part of the worksheet. Where the data are not available the requirements should be calculated from the production figures for the processes and where necessary, using expert judgement based on the emissions estimation used for the process(es). The figure for the process requirement is likely to be identical to the quantity supplied (taken from energy statistics) *only when* the latter has been obtained from industry sources.

When requirements are calculated from production using the spreadsheet the production figures are those relevant to the process for the given feedstock. If two or more feedstocks supply a single process then the corresponding production figures should be used for each feedstock.

Table 1.5b provides SFC factors linking production figures to feedstock requirements. The factors are the specific feedstock requirements of the process and include fuel use of the feedstock. The factors provided in Table 1.5b have been derived from the methods described in this volume of these *Guidelines* and may be considered as default values. It is *good practice* to use national factors if they are demonstrably more relevant than the default factors given here.

If $R_{ij}$ represents the feedstock requirements of process $i$ for feedstock $j$, then the total requirement for feedstock $j$ ($R_j$), can be expressed as:

**EQUATION 1.1**
**TOTAL FEEDSTOCK REQUIREMENT**

$$R_j = \sum_i R_{ij} = \sum_i \left(SFC_{ij} \bullet P_{ij}\right)$$

Where:

$R_j$ = total requirement for feedstock *j*, TJ

$R_{ij}$ = feedstock requirements of process *i* for feedstock *j*, TJ

$SFC_{ij}$ = Specific Feedstock Consumption of feedstock *j* in process *i*, TJ/Gg

$P_{ij}$ = production from process *i* using feedstock *j*, Gg

The $R_j$ is then compared with the figure for the supply of feedstock *j.* The difference appears in the Table 1.5a. The implementation procedure for this check is set out in the flowchart in Figure 1.3.

### Step 3: Actions arising from the comparison

It is suggested that if the difference observed exceeds 10 percent of the feedstock supply action should be taken to check the data and, if the difference is confirmed, it should be investigated. The 10 percent threshold is necessarily arbitrary and chosen to reflect the likely overall inherent uncertainties in the data.

It is considered *good practice* to focus the investigation on differences in which feedstock supply significantly exceeds the apparent requirements because this suggests that:

- Processes and therefore sources of emissions may have been omitted; or
- The specific energy requirements used in the method are too low. The specific energy requirements should then be adjusted to reflect the national situation.

When the calculated requirements exceed the apparent feedstock supply it suggests that:

- Uses of feedstock fuels are reported elsewhere as fuel combustion or fuel conversion uses.
- A 'net' definition of feedstock supply may have been used in the energy statistics instead of a 'gross' definition (see the reference to ethylene and other chemicals in Section 1.3.2).
- Feedstock requirements, obtained directly from industry sources, are overstated through the inclusion of fuels entering the plant (or more generally, the source category) which are not used in the process and therefore not for feedstock use. The inclusion of non-feedstock fuels should not occur when the feedstock requirements are derived from production data.

Where significant discrepancies remain the likely causes of differences should be listed, taking into account the accuracy of the calculation with default Specific Feedstock Consumption values per source category/feedstock combination.

**TABLE 1.5a COMPARISON OF FEEDSTOCK SUPPLY WITH REQUIREMENTS IMPLIED BY PRODUCTION**

| **YEAR** | | Feedstock or Reductant (TJ) | Process SFC (TJ/Gg) | Production (Gg [= kt]) |
|---|---|---|---|---|
| | Feedstock Quantity delivered | | | |
| | Difference | | | |
| Chemicals | Ammonia prodn | | ↑<br>Values from Table 1.5b<br>↓ | |
| | Silicon carbide | | | |
| | Calcium carbide | | | |
| | Ethylene | | | |
| | Methanol | | | |
| | Carbon black | | | |
| | Other | | | |
| Metals | Iron and steel | | | |
| | Ferroalloys | | | |
| | Aluminium | | | |
| | Zinc | | | |
| | Lead | | | |
| | Other | | | |

Table 1.5a is a reduced form of the full table in which the tabular part is replicated as many times as there are types of feedstock or reductant. In each of the replications the 'Feedstock or Reductant' heading in column 1 is replaced by the name of the fuel. The corresponding SFC values are then entered in column 2. The default SFC values are given in Table 1.5b below.

An Excel workbook is provided in the *2006 Guidelines* CDROM containing the full table, the default values and the formulae to carry out automatically the requirements calculation.

### TABLE 1.5b SPECIFIC FEEDSTOCK CONSUMPTION (TJ/Gg) FOR FEEDSTOCK/REDUCTANTS

| | | Coal | Met coke | Pet Coke | Coal tars and oils | Ref gas | Ethane | Propane | Butane | LPG | Naphtha | Kerosene | Gas oil | Fuel oil | Waste oils | Natural gas |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Chemicals | Ammonia prodn | | | | | | | | | | | | | 43(l) | | 38(o) |
| | Silicon carbide | | | 37(e) | | | | | | | | | | | | |
| | Calcium carbide | | | 21(f) | | | | | | | | | | | | |
| | Ethylene | | | | | | 58(j) | 100(k) | 104(k) | 102(k) | 137(k) | | | | | |
| | Methanol | 72(a) | | | | | | | | | | | | 37(m) | | 34(p) |
| | Carbon black | | | | 60(h) | | | | | | | | | 60(n) | | 12(q) |
| | Other | | | | | | | | | | | | | | | |
| Metals | Iron and steel | | 10(b) | | | | | | | | | | | | | |
| | Ferroalloys | | | | | | | | | | | | | | | |
| | Aluminium | | | 12(g) | 3(i) | | | | | | | | | | | |
| | Zinc | | 21(c) | | | | | | | | | | | | | |
| | Lead | | 7(d) | | | | | | | | | | | | | |
| | Other | | | | | | | | | | | | | | | |

NOTES

**(a) Methanol:** From Section 3.9.2.2; Table 3.13 Consult table for precise value according to process used.

**(b) Iron and Steel:** From Section 4.2.2.3: "The conversion factors provided in Table 6.2 of the IPPC Document are 940 kg pig iron per tonne liquid steel and 358 kg coke per tonne pig iron." so coke requirement is 0.358 x 28.2 GJ/tonne (cv coke) = 10 GJ/tonne iron.

**(c) Zinc:** From Section 4.7.1 (pyrometallurgical process only) taken from Sjardin(2003) Coke consumption is 0.74 tonnes coke/tonne zinc. That is: 0.74 x 28.2 GJ/tonne (cv coke) = 21 GJ/tonne zinc.

**(d) Lead:** Taken from Sjardin(2003) Coke consumption is 0.26 tonnes coke/tonne lead. That is: 0.26 x 28.2 GJ/tonne (cv coke) = 7 GJ/tonne lead.

**(e) Silicon carbide:** From Section 3.6.2.2: "This implies a typical emission factor of 2.3 tonnes $CO_2$/tonne petroleum coke used (IPCC, 1996), or 2.62 tonnes $CO_2$/tonne carbide produced."

So coke requirement is 2.62/2.3 = 1.14 tonne pet coke/tonne carbide. That is; 1.14 x 32.5 GJ/tonne (cv pet coke) = 37 GJ/tonne SiC.

**(f) Calcium carbide:** From: Section 3.6.2.2 "1 750 kg limestone (or 950 kg CaO), 640 kg of petroleum coke and 20 kg carbon electrodes are required to produce 1 tonne of carbide."
So coke requirement is 0.64 x 32.5 GJ/tonne (cv pet coke) = 21 GJ/tonne $CaC_2$.

**(g) Aluminium:** From Section 4.4.2.2; Table 4.11 average of two processes 1.65 tonnes CO2/tonne Al = 0.45 tonnes C/tonne Al. Assume anodes contain 84% coke and 16% pitch. (Sjardin 2003).

Assume coke is 92% C and pitch is 93% C. Assume NCV for calcined coke is 30 MJ/kg and NCV for pitch 35.6 MJ/kg.

Then coke requirement is 12 GJ/tonne Al and pitch requirement 3 GJ/tonne Al.

**(h) Carbon black:** Assumed identical to fuel oil. See note (n) below.

**(i) Aluminium:** See note (g) above.

**(j) Ethylene:** From Section 3.9.2.3; Table 3.25 Ethane requirement is: NCV for ethane x 1/yield matrix value. That is: 46.4 x 1/0.803 = 58 GJ/tonne.

**(k) Ethylene:** Feedstock requirement can be derived as is derived for ethane. See note (j) above.

**(l) Ammonia:** From Section 3.2.2.2; Table 3.1;Partial oxidation assumed.

**(m) Methanol:** From Section 3.9.2.2; Table 3.13. Consult table for precise value according to process used.

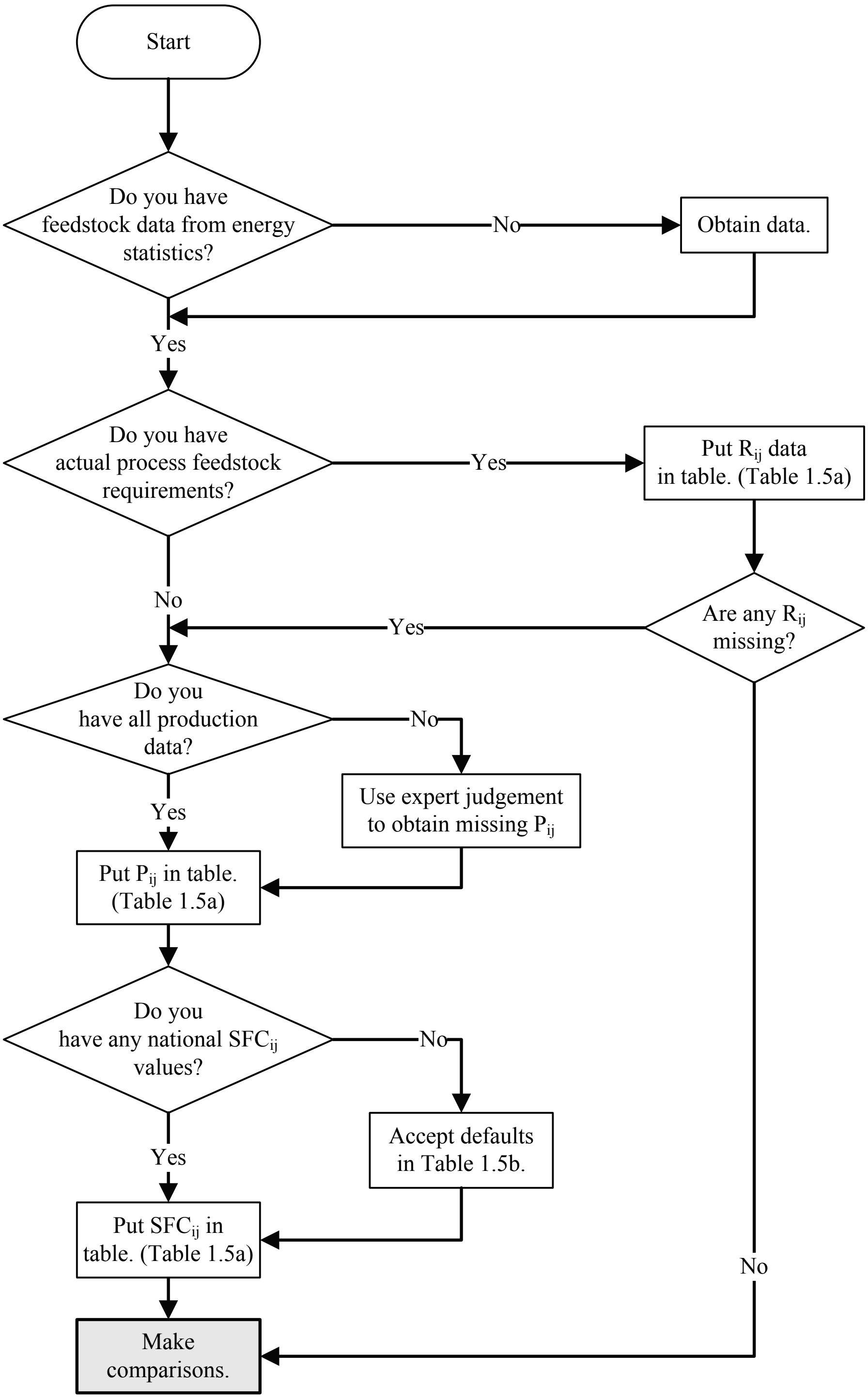
**(n) Carbon Black:** Based on Voll *et al*. (1997) and EU Integrated Pollution Prevention and Control (2004), Table 4.13.

**(o) Ammonia:** From Section 3.2.2.2; Table 3.1.

**(p) Methanol:** From Section 3.9.2.2; Table 3.13;Consult table for precise value according to process used.

**(q) Carbon Black:** Based on Voll *et al*. (1997) and EU Integrated Pollution Prevention and Control (2004), Table 4.13.

**Figure 1.3** **Flowchart for verification of completeness of accounting for non-energy uses of fuels**



Note:
$R_{ij}$ = feedstock requirements of process i for feedstock j, TJ
$SFC_{ij}$ = Specific Feedstock Consumption of feedstock j in process i, TJ/Gg
$P_{ij}$ = production from process i using feedstock j, Gg

## 1.4.4 Reporting and documentation of allocation and QC of completeness

It is *good practice* to review, summarise and document the completeness checks, if performed, for non-energy uses of fuels and fugitive emissions from fuel manufacture. This involves identifying the uses within the IPPU Sector and Fuel Combustion Activities (Category 1A) in the Energy Sectors, as discussed in this section.

Different national methods exist for accounting for feedstock use of fuels in energy statistics and there is a possibility, in exceptional cases, of reporting part of the $CO_2$ in the Energy Sector (see Sections 1.2.1 and 1.3.2). Consequently, it is *good practice* to show in the inventory report:

- Where and how *non-energy* use of fuels has been accounted for in the inventory (whether in the Energy Sector or the Industrial Processes and Product Use Sector.) (Section 1.4.4.1).
- Where and how carbon emissions, other than $CO_2$, have been accounted for in the inventory. These arise from non-combustion and non-biogenic processes involving fossil carbon such as solvent use.
- Results of *completeness checks* performed, when applicable. Details on the QC activities on completeness should be kept as internal documentation (Section 1.4.4.2), in accordance with the guidance on QA/QC (see Chapter 6 of Volume 1).

The first bullet point refers to the allocation of corresponding emissions, in the IPPU Sector or, possibly, also in the Fuel Combustion Activities (Category 1A) in the Energy Sector, and to the definition of 'non-energy' or 'feedstock' used in the national energy statistics. Depending on the definition of the source categories, the contribution of feedstock and non-energy use $CO_2$ emissions varies from less than a percent up to about 5 percent of national total fossil fuel related $CO_2$ emissions.

The description of the completeness check should explain any allocation of a particular source to several sectors. In particular, how adjustments have been made to industrial process emissions should be explained in cases where fuel by-products (off-gases or process vent gas) are transferred to another source category in the IPPU Sector or in the Energy Sector.

### 1.4.4.1 ALLOCATION OF $CO_2$ FROM NON-ENERGY USE

Table 1.6 can be used to document and report the following information, summarising the subcategories in which the sectoral $CO_2$ emissions (other than those from fuel combustion) from the fossil fuels used are reported. The amounts of each fuel type consumed for non-combustion purposes (which correspond to excluded carbon in the $CO_2$ Reference Approach) should be recorded as internal documentation. This relates to:

- The division between *manufacturing process emissions* reported in the IPPU Sector and *fuel combustion emissions* reported in the Energy Sector.
- The allocation of $CO_2$ emissions from the *direct use* of 'fuels' for their physical properties and from the *use* of chemical products in the IPPU Sector. The emissions from the *waste disposal* of these products (e.g., incineration) are dealt with in the Waste Sector.

In the allocation reporting table (Table1.6) the 'Primary NEU fuel type' and 'Other NEU fuel types' should be entered for each category. The same $CO_2$ emissions reported in the IPPU sectoral background table are entered into the IPPU emissions column (or the notation keys NE, NO, IE, where applicable). Then $CO_2$ emissions related to the use of fossil fuels for non-energy purposes reported in source categories other than IPPU are added to the appropriate 1A subcategories. These are labelled in the IPPU source categories as (partly) included elsewhere in the IPPU reporting with a reference to where they are reported. Thus the table includes all emissions from the IPPU Sector wherever they are reported and so documents the complete reporting of these emissions in the IPPU and Energy Sectors.

The inclusion of the Energy Sector improves transparency of complete $CO_2$ emissions reporting as regards the emissions from waste gases and other gases such as blast furnace gas produced from industrial processes but used for fuel combustion in other economic sectors and thus reported in the Energy Sector.

### 1.4.4.2 COMPLETENESS OF $CO_2$ FROM NON-ENERGY USE

In addition to the summary of the review of the allocation and completeness of emissions from non-energy uses of fossil fuels it is *good practice* to document:

- A description of the emission calculation methods used, in the respective source category sections of the report. This should include the reason for any departure of allocations compared to the suggested IPCC source classification, if applicable.
- The results of the *$CO_2$ completeness check* if used, for at least the base year (where data permit) and the last reported year, presented in a table such as Table 1.3, as internal documentation.
- If the *feedstock balance check* for completeness was also used, a table showing the difference between the inferred estimate of feedstock consumption and the reported feedstock deliveries; at minimum for the base year (where data permit) and the two most recent years (i.e., as in Table 1.5a) as internal documentation.
- An explanation of significant unexpected discrepancies, if any, in level or trend. This should include the main cause of these differences.
- Conclusions from the comparison in terms of whether significant $CO_2$ emissions seem to be missing, and if so, in which part of the inventory they occur, and an estimate of the sizes of the omissions.

### TABLE 1.6
### ALLOCATION OF $CO_2$ FROM NON-ENERGY USE OF FOSSILS FUELS: IPPU AND OTHER SECTORS

| Category | Reported in year: …….. | | | | Notes |
|---|---|---|---|---|---|
| | Primary NEU fuel (1) | Other NEU fuel(s) (1) | Emissions Amount Reported in IPPU Sector $CO_2$ (2) (Gg) | In case reported elsewhere: Sub-category in 1A where these emissions are (partly) reported | |
| **2 Industrial Processes and Product Use** | | | | | |
| **2A Mineral Industry** | | | | | |
| (Please specify the sub-category) | (coal, ..) | | | | 4 |
| **2B Chemical Industry** | | | | | |
| 2B1 Ammonia Production | natural gas | oil, coal | | | |
| 2B5 Carbide Production | pet coke | oil | | | |
| 2B6 Titanium Dioxide Production | coal | | | | |
| 2B8 Petrochemical and Carbon Black Production | | | | | |
| 2B8a Methanol | natural gas | coal, oil | | | 5 |
| 2B8b Ethylene | naphtha | gas oil; butane, ethane, propane, LPG | | | 5 |
| 2B8f Carbon Black | natural gas | oil, coke oven gas | | | |
| 2B10 Other | | | | | |
| **2C Metal Industry** | | | | | |
| 2C1 Iron and Steel Production | coke | coal, pet coke (carbon electrode) | | | 6 |
| 2C2 Ferroalloys Production | (carbon electrode) | coke, coal | | | 7 |
| 2C3 Aluminium Production | (carbon electrode) | coke, coal | | | 7 |
| 2C5 Lead Production | coke | | | | |
| 2C6 Zinc Production | coke | | | | |
| 2C7 Other | (carbon electrode) | coke, coal | | | |
| **2D Non-Energy Products from Fuels and Solvent Use** | | | | | |
| 2D1 Lubricant Use | lubricants | greases | | | |
| 2D2 Paraffin Wax Use | waxes | | | | |
| 2D3 Solvent Use | (mineral turpentine) | coal tars and oils | | | 8 |
| 2D4 Other | | | | | 9 |
| **2H Other** | | | | | |
| 2H1 Pulp and Paper Industry | | | | | |
| 2H2 Food and Beverages Industry | coke | | | | |
| 2H3 Other | | | | | |
| **1 ENERGY** | | | | | |
| **1A Fuel Combustion Activities** | | | **Reported in Sector 1A (3)** | | |
| 1A1a Main Activity Electricity and Heat Production | (BF gas) | (chemical off-gases) | | | 10 |
| 1A1b Petroleum Refining | | | | | |
| 1A1c Manufacture of Solid Fuels and Other Energy Industries | BF gas | | | | |
| 1A2 Manufacturing Industries and Construction | (BF gas) | (lubricants, chemical off-gases)) | | | |

(1) The columns 'Primary NEU fuel' and 'Other NEU fuel' should be completed with the actual fuel types used.

(2) These are the same emissions reported in the sectoral background table (also the same emissions notation keys NE, NO, IE, where applicable). If (partly) reported elsewhere, a reference to that other source category should be added in the next column.

(3) Report here only the $CO_2$ emissions from combustion of waste gases produced from industrial processes but used for fuel combustion in other economic sectors and reported in the Energy sector.(e.g. from combustion of blast furnace gas or chemical off-gases transferred offsite to another source category).

(4) For example powdered anthracite coal may be used in Glass Production (2A3).

(5) In cases where the production of off-gases (i.e. byproduct gases) is fully accounted for in the energy statistics, the combustion of these gases may be used to calculate and report $CO_2$ emissions from the feedstock losses. Part of these off-gases may be combusted off-site (i.e. in a sector other than the petrochemical industry) and should thus be accounted for separately as fuel combustion in the Energy Sector.

(6) Part of the blast furnace gas produced from coke used in blast furnaces may be combusted off-site (i.e. in a sector other than the iron and steel industry) and should thus be accounted for separately as fuel combustion in the Energy Sector.

(7) Carbon electrodes are generally manufactured from coke, coal or tar either on-site by the users themselves or separately by anode production plants and then sold to users domestically and/or exported. If anodes are also imported and/or exported, there is no direct correspondence between fuels used for anode production and the amounts of anodes used in the country.

(8) Mineral turpentines are often used as solvent, possibly blended with other liquids. Aromatics derived from coal oils may also be used as solvents.

(9) Emissions from asphalt production, paving of roads and roofing should be reported under 2D4. However, bitumen - and other oil as diluent or 'road oil' - used for this activity does not result in $CO_2$ emissions.

(10) $CO_2$ from blast furnace gas and chemical off-gases should be reported here only when utilised in public power or heat production.

# 1.5 CHOOSING BETWEEN THE MASS-BALANCE AND EMISSION-FACTOR APPROACHES

## 1.5.1 Introduction

Chapters 7 and 8 describe several different methods for estimating HFC, PFC, and $SF_6$ emissions from long-lived, pressurized equipment, including air-conditioning and refrigeration equipment, electrical equipment, and fire-protection equipment. These methods generally fall into two categories: (1) approaches based on a mass-balance of chemical consumption and changes in equipment stocks, and (2) approaches based on chemical banks and emission factors. Both the mass-balance and the emission-factor approaches can be applied at several levels of aggregation, including, from most to least aggregated, global, regional and national. Further levels of disaggregation vary depending on the type of emissions. For emissions described in Chapter 8 (e.g., $SF_6$ from electrical equipment), it is possible to apply methods at the facility level or the lifecycle stage of the equipment at the facility. For Chapter 7 (e.g., HFCs and PFCs from air-conditioning, refrigeration and fire-protection equipment), methods can be applied at the application (Tier 1) or sub-application (Tier 2) level. Both types of approaches can also be highly accurate, but depending on the circumstances and data availability, one may be more accurate than the other. This section describes the mass-balance and emission-factor approaches and *good practice* for choosing between them based on national circumstances.

## 1.5.2 Strengths and weaknesses of the mass-balance approach

The *mass-balance approach* tracks the amount of new chemical introduced into the country, facility, or stock of equipment (at the application or sub-application level) each year. This approach then accounts for the share of this new chemical that is used to fill new equipment capacity or to replace destroyed gas. The consumption that cannot be accounted for is assumed either to replace emitted gas or to be emitted itself.

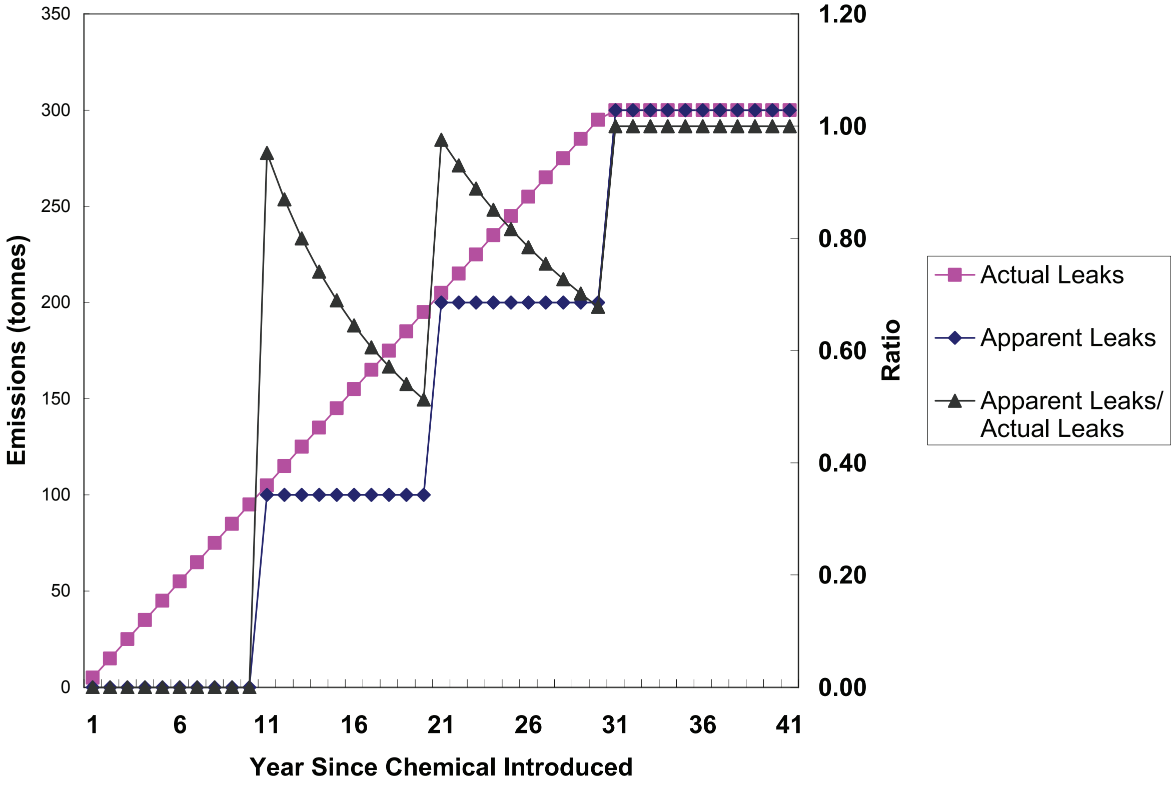
The mass-balance approach has the important advantage of reflecting actual emissions at the place where they occurred, capturing differences not only among types of facilities and equipment, but among individual facilities and pieces of equipment. Thus, the mass-balance approach is likely to be more accurate where emission rates vary across equipment and facilities, and to some extent, where emission rates vary over time. Because emission rates frequently do vary, often unpredictably, it is *good practice* to use the mass-balance approach rather than the emission-factor approach as long as (1) accurate activity data for the mass-balance approach are available, and (2) neither of the drawbacks described below applies to the process or equipment whose emissions are being estimated.

The mass-balance approach has two drawbacks. First, the accuracy of the approach is limited by the precision of mass-, density-, and pressure-measuring devices, which tends to fall around ±1 or 2 percent. If the emission rate from a process (such as equipment installation) is in this range (i.e., 3 percent of nameplate capacity per year or less), then the mass-balance approach will be inaccurate for that process.

Second, the mass-balance approach detects some emissions after they occur, sometimes several years later. This is because equipment that leaks slowly can operate for years or even decades with less than a full charge. This time lag can sharply reduce accuracy where servicing is infrequent and/or stocks are growing quickly. This is likely to be the case for (1) types of equipment that are almost never refilled during their lifetimes (e.g., sealed-pressure electrical equipment and hermetically sealed air-conditioning and refrigeration equipment, such as household refrigerators), and (2) countries that have only recently begun using electrical equipment containing $SF_6$ and/or air conditioning and refrigeration equipment containing HFCs. In the latter case, the mass-balance approach will significantly underestimate emissions during the first few years of equipment use, because chemical consumption for refilling equipment will be close to zero until the first set of equipment is refilled for the first time. For electrical equipment, this may not occur until 10 to 20 years after the introduction of the equipment into the country, depending on the leak rate of the equipment. For air-conditioning and refrigeration equipment, this may not occur until 5 to 20 years after the introduction of the equipment, again depending on the leak rate of the equipment.

Figures 1.4 and 1.5 illustrate the ‘lag error’ associated with the mass-balance approach for these two situations. Figure 1.4 focuses on the error that can occur when countries have only recently begun using electrical equipment containing $SF_6$ or air-conditioning equipment containing HFCs. In this example, equipment is serviced (refilled) every 10 years and has a lifetime of 30 years. Annual equipment sales are assumed to remain constant, but the total stock of equipment grows until the lifetime of the equipment is reached. For illustrative purposes, leaks are assumed to make up 100 percent of emissions (e.g., emissions at equipment installation, servicing and disposal are assumed to be zero).[7]

**Figure 1.4** **Apparent versus Actual Leaks; No growth in annual sales of equipment (10-yr service, 30-yr life)**



In Figure 1.4, after the chemical is first introduced into the equipment, emissions (‘Actual Leaks’) grow rapidly as the bank of chemical in the equipment stock doubles in the second year, triples in the third, and quadruples in the fourth. However, sales of the chemical for refilling (‘Apparent Leaks’) remain close to zero until year 11, when the equipment installed in year 1 is recharged for the first time. In year 21, sales jump again, as, for the first time, two sets of equipment are serviced. When equipment begins to retire, apparent leaks rise to equal actual leaks (resulting in a ratio of 1.0), and the lag error disappears.

Figure 1.5 describes the same situation as Figure 1.4, except in this case, annual equipment sales are assumed to grow by 5 percent per year. The relationship between apparent and actual leaks is very similar to that shown in Figure 1.4 until the equipment begins to retire. At that point, apparent leaks rise, but they never quite equal actual leaks. Instead, the relationship between apparent leaks and actual leaks stabilizes at a constant, equilibrium value, 0.78 for this scenario.

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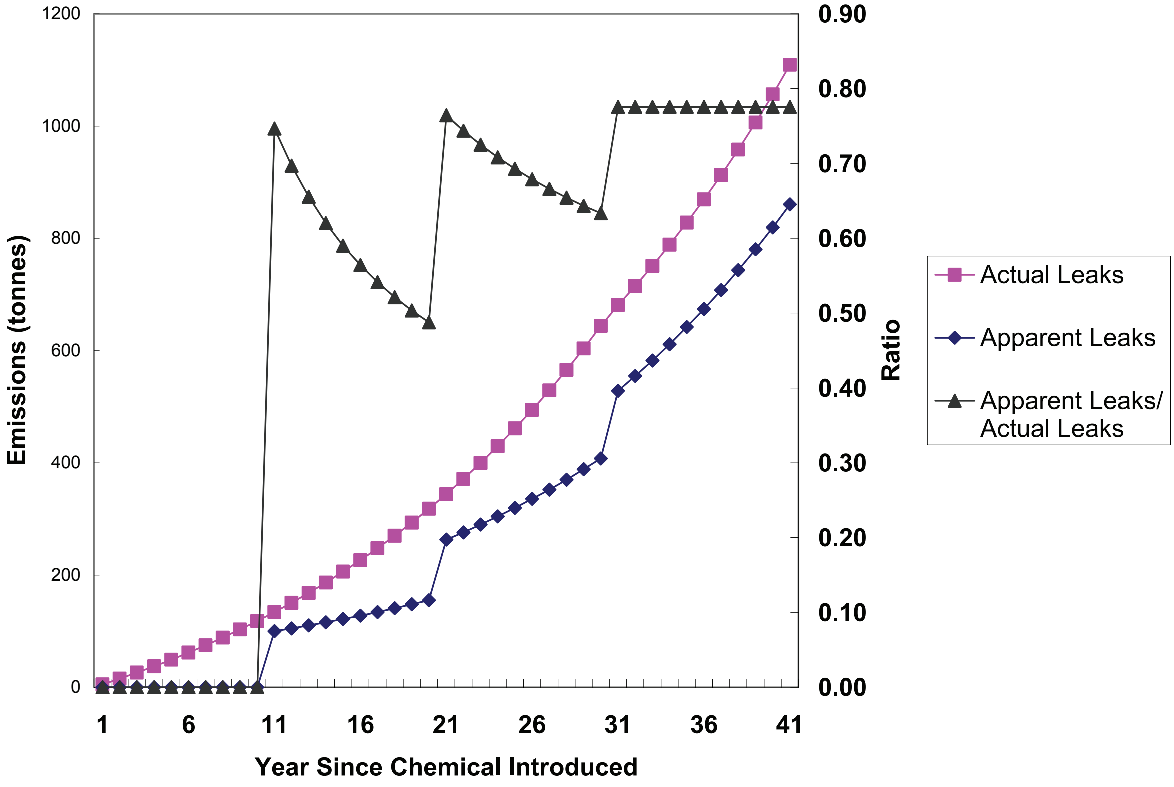
[7] In this example, the nameplate capacity of the equipment sold each year is assumed to equal 1 000 tonnes, and the leak rate is assumed to equal one percent per year. Note, however, that the relationship between apparent and actual leaks is actually independent of the sizes of the annual sales and the leak rate.

**Figure 1.5** **Apparent versus Actual Leaks; 5% growth in annual sales of equipment (10-yr service, 30-yr life)**



In general, if the average time between refilling events is R, then the mass balance approach will yield a very poor estimate of emissions until R+1 years have passed since the chemical was introduced into the country. The accuracy of the estimate will fluctuate in following years, reaching a maximum once the equipment begins to retire.[8]

## 1.5.3 Strengths and weaknesses of the emission-factor approach

The *emission-factor approach* equates emissions to the product of an emission factor and either (1) the nameplate capacity of the equipment that uses or holds a chemical, or (2) the bank of a chemical. (These quantities are similar but not necessarily identical.) Fortunately, where the mass-balance approach is likely to be inaccurate, the emission-factor approach can be used. However, the robustness and reliability of an emission-

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[8] The maximum, long-term accuracy of the mass-balance approach depends on the frequency with which equipment is refilled, the growth rate of new equipment sales, and the fraction of emissions represented by leaks. The accuracy can be estimated using the following expressions (for exponentially growing equipment stock):

$$\frac{ApparentLeaks}{ActualLeaks} = \frac{R[\ln(1+g)]}{(1+g)^R - 1}$$

where R = number of years between recharges and g = the annual growth rate of equipment sales. (Note that this is the same as the growth rate of the stock once equilibrium has been reached.)

Where F = the fraction of total emissions comprised of leaks, the following equation also applies:

$$\frac{ApparentEmissions}{ActualEmissions} = F\left(\frac{ApparentLeaks}{ActualLeaks}\right) + (1-F)$$

If inventory compilers can obtain data on the variables in these equations, they can use them both to quantify and to compensate for the long-term lag error associated with the mass-balance approach (Schaefer, 2002).

factor model depend heavily on the continuing accuracy of its emission factors. In addition, emission factors for these categories (i.e., ODS substitutes and $SF_6$ from electrical equipment) do not exist for all regions of the world.

Emission rates can vary widely among facilities and types of equipment and over time, depending on the design of the equipment (which varies depending on when and where the equipment was manufactured), chemical handling practices, availability of state-of-the-art handling equipment, chemical prices, legislation (e.g., chemical recovery requirements), and other factors. It is therefore *good practice* to develop emission factors using a representative sample of facilities and types of equipment, and to check these factors at least every five years.

The Tier 3 emission-factor methods in Chapters 8 as well as the Tier 2 emission-factor methods (Tier 2a methods) in Chapter 7 require that the country and/or its facilities keep detailed records of the chosen methods for verifying and validating the emission factors. If necessary, emission factors will have to be adjusted to ensure that emission estimates are ultimately linked to measurements of actual gas loss (e.g., as determined by chemical sales and/or equipment recharging).

Table 1.7 summarises the principles, strengths, and weaknesses of the mass-balance and emission-factor approaches.

**TABLE 1.7**
**CHOOSING BETWEEN THE MASS-BALANCE AND EMISSION-FACTOR APPROACHES**

<table>
<tr><th>Mass-Balance Approach</th><th>Emission-Factor Approach</th></tr>
<tr><td><b>How it works:</b> Tracks the amount of new chemical introduced into the country or facility each year, accounting for gas that is used to fill new equipment capacity or to replace destroyed gas. The consumption that cannot be accounted for is assumed to be emitted or to replace emitted gas.</td><td><b>How it works:</b> Equates emissions to the product of an emission factor and either (1) the nameplate capacity of the equipment that uses or holds a chemical, or (2) the bank of a chemical. (These quantities are similar but not necessarily identical.)</td></tr>
<tr><td colspan="2"><b>Level of aggregation:</b> Both the mass-balance and the emission-factor-based approaches can be applied at several levels of aggregation. For electrical equipment, these include the country, the facility, and the lifecycle stage of the equipment at the facility. For refrigeration, air-conditioning and fire-protection equipment, they include the application, sub-application or further-disaggregated equipment types..</td></tr>
<tr><td><b>More accurate where:</b><br>• Emission rates vary across facilities and/or equipment, and to some extent, over time<br>• Process emission rates are above 3%/year<br>• Equipment is refilled frequently<br>• Equipment stock is growing slowly<br>• Equipment containing HFCs, PFCs, or $SF_6$ has been in use in the country for at least as long as the typical time between refills for that equipment.<br>o 10-20 years for electrical equipment<br>o 5-20 years for air-conditioning and refrigeration equipment</td><td><b>More accurate where:</b><br>• Emission rates are fairly constant within defined types of equipment and/or facilities<br>• Process emission rates are below 3%/year<br>• Equipment is rarely or never refilled<br>• Equipment stock is growing quickly<br>• Equipment containing HFCs, PFCs, or $SF_6$ has been in use in the country for less than the typical time between refills for that equipment.<br>o 10-20 years for electrical equipment<br>o 5-20 years for air-conditioning and refrigeration equipment</td></tr>
<tr><td><b>Other considerations:</b> In the long run, this approach will reflect actual emissions, but there may be a significant time lag (in some cases, 20 years or more) between emissions and their detection.</td><td><b>Other considerations:</b> Emission factors should be periodically checked to ensure that they remain consistent with reality.</td></tr>
</table>

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# CHAPTER 2

# MINERAL INDUSTRY EMISSIONS

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# 2 MINERAL INDUSTRY EMISSIONS

## 2.1 INTRODUCTION

This chapter outlines methodologies for estimating process-related carbon dioxide ($CO_2$) emissions resulting from the use of carbonate raw materials in the production and use of a variety of mineral industry products. There are two broad pathways for release of $CO_2$ from carbonates: calcination and the acid-induced release of $CO_2$. The primary process resulting in the release of $CO_2$ is the calcination of carbonate compounds, during which, through heating, a metallic oxide is formed. A typical calcination reaction, here shown for the mineral calcite or calcium carbonate, would be:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

Acid-induced release of $CO_2$, for example, via an equation such as:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

This occurs in a variety of industries, but is typically the result of small quantities of carbonate being present as an impurity in an acidification process to upgrade a non-carbonate material. For example, in the treatment of phosphate ores with sulphuric acid to produce phosphoric acid, the phosphate concentrate that is to be acidified may contain a small percentage of carbonate minerals. In general, the amount of $CO_2$ released by acidification of these carbonate impurities will be small.

The focus of this chapter is therefore on the emissions resulting from calcination of carbonate materials. Although the principal process by which calcination-related emissions are released is similar among the source categories in the mineral industry, three source categories are highlighted because of their relatively significant contribution to global emissions. These source categories are Cement Production, Lime Production and Glass Production. In addition to these source categories, this chapter considers emissions resulting from the consumption of carbonates in a variety of other mineral industries including ceramics, soda ash use, and carbonate consumption for non-metallurgical magnesia production.

Limestone and other carbonate materials also are consumed in a variety of other industries not covered in this chapter. Examples include carbonates used as fluxes[1] and slagging[2] agents in metals smelting and refining (e.g., iron and steel production and base metals such as copper), and as inputs to the chemical industry (e.g., fertiliser). The methods outlined in this chapter for estimating emissions from the use of carbonates are applicable to these other industries as well. It is *good practice* to allocate emissions from the use of limestone, dolomite and other carbonates to the industrial source category where they are emitted (e.g., iron and steel production).

As noted throughout Volume 3 on Industrial Processes and Product Use (IPPU), the emission estimation methodologies outlined below consider only process-related emissions and do not consider energy-related emissions. Inventory compilers should ensure that energy-related emissions from these industries 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 cement manufacture should consider the combustion of both fossil fuels and waste fuels (tyres, waste oils, paints, etc.) These combustion-related emissions, however, should be included with energy-related emissions and not with IPPU, which should include only the emissions from calcination.

Although methane ($CH_4$) and nitrous oxide ($N_2O$) may be emitted from some minerals industry source categories, given current scientific knowledge, these emissions are assumed to be negligible and thus are not addressed in this chapter. $CO_2$ emissions may result from additional mineral-related activities not identified here; where these are known and can be estimated, they should be included in the inventory.

The source categories in this chapter share a common approach to methodological tiers. Tiers 1 and 2 are based on estimates of the amount of raw materials consumed or products manufactured, along with emission factors that represent the amount of $CO_2$ emitted per unit of mass. Tier 3 describes direct calculations based on the site-

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[1] Fluxes are raw materials, such as limestone, dolomite, lime and silica sand, which are used to reduce the heat or other energy requirements of thermal processing of minerals (such as smelting of metals). Fluxes also may serve a dual function as a slagging agent.

[2] Slag is a residual silicate melt deliberately formed during the smelting of metallic ores, or in subsequent furnaces (e.g., steel), by the addition of slagging agents (commonly lime, limestone and/or dolomite). Slag contains most of the non-volatile impurities stripped from the ores as well as components derived from any fluxes added to the smelting process.

specific chemistry of raw materials. If site-specific raw materials data are used, it is vital that all sources of carbonate in the raw materials and fuels are accounted for (not just the limestone). The basic emissions calculations for all carbonate-burning industries are similar. They are based on common formula weights and $CO_2$ ratios, which are presented in Table 2.1 below for convenience.

**TABLE 2.1**
**FORMULAE, FORMULA WEIGHTS, AND CARBON DIOXIDE CONTENTS OF COMMON CARBONATE SPECIES***

| Carbonate | Mineral Name(s) | Formula Weight | Emission Factor (tonnes $CO_2$/tonne carbonate)** |
|---|---|---|---|
| $CaCO_3$ | Calcite*** or aragonite | 100.0869 | 0.43971 |
| $MgCO_3$ | Magnesite | 84.3139 | 0.52197 |
| $CaMg(CO_3)_2$ | Dolomite*** | 184.4008 | 0.47732 |
| $FeCO_3$ | Siderite | 115.8539 | 0.37987 |
| $Ca(Fe,Mg,Mn)(CO_3)_2$ | Ankerite**** | 185.0225−215.6160 | 0.40822−0.47572 |
| $MnCO_3$ | Rhodochrosite | 114.9470 | 0.38286 |
| $Na_2CO_3$ | Sodium carbonate or soda ash | 106.0685 | 0.41492 |

Source: CRC Handbook of Chemistry and Physics (2004)

* Final results (i.e., emission estimates) using these data should be rounded to no more than two significant figures.

** The fraction of emitted $CO_2$ assuming 100 percent calcination; e.g., 1 tonne calcite, if fully calcined, would yield 0.43971 tonnes of $CO_2$.

*** Calcite is the principal mineral in limestone. Terms like high-magnesium or dolomitic limestones refer to a relatively small substitution of Mg for Ca in the general $CaCO_3$ formula commonly shown for limestone.

**** Formulae weight range shown for ankerite assumes that Fe, Mg, and Mn are present in amounts of at least 1.0 percent.

# 2.2 CEMENT PRODUCTION

## 2.2.1 Methodological issues

In cement manufacture, $CO_2$ is produced during the production of clinker, a nodular intermediate product that is then finely ground, along with a small proportion of calcium sulfate [gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$)], into hydraulic (typically portland) cement. During the production of clinker, limestone, which is mainly calcium carbonate ($CaCO_3$), is heated, or calcined, to produce lime ($CaO$) and $CO_2$ as a by-product. The CaO then reacts with silica ($SiO_2$), alumina ($Al_2O_3$), and iron oxide ($Fe_2O_3$) in the raw materials to make the clinker minerals (chiefly calcium silicates). The proportion in the raw materials of carbonates other than $CaCO_3$ is generally very small. The other carbonates, if present, exist mainly as impurities in the primary limestone raw material. A small amount of MgO (typically 1-2 percent) in the clinker-making process is desirable as it acts as a flux, but much more than this amount can lead to problems with the cement (van Oss and Padovani, 2002). Cement may be made (ground) entirely from imported clinker, in which case the cement production facility may be considered to have zero process-related $CO_2$ emissions. As discussed in Section 2.2.1.2, cement kiln dust (CKD) may be generated during the manufacture of clinker. Emission estimates should account for emissions associated with the CKD.

There are no additional emissions associated with the production of masonry cement. Where masonry cement is produced by adding lime to portland cement (or its clinker), the emissions associated with the lime should already be accounted for under lime production. The addition of ground limestone to portland cement or its clinker to produce masonry cement does not lead to additional emissions.

### 2.2.1.1 CHOICE OF METHOD

The decision tree in Figure 2.1 describes *good practice* in choosing the most appropriate method based on national circumstances. In the Tier 1 method, emissions are based on clinker production estimates inferred from cement production data, correcting for imports and exports of clinker. The estimation of emissions directly from cement production (i.e., applying an emission factor directly to cement production without first estimating clinker production) is not considered to be a *good practice* method because it does not account for clinker imports and exports.

In Tier 2, emissions are estimated directly from clinker production data (rather than clinker production inferred from cement production) and a national or default emission factor. The Tier 3 approach is a calculation based on the weights and compositions of all carbonate inputs from all raw material and fuel sources, the emission factor(s) for the carbonate(s), and the fraction of calcination achieved. The Tier 3 approach relies on plant specific data. If the inventory compiler considers plant-level data to be unreliable or highly uncertain, then it is *good practice* to use Tier 2.

Tier 2 and Tier 3 should also include a correction for CKD. Tier 2 includes a correction addition for emissions associated with CKD not recycled to the kiln. Tier 3 also should account for CKD. Unlike the Tier 2 approach, when using Tier 3, emissions attributed to uncalcined CKD not recycled to the kiln should be subtracted from the total emissions estimate.

Should $CO_2$ capture technology be installed and used at a plant, it is *good practice* to deduct the $CO_2$ captured in a higher tier emissions calculation. The default assumption is that there is no $CO_2$ capture and storage (CCS) taking place. Any methodology taking into account $CO_2$ capture should consider that $CO_2$ emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately, e.g. for cement production, inventory compilers should ensure that the same quantities of $CO_2$ are not double counted. In these cases the total amount of $CO_2$ captured should preferably be reported in the corresponding energy combustion and IPPU source categories in proportion to the amounts of $CO_2$ generated in these source categories. For additional information on $CO_2$ capture and storage refer to Volume 3, Section 1.2.2 and for more details on capture and storage to Volume 2, Section 2.3.4.

### TIER 1 METHOD: ESTIMATING CLINKER PRODUCTION THROUGH USE OF CEMENT PRODUCTION DATA

As noted above, calculating $CO_2$ emissions directly from cement production (i.e., using a fixed cement-based emission factor) is not consistent with *good practice*. Instead, in the absence of data on carbonate inputs or national clinker production data, cement production data may be used to estimate clinker production by taking into account the amounts and types of cement produced and their clinker contents and including a correction for clinker imports and exports. Accounting for imports and exports of clinker is an important factor in the estimation of emissions from this source. Emissions from the production of imported clinker should not be included in national emissions estimates as these emissions were produced and accounted for in another country. Similarly, emissions from clinker that is ultimately exported should be factored into national estimates of the country where the clinker is produced. An emission factor for clinker is then applied and the $CO_2$ emissions are calculated according to Equation 2.1.

**EQUATION 2.1**
**TIER 1: EMISSIONS BASED ON CEMENT PRODUCTION**

$$CO_2\ Emissions = \left[ \sum_i (M_{ci} \bullet C_{cl\,i}) - Im + Ex \right] \bullet EF_{clc}$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from cement production, tonnes

$M_{ci}$ = weight (mass) of cement produced[3] of type *i*, tonnes

$C_{cli}$ = clinker fraction of cement of type *i*, fraction

Im = imports for consumption of clinker, tonnes

Ex = exports of clinker, tonnes

$EF_{clc}$ = emission factor for clinker in the particular cement, tonnes $CO_2$/tonne clinker
The default clinker emission factor ($EF_{clc}$) is corrected for CKD.

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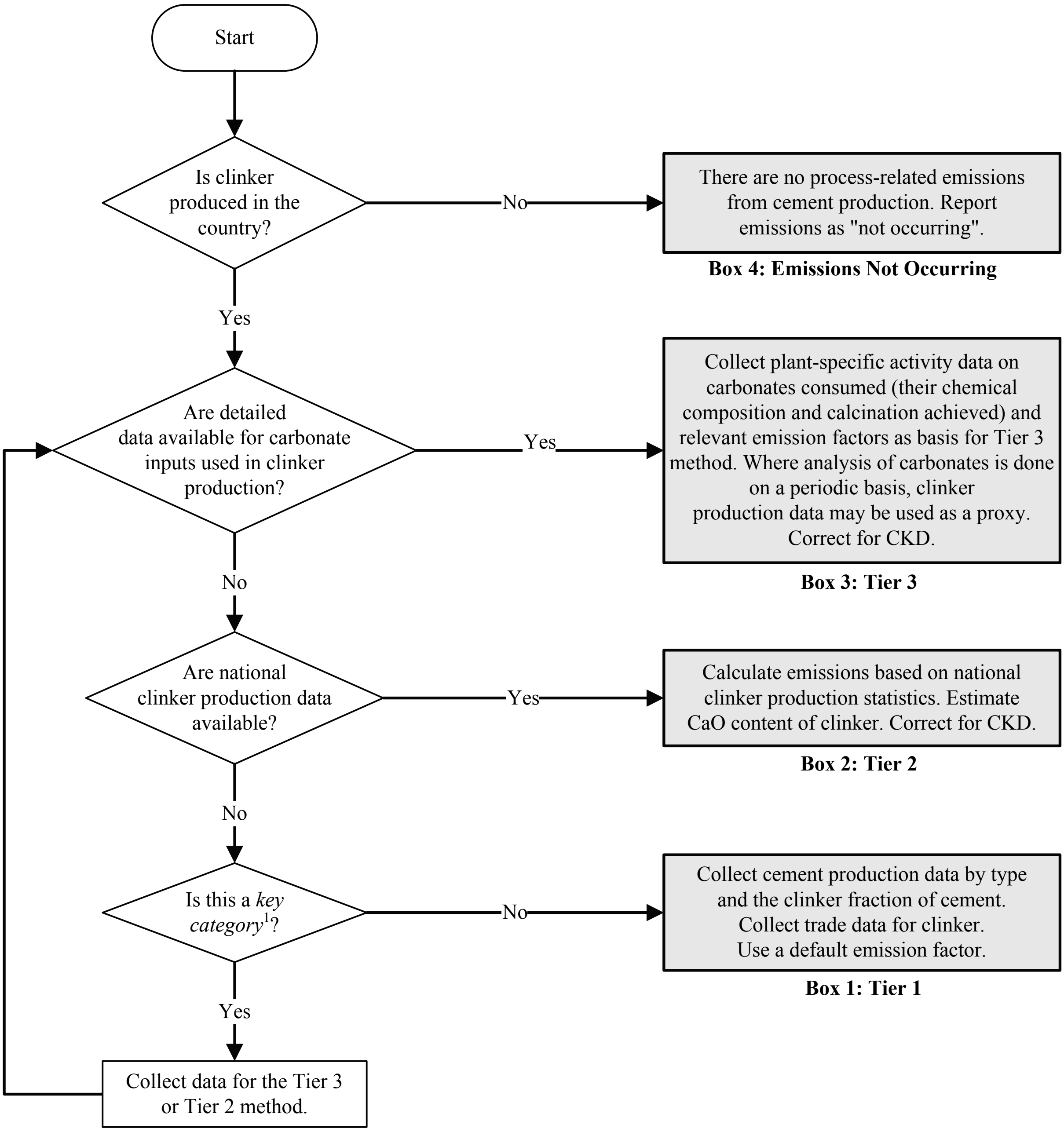
[3] In some statistical compendia production of cement is taken to mean production of cement plus the exports of clinker. If this is the case, it is *good practice* to subtract clinker exports from the $M_{ci}$ factor in Equation 2.1.

**Figure 2.1 Decision tree for estimation of $CO_2$ emissions from cement 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: USE OF CLINKER PRODUCTION DATA

If detailed and complete data (including weights and composition) for carbonate(s) consumed in clinker production are not available (Tier 3), or if a rigorous Tier 3 approach is otherwise deemed impractical, it is *good practice* to use aggregated plant or national clinker production data and data on the CaO content in clinker, expressed as an emission factor in the following Equation 2.2:

**EQUATION 2.2**
**TIER 2: EMISSIONS BASED ON CLINKER PRODUCTION DATA**

$$CO_2\ Emissions = M_{cl} \bullet EF_{cl} \bullet CF_{ckd}$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from cement production, tonnes

$M_{cl}$ = weight (mass) of clinker produced, tonnes

$EF_{cl}$ = emission factor for clinker, tonnes $CO_2$/tonne clinker (See discussion under Section 2.2.1.2, Choice of Emission Factors, for Tiers 1 and 2 below.) This clinker emission factor ($EF_{cl}$) is not corrected for CKD.

$CF_{ckd}$ = emissions correction factor for CKD, dimensionless (see Equation 2.5)

The Tier 2 approach is based on the following assumptions about the cement industry and clinker production:

1. The majority of hydraulic cement is either portland cement or a similar cement, which requires portland cement clinker;
2. There is a very limited range in the CaO composition of clinker and the MgO content is kept very low;
3. Plants are generally able to control the CaO content of the raw material inputs and of the clinker within close tolerances;
4. Even where the output of clinker is calculated by a plant rather than directly measured, there is generally close agreement between the two determination methods when audits are performed;
5. The CaO content of clinker from a given plant tends not to change significantly over the years;
6. The main source of the CaO for most plants is $CaCO_3$ and, at least at the plant level, any major non-carbonate sources of CaO are readily quantified (see Section 2.2.1.2 below);
7. A 100 percent (or very close to it) calcination factor is achieved for the carbonate inputs for clinker manufacture, including (commonly to a lesser degree) material lost to the system as non-recycled CKD; and
8. Dust collectors at plants capture essentially all of the CKD, although this material is not necessarily recycled to the kiln.

### TIER 3 METHOD: USE OF CARBONATE(S) INPUT DATA

Tier 3 is based on the collection of disaggregated data on the types (compositions) and quantities of carbonate(s) consumed to produce clinker, as well as the respective emission factor(s) of the carbonate(s) consumed. Emissions are then calculated using Equation 2.3. The Tier 3 approach includes an adjustment to subtract any uncalcined carbonate within CKD not returned to the kiln. If the CKD is fully calcined, or all of it is returned to the kiln, this CKD 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 CKD. However, excluding uncalcined CKD may slightly overestimate emissions.

Limestones and shales (raw materials) also may contain a proportion of organic carbon (kerogen), and other raw materials (e.g., fly ash) may contain carbon residues, which would yield additional $CO_2$ when burned. These emissions typically are not accounted for in the Energy Sector, but, if used extensively, inventory compilers should make an effort to see if they are included in the Energy Sector. Currently, however, too few data exist 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 percent 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 on 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 clinker production, the clinker 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 clinker, based on periodic calibration to the carbonate inputs.

**EQUATION 2.3**
**TIER 3: EMISSIONS BASED ON CARBONATE RAW MATERIAL INPUTS TO THE KILN**

$$CO_2\ Emissions = \underbrace{\sum_i (EF_i \bullet M_i \bullet F_i)}_{\text{Emissions from carbonates}} - \underbrace{M_d \bullet C_d \bullet (1 - F_d) \bullet EF_d}_{\text{Emissions from uncalcined CKD not recycled to the kiln}} + \underbrace{\sum_k (M_k \bullet X_k \bullet EF_k)}_{\text{Emissions from carbon-bearing non-fuel materials}}$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from cement production, tonnes

$EF_i$ = emission factor for the particular carbonate *i*, tonnes $CO_2$/tonne carbonate (see Table 2.1)

$M_i$ = weight or mass of carbonate *i* consumed in the kiln, tonnes

$F_i$ = fraction calcination achieved for carbonate *i*, fraction[a]

$M_d$ = weight or mass of CKD not recycled to the kiln (= 'lost' CKD), tonnes

$C_d$ = weight fraction of original carbonate in the CKD not recycled to the kiln, fraction[b]

$F_d$ = fraction calcination achieved for CKD not recycled to kiln, fraction[a]

$EF_d$ = emission factor for the uncalcined carbonate in CKD not recycled to the kiln, tonnes $CO_2$/tonne carbonate[b]

$M_k$ = weight or mass of organic or other carbon-bearing nonfuel raw material *k*, tonnes[c]

$X_k$ = fraction of total organic or other carbon in specific nonfuel raw material *k*, fraction[c]

$EF_k$ = emission factor for kerogen (or other carbon)-bearing nonfuel raw material *k*, tonnes $CO_2$/tonne carbonate[c]

Notes on defaults for Equation 2.3:

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

b: Because calcium carbonate is overwhelmingly the dominant carbonate in the raw materials, it may be assumed that it makes up 100 percent of the carbonate remaining in the CKD not recycled to the kiln. It is thus acceptable within *good practice* to set $C_d$ as equal to the calcium carbonate ratio in the raw material feed to the kiln. Likewise, it is acceptable to use the emission factor for calcium carbonate for $EF_d$.

c: The $CO_2$ emissions from non-carbonate carbon (e.g., carbon in kerogen, carbon in fly ash) in the non-fuel raw materials can be ignored (set $M_k \bullet X_k \bullet EF_k = 0$) if the heat contribution from kerogen or other carbon is < 5 percent of total heat (from fuels).

## 2.2.1.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

In Tier 1, it is *good practice* to use a default CaO content for clinker of 65 percent; assume that 100 percent of the CaO is from calcium carbonate material; and to incorporate a 2 percent correction factor for CKD (for more discussion on CKD, please refer to the Tier 2 method discussion below.)

For the default CaO composition, 1 tonne of clinker contains 0.65 tonnes CaO from $CaCO_3$. This carbonate is 56.03 percent CaO and 43.97 percent $CO_2$ by weight (Table 2.1). The amount (X) of $CaCO_3$ needed to yield 0.65 tonnes CaO is: $X = 0.65/0.5603 = 1.1601$ tonnes $CaCO_3$ (unrounded). The amount of $CO_2$ released by calcining this $CaCO_3 = 1.1601 \bullet 0.4397 = 0.5101$ tonnes $CO_2$ (unrounded). Assuming a correction addition of 2 percent to account for CKD, the rounded default emission factor ($EF_{clc}$) for clinker is:

EQUATION 2.4
EMISSION FACTOR FOR CLINKER

$$EF_{clc} = 0.51 \bullet 1.02 \text{ (CKD correction)} = 0.52 \text{ tonnes}CO_2 / \text{tonne clinker}$$

Under Tier 1, the default $EF_{clc}$ incorporates the correction for CKD. This should not be confused with $EF_{cl}$ under Tier 2, which does not account for the CKD. $EF_{cl}$ should be multiplied by a correction factor, $CF_{ckd}$ (see Equation 2.5) to generate the combined EF for clinker and CKD.

## TIER 2 METHOD

### *Emission factor for clinker ($EF_{cl}$)*

In the Tier 2 method, if sufficient country-specific data on CaO content of clinker and inputs of non-carbonate CaO sources are available, it is *good practice* to estimate a country-specific $CO_2$ emission factor for clinker. As noted above, the derivation of an emission factor for clinker requires that the CaO content of the clinker be known, as well as the fraction of CaO that was derived from a carbonate source (generally $CaCO_3$). The CaO content of clinker is generally within the range of 60 to 67 percent. At a given plant the CaO content will remain stable to within 1 to 2 percent. The basic default emission factor, as recommended under Tier 1, assumes that the clinker is 65 percent CaO and that this is 100 percent derived from $CaCO_3$ and that 100 percent calcination is achieved in the kiln.

The base (i.e., uncorrected for CKD) 0.51 emission factor in Equation 2.4 assumes a 65 percent CaO content in clinker. A similar calculation would yield emission factors for different CaO contents, if these contents are known. For example, for a clinker with 60 percent CaO all derived from $CaCO_3$ the $EF_{cl}$ (not including a correction for CKD) is 0.47, and for 67 percent CaO the $EF_{cl}$ is 0.53.

If it is known that a plant is deriving a significant fraction of CaO from a non-carbonate source (such as steel slag or fly ash), then this component of CaO should first be subtracted. For example, if 4 percent of the CaO in a 65 percent CaO clinker is from slag, then the CaO from carbonate is 61 percent and the calculation for this yields an $EF_{cl}$ of 0.48.

The default emission factor does not include a correction for MgO. For every 1 percent of MgO derived from carbonate the emission factor is an additional 0.011 tonne $CO_2$/tonne clinker (i.e., $EF_{cl} = 0.510 + 0.011 = 0.52$ tonne $CO_2$/tonne clinker). Because MgO also may come from a non-carbonate source and because the MgO is deliberately kept low in portland cement, the true MgO from carbonate is likely to be very small. Given the fact that the assumption of a 100 percent carbonate source for the CaO already yields an overestimation of emissions (there is likely to be at least some contribution of CaO from non-carbonate sources) and the fact that some of the MgO is also likely to be from a non-carbonate source, a correction for MgO is not required for a Tier 2 calculation. For uncertainties associated with these assumptions please refer to Table 2.3.

### *Emissions correction factor for cement kiln dust ($CF_{ckd}$)*

Dust may be generated at various points in the kiln line apparatus used to make clinker. The composition of this dust can vary depending on where it is generated but all may be included under the term ‘cement kiln dust’ (CKD). CKD includes particulates derived from the raw materials, and the original carbonate component of the dust may be incompletely calcined. CKD 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 (after capture) it may be disposed of. The degree to which CKD can be recycled to the kiln depends on whether or not this causes a quality problem (e.g., excessive alkali content) with the clinker or subsequent finished cement. Any CKD not recycled to the kiln is considered to be ‘lost’ to the process and emissions associated with it will not be accounted for by the clinker. To the degree that the lost CKD represents calcined carbonate raw materials, the emissions from these calcined raw materials represent an addition to the clinker emissions in the Tier 1 and 2 calculations, and a subtraction in the Tier 3 calculation.

As data on the amount of CKD produced may be scarce (except possibly for plant-level reporting), estimating emissions from lost CKD based on a default value can be considered *good practice*. The amount of $CO_2$ from lost CKD can vary, but ranges typically from about 1.5 percent (additional $CO_2$ relative to that calculated for clinker) for a modern plant to about 20 percent for a plant losing a lot of highly calcinated CKD (van Oss, 2005). In the absence of data, the default CKD correction factor ($CF_{ckd}$) is 1.02 (i.e., add 2 percent to the $CO_2$ calculated for clinker). If no calcined CKD is believed to be lost to the system, the CKD correction factor will be 1.00 (van Oss, 2005). In addition to CKD, the World Business Council for Sustainable Development (WBCSD) separately addresses emissions from bypass dust (which is fully calcined). If the data are available, countries may refer to the WBCSD Protocol to estimate these emissions (WBCSD, 2005).

Where data are available, a correction factor ($CF_{ckd}$ in Equation 2.2) for the ‘lost’ $CO_2$ emissions can be calculated using Equation 2.5.

The CKD correction factor ($CF_{ckd}$) for use in Equation 2.2 can be derived as:

**EQUATION 2.5**
**CORRECTION FACTOR FOR CKD NOT RECYCLED TO THE KILN**

$$CF_{ckd} = 1 + (M_d / M_{cl}) \bullet C_d \bullet F_d \bullet (EF_c / EF_{cl})$$

Where:

$CF_{ckd}$ = emissions correction factor for CKD, dimensionless

$M_d$ = weight of CKD not recycled to the kiln, tonnes[a]

$M_{cl}$ = weight of clinker produced, tonnes

$C_d$ = fraction of original carbonate in the CKD (i.e., before calcination), fraction[b]

$F_d$ = fraction calcination of the original carbonate in the CKD, fraction[b]

$EF_c$ = emission factor for the carbonate (Table 2.1), tonnes $CO_2$/tonne carbonate

$EF_{cl}$ = emission factor for clinker uncorrected for CKD (i.e., 0.51 tonnes $CO_2$/tonne clinker), tonnes $CO_2$/tonne clinker

Notes:

a: It is assumed that 100 percent of the CKD is first captured. If any CKD vents to the atmosphere, an estimate of this quantity must be made and included in the $M_d$.

b: It is acceptable to assume that the original carbonate is all $CaCO_3$ and that the proportion of original carbonate in the CKD is essentially the same as that in the raw mix kiln feed.

For example, for $M_d/M_{cl}$ = 0.2, $C_d$ = 0.85, $F_d$ = 0.5, original carbonate all $CaCO_3$ (hence $EF_c$ = 0.4397 tonne $CO_2$/tonne carbonate), and $EF_{cl}$ = default value of 0.51 tonne $CO_2$/tonne clinker, the $CF_{ckd}$ = 1.073 (unrounded) - that is, this represents about a 7 percent addition to the $CO_2$ calculated for the clinker alone.

### TIER 3 METHOD

The Tier 3 emission factors are based on the actual $CO_2$ contents of the carbonates present (see Equation 2.3 and Table 2.1). The Tier 3 approach requires the full accounting of carbonates (species and sources).

## 2.2.1.3 CHOICE OF ACTIVITY DATA

### TIER 1 METHOD

In Tier 1, national-level (or where available, plant-level), data should be collected on the types of cement produced and the clinker fraction of the cement in order to estimate clinker production. Most hydraulic cement produced worldwide is either portland cement, or blended (composite) cements based on portland cement (i.e., portland cement (or clinker) plus pozzolanic or cementitious additives) or masonry-type cements (portland cement plus plasticizing materials such as ground limestone). If cement production cannot be disaggregated by type and it is suspected that significant amounts of blended and/or masonry cements are being produced in addition to portland cement, it is acceptable within *good practice* to assume an overall clinker fraction of 75 percent. If cement production is known to be essentially all portland cement, then it is *good practice* to use a default value of 95 percent clinker. Unfortunately, even if the types of cement produced in the country are known, there can be large variability in the clinker fraction of cement within a given blended or masonry cement type. Table 2.2 provides an illustration of the range of clinker fractions in various cement types. For additional information see DIN (1994) and ASTM (2004a, 2004b). Countries should document clearly any assumptions about the composition of cement and the clinker fraction used to estimate emissions.

**TABLE 2.2**
**CLINKER FRACTION OF BLENDED CEMENT 'RECIPES' AND OVERALL PRODUCT MIXES (BASED ON U.S. STANDARDS ASTM C-150 AND C-595; U.S. DATA MAY BE ILLUSTRATIVE FOR OTHER COUNTRIES)**

| Cement Name | Symbol | Recipe | % Clinker | Notes |
|---|---|---|---|---|
| Portland | 'PC' | 100% PC | 95 - 97<br>90 - 92 | Some U.S. states allow inclusion of 3% GGBFS.<br>Latest standards allow inclusion of ≤ 5% ground limestone. |
| Masonry | 'MC' | 2/3 PC | 64 | varies considerably |
| Slag-modified portland | I(SM) | slag < 25% | >70 - 93 | |
| Portland BF Slag | IS | slag 25-70% | 28 - 70 | |
| Portland pozzolan | IP and P | pozz 15-40% | 28 - 79/81 | base is PC and/or IS |
| Pozzolan-modified portland | I(PM) | pozz <15% | 28 - 93/95 | base is PC and/or IS |
| Slag cement | S | slag 70+% | <28/29 | can use CaO instead of clinker |

**PERCENT CLINKER IN THE PRODUCT MIX**

**Percent Additives (Pozzolan + Slag) in the Blended Cement***

| Product Mix (PC/blend)** | 0% | 10% | 20% | 30% | 40% | 75% |
|---|---|---|---|---|---|---|
| 100/0 | 95 - 97 | 0 | 0 | 0 | 0 | 0 |
| 0/100 | 0 | 85.5 | 76 | 66.5 | 57 | 23.8 |
| 15/85 | 14.2 | 86.9 | 78.9 | 70.8 | 62.7 | 26.4 |
| 25/75 | 23.8 | 87.9 | 80.8 | 73.6 | 66.5 | 41.6 |
| 30/70 | 28.5 | 88.35 | 81.7 | 75.1 | 68.4 | 45.2 |
| 40/60 | 38 | 89.3 | 83.6 | 77.9 | 72.2 | 52.3 |
| 50/50 | 47.5 | 90.3 | 85.5 | 80.8 *** | 76 | 59.4 |
| 60/40 | 57 | 91.2 | 87.4 | 83.6 | 79.8 | 66.5 |
| 70/30 | 66.5 | 92.2 | 89.3 | 86.5 | 83.6 | 73.6 |
| 75/25 | 71.1 | 92.6 | 90.1 | 87.8 | 85.4 | 77.1 |
| 85/15 | 80.8 | 93.6 | 92.2 | 90.7 | 89.3 | 84.3 |

Notes:

* The inclusion of slag allows for the blend to be portland and/or portland blast furnace slag cement.

Except for 100 percent portland range itself, all other portland assumed to be 95 percent clinker.

** Product Mix refers to range of products of a country, e.g., 75 percent of total production is portland and the rest is blended.

It is assumed that all the hydraulic cement is portland and/or blended, or pure pozzolan. Masonry would approximate a product mix of 60/40 to 70/30 portland/blended, for the 75 percent additive column. Other hydraulic cements (e.g., aluminous) are assumed to be zero.

*** Example: Clinker fraction where a country's cement output is 50 percent portland cement and 50 percent blended cement, and the blended cement contains 70 percent portland cement and 30 percent additives.

Tier 1 also requires a correction for imports and exports of clinker. Data on the quantity of clinker imported and exported from a country are usually available from national customs agencies, the United Nations, national cement associations or trade associations and/or departments of commerce. The typical tariff codes in use for clinker trade are 661.21 (SITC) and 2523.10.00 (HTS). It is important to distinguish trade data for clinker itself from those for the combined category of hydraulic cement and clinker: [codes 661.2 (SITC) and 25.23.0000 (HTS)], and from data on cement imports: [codes 661.22 – 661.29 (SITC) and 2523.21 – 2523.90 (HTS)].

## TIER 2 METHOD

The Tier 2 method requires collection of clinker production data. It is suggested that if national surveys currently canvass cement production data, the inventory compiler should investigate the possibility of expanding them to collect clinker production data. It is *good practice* to collect clinker production data directly from national statistics or, preferably, from individual plants. It is also suggested that inventory compilers collect information on the CaO content of the clinker and the fraction of this CaO from carbonate. Where data are available on CaO from non-carbonate sources (e.g., slags and fly ash), this CaO should not be included in the CaO content of clinker used for calculating emissions. If possible, data should be collected to document CKD collection and recycling practices at the plants and likewise on the average or typical composition and calcination fraction of the CKD. 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 plant level conditions.

### TIER 3 METHOD

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 clinker production (which is typically calculated daily). Subsequently, the clinker production data may then be used as a proxy for the carbonate calculations to estimate emissions. To be consistent with *good practice*, this linkage should be periodically recalibrated.

In general, limestone or similar carbonate rocks will be the dominant (80-90 percent) raw materials used at a typical cement plant, and these data should be collected annually. However it is likely that there could be a carbonate component within clay, shale, sandstone, and other supplementary raw materials, as well as in coal and perhaps some other fuels. If, during the full investigation, it is determined that the amount of carbonates from non-major sources is small (e.g., less than 5 percent 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 but are merely introduced into the finish (grinding) mill. For example, a plant may ‘dilute’ its finished portland cement by blending in a small percentage (1-5 percent) of ground limestone. Carbonates added in the finish mill are not calcined and so do not contribute $CO_2$.

## 2.2.1.4 COMPLETENESS

When following a Tier 1 method, inventory compilers should be sure to account for imports and exports of clinker. For countries that are net importers of clinker, failure to deduct the net clinker imports would result in an overestimation of emissions from cement production. For countries that are net exporters of clinker, failure to include the net exports would result in an underestimation of emissions from the cement plants. Potential sources of trade data are discussed in Section 2.2.1.3.

Clinker production data may be available in national statistical databases, or could be collected, even if such data have not been published in national statistics. Cement and/or clinker production data from national statistics may not be complete in some countries where a substantial part of production comes from numerous small kilns, particularly vertical shaft kilns, for which data are difficult to obtain.

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 clinker-producing plants are considered, and that all carbonates consumed to make clinker are included in the emission calculation. Clinker production plants are well identified in each country, but data on the fraction weight of carbonate(s) 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 clinker plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, 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 2 in order to ensure completeness during the transition period. A similar approach could be undertaken as a country moves from Tier 1 to Tier 2.

The potential for double counting also should be considered. For example, inventory compilers should review statistics used to estimate emissions from the source category ‘Other Process Uses of Carbonates’ to ensure that emissions reported in that source category do not result from the use of these carbonates in cement production. Where carbonates are used for cement production, the emission should be reported under Cement Production. Finally, inventory compilers should include only process-related emissions from cement 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. Free lime (CaO not part of the formulae of the clinker minerals mentioned above) released during the curing of concrete (i.e., from the hydration of the clinker minerals) can potentially re-absorb atmospheric $CO_2$ - a process called carbonation. However, the rate of carbonation is very slow (years to centuries) and, as a practical matter, should not be considered for *good practice*. This is an area for future work before inclusion into national inventories.

### 2.2.1.5 DEVELOPING A CONSISTENT TIME SERIES

These *Guidelines* introduce two changes in the estimation of emissions from cement production. First, under Tier 1, the default emission factor now includes a correction factor for CKD of 2 percent. The correction factor for CKD is now included in Tier 1 because it better reflects the sources of emissions during clinker production It is *good practice* to recalculate previous Tier 1 emissions estimates using the emission factor presented in Section 2.2.1.2.

Also, a new Tier 3 approach based on carbonate inputs to clinker production has been introduced. These data may or may not be available historically. If the inventory compiler chooses to implement Tier 3 (vs. a historical Tier 2 approach) for current and future inventories, they are encouraged to collect these data for historical years to ensure time series consistency. Where these data are not available, the inventory compiler may refer to the 'Overlap approach' (see Volume 1, Section 5.3) to attempt to recalculate previous estimates. The relationship between emissions estimated from the carbonate input approach (Tier 3) and the output-based clinker production approach (Tier 2) should be relatively constant over time for a given plant, but may fail if the number of plants or their technologies or raw materials has changed significantly over time. Once that relationship is established, previous estimates can be recalculated based on this relationship (see Volume 1, Section 5.3). A similar approach could be used where inventory compilers move from a Tier 1 to a Tier 2 approach.

## 2.2.2 Uncertainty assessment

Uncertainty estimates for cement production result predominantly from uncertainties associated with activity data, and to a lesser extent from uncertainty related to the emission factor for clinker.

### 2.2.2.1 EMISSION FACTOR UNCERTAINTIES

For Tier 1, the major uncertainty component is the clinker fraction of the cement(s) produced. If reliable clinker import and export data are not available, then the uncertainty of the clinker production estimate will be higher. Although the default CKD correction factor itself has a very large uncertainty, its effect on the overall emissions calculation is still less than the uncertainty associated with the clinker fraction. Under Tier 2, the major source of uncertainty is associated with determining the CaO content of clinker. If clinker data are available, the uncertainty of the emission factor is equal to the uncertainty of the CaO fraction and the assumption that it was all derived from $CaCO_3$ (Table 2.3). For Tier 3, there is relatively little uncertainty associated with the emission factors of the source carbonates because they are based on stoichiometric ratios. There may be some uncertainty associated with assuming, in Tier 3, that there is 100 percent calcination of carbonates in the CKD.

In general, CKD is the least characterised factor for estimating $CO_2$ emissions from cement production, regardless of the Tier implemented.

### 2.2.2.2 ACTIVITY DATA UNCERTAINTIES

Where clinker production data are estimated from cement production, the uncertainty of the activity data can be as high as about 35 percent. For Tier 2, the uncertainty in data on clinker production tonnages, when available, 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. This is particularly important for determining possible differences in clinker composition and irregularities in annual production (i.e. using clinker stockpiles instead of production to produce cement at various times). Except for CKD the greatest sources of uncertainty associated with Tier 3 are the uncertainties associated with identification of carbonate species (1-5 percent) and the weight of raw materials.

Although emissions are much smaller than from carbonates, there may be considerable uncertainty associated with estimating emissions from CKD in Tier 2 estimates, and also in Tier 3 if plants do not weigh the CKD that is not recycled to the kiln or if the plants lack CKD scrubbers. Where the weight and composition of CKD are unknown for a plant, the uncertainty will be higher. As an example, an attempt has been made to estimate the approximate uncertainties for different factors in Equations 2.1-2.5 and/or the steps in the manufacture of clinker and cement. The uncertainties are presented in Table 2.3 and are approximate component uncertainties - that is, they are those associated with a particular step or activity in clinker manufacturing. In order to quantify uncertainty for cement (clinker) production, the default uncertainties provided in Table 2.3 should be combined according to the guidance in Volume 1, Section 3.2.3. Where ranges are given for the uncertainty values, the mid-range should be used unless country-specific or plant-specific circumstances suggest that another value should be used.

**TABLE 2.3**
**DEFAULT UNCERTAINTY VALUES FOR CEMENT PRODUCTION**

| Uncertainty[a] | Comment | Tier |
|---|---|---|
| **Chemical Analysis/Composition** | | |
| 2-7% | Assumption of 95% clinker factor in portland cement | 1 |
| 1-2% | Chemical analysis of clinker to determine CaO | 2 |
| 3-8% | Assumption of 65% CaO in clinker | 2 |
| 1-3% | Assumption that 100% CaO is from $CaCO_3$ (uncertainty is higher if ash or slag feeds are used but not accounted for.) | 2 |
| 1% | Assumption of 100% calcination of carbonate destined to become clinker | 2, 3 |
| 1-3% | Kerogen (or other non-carbonate carbon) determination | 3 |
| 1-3% | Overall chemical analysis pertaining to carbonate content (mass) & type | 3 |
| 1-5% | Assumption that the carbonate species is 100% $CaCO_3$ | 3 |
| **Production Data** | | |
| 1-2% | Reported (plant-level) cement production data | 1 |
| 35% | Assumption that country output is 100% portland cement | 1 |
| 10% | Use of estimated country (or aggregated plant) production data (national statistics). | 1, 2 |
| Variable | Use of reported but rounded weight data in cement or clinker (e.g., national-level reporting in large units); uncertainty is one unit in last significant digit shown) | 1, 2 |
| 1-2% | Weighing or calculation of clinker production, assumes complete reporting | 2 |
| 1-3% | Uncertainty of plant-level weighing of raw materials | 3 |
| **CKD** | | |
| 25-35% | Default assumption that emissions from CKD are 2% of process-related emissions from clinker production. Uncertainty assumes that 33-50% of clinker not recycled. If no recycling takes place or if the calcination percentage significantly exceeds 50%, uncertainty could be 50% or more | |
| 1% | Assumption that original components in CKD are same as raw mix | 2, 3 |
| 1% | Assumption that all carbonate (calcined or remaining) in CKD is $CaCO_3$ | 2, 3 |
| 10-35% | Estimation of % calcination of CKD | 2, 3 |
| 20-80% | Assumption of 100% calcination of CKD | 2, 3 |
| up to 60% | Assumption of 50% calcination of CKD | 2, 3 |
| 5% | Weighing of CKD captured by scrubbers | 2, 3 |
| 1-3% | Weighing of scrubber-captured CKD returned to kiln | 2, 3 |
| 5-10% | Weighing of scrubber-captured CKD not recycled to kiln (other disposal) | 2, 3 |
| 10-15% | Estimation of weight of CKD automatically rerouted to kiln | 2, 3 |
| 20-30% | Estimation of weight of CKD if none is recovered or scrubbed | 2, 3 |
| **Imports/Exports** | | |
| 10% | Trade data for clinker (if tariff codes are correctly isolated and cement is not included) | 1 |
| 50% of import tonnage | Overestimation from failure to deduct for net clinker imports for consumption (this is because, per Equation 2.4, $CO_2$ is approximately one half the weight of clinker) | 1 |

[a] Estimates are based on expert judgement.

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

## 2.2.3.1 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 emissions estimated 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 for cement or clinker (top-down approach). In cases where a hybrid Tier 1/2 or Tier 2/3 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 representativity 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 conditions or technology. For cement production, inventory compilers should compare plant data (content of CaO in clinker, content of clinker in cement) with other plants in the country.

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

## 2.2.3.2 REPORTING AND DOCUMENTATION

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

### TIER 1 METHOD

In addition to cement production data, the quantity of clinker imports and exports also should be reported. Any information regarding the CaO content of clinker should be documented, including use of default values different from those discussed in section 2.2.1.2.

### TIER 2 METHOD

Tier 2 documentation should include a description of how clinker production was estimated by the reporting entity (i.e., directly weighed, weight determined by volume of clinker pile, calculated from raw material inputs, etc.) and at what level the activity data were collected (i.e., plant level or national level). The method (e.g., country specific or IPCC default) for determining the CaO content of clinker should be documented along with any plant-specific information regarding the quantity and type of non-carbonate feeds to the kiln, such as slags or fly ash. All procedures used to quantify and determine the degree of calcination of CKD should be documented. Where the assumption that emissions of CKD are equal to 2 percent of emissions from clinker production is made, this should be transparently reported.

### TIER 3 METHOD

When documenting the Tier 3 method it is important to document all the procedures undertaken and methodologies used to identify the weight fraction and identities of all carbonates, including carbonates incorporated in any clay, shales, sandstone or other supplementary raw materials, consumed as raw materials, along with the corresponding emission factors.

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

It is likely that plants will find it impractical to undertake chemical analyses of all raw material inputs on a daily basis for the purpose of $CO_2$ calculations. Instead, a full investigation will take place at each facility on a number of occasions throughout the year to fully characterise the carbonate inputs. Facilities will likely develop a relationship between carbonate input and clinker production that will be applied to the plant's routine calculation of clinker output for intervening periods. In addition to identifying all procedures used to calculate emissions from the carbonate inputs, all steps necessary to identify the relationship between carbonate input and clinker production should be documented.

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

# 2.3 LIME PRODUCTION

## 2.3.1 Methodological issues

Calcium oxide (CaO or quicklime) is formed by heating limestone to decompose the carbonates. This is usually done in shaft or rotary kilns at high temperatures and the process releases $CO_2$. Depending on the product requirements (e.g., metallurgy, pulp and paper, construction materials, effluent treatment, water softening, pH control, and soil stabilisation), primarily high calcium limestone (calcite) is utilized in accordance with the following reaction:

$$\boxed{CaCO_3 \text{ (high-purity limestone)} + \text{heat} \rightarrow CaO \text{ (quicklime)} + CO_2}$$

Dolomite and dolomitic (high magnesium) limestones may also be processed at high temperature to obtain dolomitic lime (and release $CO_2$) in accordance with the following reaction: $CaMg(CO_3)_2$ (dolomite) + heat → $CaO{\cdot}MgO$ (dolomitic lime) + $2CO_2$. At some facilities, hydrated (slaked) lime also is produced, using additional hydration operations.

The production of lime involves a series of steps, including the quarrying of raw materials, crushing and sizing, calcining the raw materials to produce lime, and (if required) hydrating the lime to calcium hydroxide.

The consumption of lime as a product may in some cases not result in net emissions of $CO_2$ to the atmosphere. The use of hydrated lime for water softening, for example, results in $CO_2$ reacting with lime to re-form calcium carbonate, resulting in no net emissions of $CO_2$ to the atmosphere. Similarly, precipitated calcium carbonate, which is used in the paper industry as well as for other industrial applications, is a product derived from reacting hydrated high-calcium quicklime with $CO_2$. During the process of sugar refining, lime is used to remove impurities from the raw cane juice; any excess lime can be removed through carbonation. Any recarbonation in these specific industries may be calculated and reported only where proven and validated methods are used to calculate the amount of $CO_2$ that reacts with lime to re-form calcium carbonate. Where these conditions are met, this may be reported under Category 2H, Other.

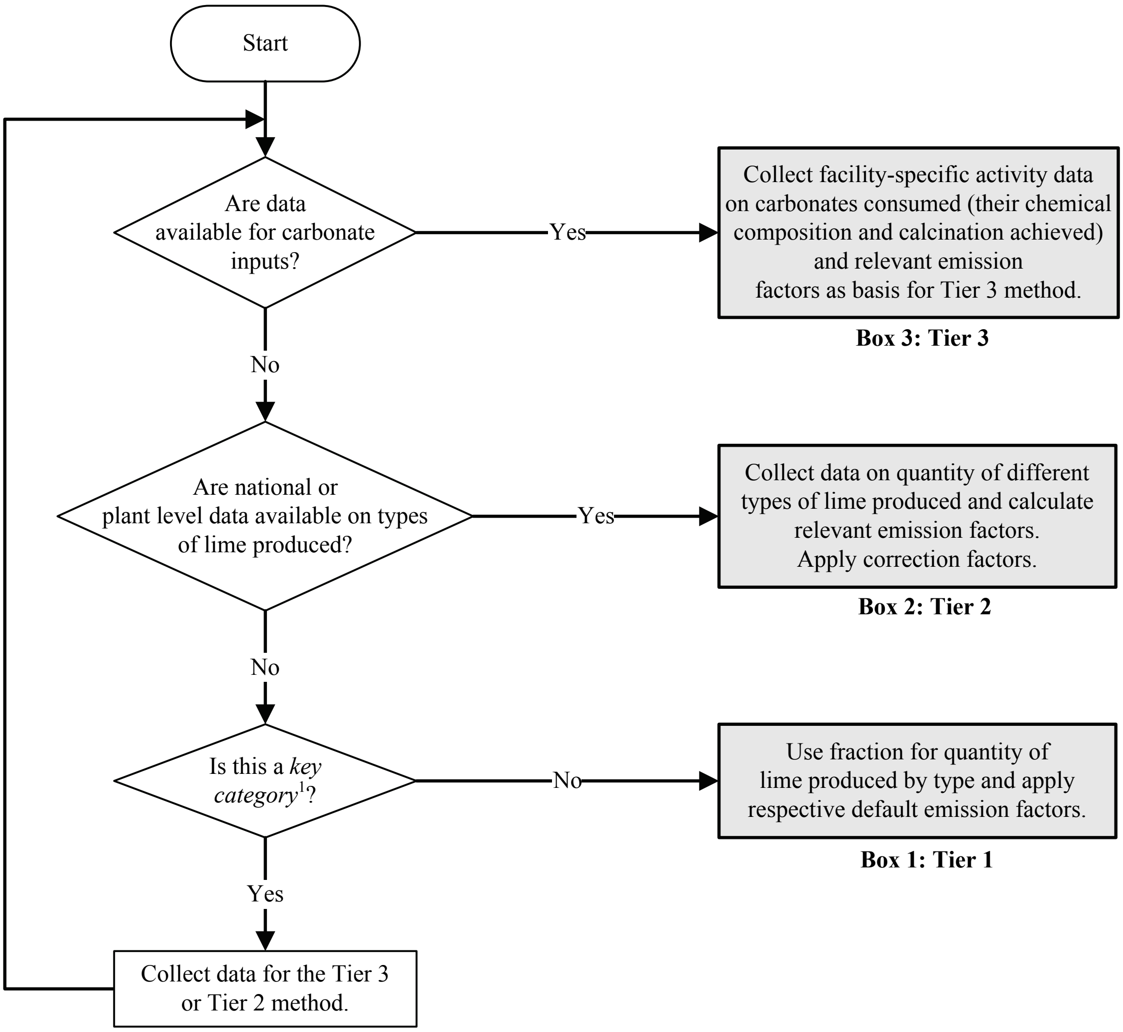
As discussed in Section 2.3.1.3, lime kiln dust (LKD) may be generated during the production of lime. Emission estimates developed using Tier 2 and Tier 3 should account for emissions associated with the LKD.

### 2.3.1.1 CHOICE OF METHOD

As is the case for emissions from cement production, there are three basic methodologies for estimating emissions from lime production: an output-based approach that uses default values (Tier 1), an output-based approach that estimates emissions from CaO and $CaO{\cdot}MgO$ production and country-specific information for correction factors (Tier 2) and an input-based carbonate approach (Tier 3). Unlike the Tier 3 method which requires a plant-specific assessment, the Tier 1 and Tier 2 methods can be applied either to national, or where possible, plant statistics. The choice of *good practice* method depends on national circumstances, as shown in Figure 2.2.

It is *good practice* to assess the available national statistics for completeness, and for the ratio of limestone to dolomite used in lime production. Some industries produce non-marketed lime reagents for their own processes (e.g., the iron and steel industry for use as a slagging agent). All lime production, whether produced as a marketed or a non-marketed product should be reported under IPCC Subcategory 2A2 Lime Production.

**Figure 2.2 Decision tree for estimation of $CO_2$ emissions from lime 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 1 METHOD

The Tier 1 method is based on applying a default emission factor to national level lime production data. While country-specific information on lime production by type (e.g., high calcium lime, dolomitic lime, or hydraulic lime) is not necessary for *good practice* in Tier 1, where data are available to identify the specific types of lime produced in the country, this may be used. It is not necessary for *good practice* to account for LKD in Tier 1.

## TIER 2 METHOD

Where national level data are available on the types of lime produced, it is *good practice* to estimate emissions using Equation 2.6. The Tier 2 method requires country-specific information on the proportion of hydrated lime produced. Typical plant-level ratios of lime product to LKD production should be obtained.

EQUATION 2.6
TIER 2: EMISSIONS BASED ON NATIONAL LIME PRODUCTION DATA BY TYPE

$$CO_2\ Emissions = \sum_i (EF_{lime,i} \bullet M_{l,i} \bullet CF_{lkd,i} \bullet C_{h,i})$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from lime production, tonnes

$EF_{lime,i}$ = emission factor for lime of type *i*, tonnes $CO_2$/tonne lime (see Equation 2.9)

$M_{l,i}$ = lime production of type *i*, tonnes

$CF_{lkd,i}$ = correction factor for LKD for lime of type *i*, dimensionless
This correction can be accounted for in a similar way as for CKD (Equation 2.5, but omitting the factor ($Ef_c/EF_{cl}$))

$C_{h,i}$ = correction factor for hydrated lime of the type *i* of lime, dimensionless (See discussion under Section 2.3.1.3, Choice of Activity Data.)

i = each of the specific lime types listed in Table 2.4

## TIER 3 METHOD

Tier 3 is based on the collection of plant-specific data on the type(s) and quantity(ies) of carbonate(s) consumed to produce lime, as well as the respective emission factor(s) of the carbonate(s) consumed. The Tier 3 method to estimate emissions from lime production is similar to Equation 2.3 for cement production, except there is a correction for LKD, as opposed to CKD and there is no need to correct for emissions from carbon-bearing non-fuel materials. Unlike the case with CKD and cement kilns, LKD is seldom recycled to the lime kiln (but LKD can be used as a feed to a cement kiln). For purposes of estimating emissions in Equation 2.7 it is assumed that no LKD is recycled to the kiln.

EQUATION 2.7
TIER 3: EMISSIONS BASED ON CARBONATE INPUTS

$$CO_2\ Emissions = \sum_i (EF_i \bullet M_i \bullet F_i) - M_d \bullet C_d \bullet (1 - F_d) \bullet EF_d$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from lime production, tonnes

$EF_i$ = emission factor for carbonate *i*, tonnes $CO_2$/tonne carbonate (see Table 2.1)

$M_i$ = weight or mass of carbonate i consumed, tonnes

$F_i$ = fraction calcination achieved for carbonate *i*, fraction[a]

$M_d$ = weight or mass of LKD, tonnes

$C_d$ = weight fraction of original carbonate in the LKD, fraction[a]. This factor can be accounted for in a similar way as CKD.

$F_d$ = fraction calcination achieved for LKD, fraction[a]

$EF_d$ = emission factor for the uncalcined carbonate in LKD, tonnes $CO_2$/tonne carbonate[b]

Notes on defaults for Equation 2.7

a: Calcination fractions: In the absence of actual data, it is consistent with *good practice* to assume that the degree of calcination achieved is 100 percent (i.e., $F_i = 1.00$) or very close to it. For LKD, a $F_d$ of <1.00 is more likely but the data may show high variability and relatively low reliability. In the absence of reliable data for LKD, an assumption of $F_d = 1.00$ will zero out the subtraction correction for uncalcined carbonate remaining in LKD.

b: Because calcium carbonate is overwhelmingly the dominant carbonate in the raw materials, in the absence of better data it may be assumed that it makes up 100 percent of the carbonate remaining in the LKD. It is thus consistent with *good practice* to set $C_d$ equal to the calcium carbonate ratio in the raw material feed to the kiln. Likewise, in the absence of better data it is consistent with *good practice* to use the emission factor for calcium carbonate for $EF_d$.

### 2.3.1.2 CHOICE OF EMISSION FACTORS

#### TIER 1 METHOD

Tier 1 is an output-based method and applies an emission factor to the total quantity of lime produced. The emission factor is based on the stoichiometric ratios illustrated in Table 2.4, which vary depending on the type of lime produced. The stoichiometric ratio is the amount of $CO_2$ released by the carbonate precursor to the lime, assuming that the degree of calcination was 100 percent and assuming no LKD. For example, 1 tonne of CaO requires the calcination of 1.785 tonnes of $CaCO_3$ and this releases 0.785 tonne $CO_2$ if fully calcined.

In the absence of country specific data, it is *good practice* to assume 85 percent production of high calcium lime and 15 percent production of dolomitic lime (Miller, 1999). Based on this, Equation 2.8 illustrates how to calculate the Tier 1 emission factor for lime production.

**EQUATION 2.8**
**TIER 1 DEFAULT EMISSION FACTOR FOR LIME PRODUCTION**

$$\begin{aligned} EF_{Lime} &= 0.85 \bullet EF_{high\ calcium\ lime} + 0.15 \bullet EF_{dolomitic\ lime} \\ &= 0.85 \bullet 0.75 + 0.15 \bullet 0.77^{a} \\ &= 0.6375 + 0.1155 \\ &= 0.75 \text{tonnes } CO_2 \text{ / tonne lime produced} \end{aligned}$$

Notes on defaults in Equation 2.8

a: The default EF for dolomitic lime may be 0.86 or 0.77 depending on the technology used for lime production. See Table 2.4.

**TABLE 2.4**
**BASIC PARAMETERS FOR THE CALCULATION OF EMISSION FACTORS FOR LIME PRODUCTION**

| Lime Type | Stoichiometric Ratio [tonnes $CO_2$ per tonne CaO or CaO·MgO] (1) | Range of CaO Content [%] | Range of MgO Content[d] [%] | Default Value for CaO or CaO·MgO Content [fraction] (2) | Default Emission Factor [tonnes $CO_2$ per tonne lime] (1) • (2) |
|---|---|---|---|---|---|
| High-calcium lime[a] | 0.785 | 93-98 | 0.3-2.5 | 0.95 | 0.75 |
| Dolomitic lime [b] | 0.913 | 55-57 | 38-41 | 0.95 or 0.85[c] | 0.86 or 0.77[c] |
| Hydraulic lime [b] | 0.785 | 65-92[e] | NA | 0.75[e] | 0.59 |

Source:

[a] Miller (1999b) based on ASTM (1996) and Schwarzkopf (1995).

[b] Miller (1999a) based on Boynton (1980).

[c] This value depends on technology used for lime production. The higher value is suggested for developed countries, the lower for developing ones.

[d] There is no exact chemical formula for each type of lime because the chemistry of the lime product is determined by the chemistry of the limestone or dolomite used to manufacture the lime.

[e] Total CaO content (including that in silicate phases).

#### TIER 2 METHOD

Similar to Tier 1, the emission factor for lime production in Tier 2 reflects the stoichiometric ratios between $CO_2$ and CaO and/or CaO·MgO, and an adjustment to account for the CaO or the CaO·MgO content of the lime. However, unlike Tier 1, Tier 2 requires the use of national level data on lime production by type. It is *good practice* to apply Equation 2.9 to develop the emission factors and to account for the CaO or the CaO·MgO content.

**EQUATION 2.9**
**TIER 2 EMISSION FACTORS FOR LIME PRODUCTION**

$$EF_{lime,a} = SR_{CaO} \bullet CaO\ Content$$

$$EF_{lime,b} = SR_{CaO \cdot MgO} \bullet CaO \cdot MgO\ Content$$

$$EF_{lime,c} = SR_{CaO} \bullet CaO\ Content$$

Where:

$EF_{lime\ a}$ = emission factor for quicklime (high-calcium lime), tonnes $CO_2$/tonne lime

$EF_{lime\ b}$ = emission factor for dolomitic lime, tonnes $CO_2$/tonne lime

$EF_{lime\ c}$ = emission factor for hydraulic lime, tonnes $CO_2$/tonne lime

$SR_{CaO}$ = stoichiometric ratio of $CO_2$ and CaO (see Table 2.4), tonnes $CO_2$/tonne CaO

$SR_{CaO \cdot MgO}$ = stoichiometric ratio of $CO_2$ and CaO·MgO (see Table 2.4), tonnes $CO_2$/tonne CaO·MgO

CaO Content = CaO content (see Table 2.4), tonnes CaO/tonne lime

CaO·MgO Content = CaO·MgO content (see Table 2.4), tonnes CaO·MgO/tonne lime

### TIER 3 METHOD

The Tier 3 emission factors are based on the actual carbonates present. (See Equation 2.7 and Table 2.1.) Tier 3 requires the full accounting of carbonates (species and sources) and may include a correction (i.e., subtraction) for uncalcined lime kiln dust.

## 2.3.1.3 CHOICE OF ACTIVITY DATA

Some industries produce lime and consume it for their operations. This quantity of lime may never be introduced into the market. It is important when collecting activity data for lime production that both marketed and non-marketed lime production are included. In many countries, obtaining statistics on non-marketed lime production may be challenging. It is suggested that inventory compilers identify potential industries where non-marketed lime may be produced (e.g., metallurgy, pulp and paper, sugar refining, precipitated calcium carbonate, water softeners) and inquire whether there is such production. As industries and countries may vary significantly with respect to the quantities of non-marketed lime produced, it is not possible to provide a default value to estimate this activity data.

### TIER 1 METHOD

In Tier 1, inventory compilers may use default values for either of the following variables: (1) the types of lime produced and/or (2) the proportion of hydrated lime produced. Table 2.4, provides data on stoichiometric ratios, the ranges of CaO and CaO·MgO contents and the resulting default emission factors, for the main lime types produced. Where there are no disaggregated data for the breakdown of lime types, it is *good practice* to assume that 85 percent is high-calcium lime and 15 percent dolomitic lime (Miller, 1999) and the proportion of hydraulic lime should be assumed zero unless other information is available.

The Tier 1 method for lime production does not incorporate a correction for LKD. The potential exists to exclude some lime sources in the national inventory due to problems with the activity data (see Sections 2.3.1.4 and 2.3.2.2). The Tier 1 method could considerably underestimate emissions if these issues are not carefully considered.

### TIER 2 METHOD

In implementing the Tier 2 method, it is important to collect disaggregated data for the three types of lime, as this will improve the emissions estimate. There are three main types of non-hydrated lime:

- High-calcium lime (CaO + impurities);
- Dolomitic lime (CaO·MgO + impurities);
- Hydraulic lime (CaO + hydraulic calcium silicates) that is a substance between lime and cement.

The main reason to distinguish these types is that the first two have different emission factors. It is also important to correct for the proportion of hydrated lime in production. Similar to the Tier 2 method for cement production, data should be collected on all non-carbonate sources of CaO (if applicable).

Significant amounts of LKD may be produced as a by-product during lime production. The quantities generated depend on the type of kiln used and the characteristics of the carbonates used. According to Boynton (1980) an average rotary kiln will yield a dust attrition loss of 9 to 10 percent per tonne of lime produced, or 16 to 18 percent of the raw material input. The chemical composition of the LKD varies depending on the raw material input, but a typical high-calcium lime LKD may contain 75 percent combined calcium oxide and uncalcined calcium carbonate (at roughly a 50:50 ratio), with the remaining impurities consisting of silica, aluminum and iron oxides, and sulphur (depending on the fuel used). Correction for LKD in the Tier 2 and Tier 3 methods is analogous to CKD in cement production in both methodology and default value. If possible, data should be collected on typical ratios of LKD to lime production and on the typical composition of the LKD. In the absence of data, the inventory compiler may assume a correction addition of 2 percent to account for LKD (i.e., multiply emissions by 1.02).

Vertical shaft kilns generate relatively small amounts of LKD, and it is judged that a correction factor for LKD from vertical shaft kilns would be negligible and do not need to be estimated.

### TIER 3 METHOD

It is *good practice* to collect plant specific data for the weight fraction of carbonate(s) consumed for lime production and the fraction of calcination achieved. Data should also be collected for the amount (dry weight) and composition of LKD produced. Similar to the Tier 3 method for cement production, emissions from LKD should be subtracted from the Tier 3 estimates.

A couple of key issues should be considered when estimating carbonate consumption data. Data must be available and collected on the plant level, as national level statistics on carbonate consumption for lime production may not be complete. Similar to cement production, although limestone and or dolomite are likely to be the predominant carbonates, it is important to ensure that all carbonate inputs are identified and accounted for.

### CORRECTION FOR THE PROPORTION OF HYDRATED LIME

Both high-calcium and dolomitic limes can be slaked and converted to hydrated lime that is $Ca(OH)_2$ or $Ca(OH)_2 \cdot Mg(OH)_2$. It is *good practice* to include a correction for hydrated lime under Tier 2, and where data are available, under Tier 1. If no data are available for Tier 1, it is *good practice* to assume zero production of hydrated lime.

If x is the proportion of hydrated lime and y is the water content in it, it is *good practice* to multiply the production by a correction factor $1 – (x \bullet y)$. Since the vast majority of hydrated lime produced is high-calcium (90 percent), the default values are $x=0.10$ and $y = 0.28$ (default water content), resulting in a correction factor of 0.97. This default correction factor for hydrated lime may be included in Equation 2.6.

## 2.3.1.4 COMPLETENESS

Complete activity data (i.e., lime production) are needed for *good practice*. Typically, reported production accounts for only a portion of the actual production, because lime production statistics may consider only product that is sold on the market. Use or production of lime as a non-marketed intermediate is not well accounted for or reported. For example, many plants that produce steel, synthetic soda ash, calcium carbide, magnesia and magnesium metal, as well as copper smelters and sugar mills, produce lime but may not report it to national agencies. Omission of these data may lead to an underestimation of lime production for a country by a factor of two or more. Likewise, there may be village-scale or artisanal production of lime for sanitation purposes or for whitewash. All lime production should be reported in this source category, whether produced by lime kilns as a marketed product, or whether produced as a non-marketed intermediate reagent.

Inventory compilers should be cautious to avoid double counting, or omissions, between this source category and emissions from limestone and dolomite consumption. Another potential source of double counting that the inventory compiler should be aware of is associated with hydrated lime. If lime production is corrected for hydrated lime without first establishing whether the lime used to produce hydrated lime is included in total lime production, production of this lime could be double-counted.

Similar to the discussion for cement, when using Tier 3 it is important that all carbonate inputs (e.g., limestone, dolomite, etc.) are accounted for on a plant-specific basis.

Finally, lime-based mortars used in construction gain their strength through the absorption of $CO_2$, but the rates of the carbonation reaction that occur in practice are very uncertain. As it is believed that this process for the carbonation of mortars can take months to decades, it has not been factored into emission calculations. It is not considered *good practice* to include this factor in emissions calculations at this time. This is an area for future work before inclusion into national inventories.

#### 2.3.1.5 DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to calculate emissions from lime production using the same method for every year in the time series. These *Guidelines* introduce a new Tier 3 approach based on carbonate input to lime production. These data may or may not be available historically. If the inventory compiler chooses to implement this Tier for current and future inventories they are encouraged to collect this data for historical years to ensure time series consistency. Where these data are not available, the inventory compiler may refer to the 'Overlap approach' (see Volume 1, Section 5.3) to attempt to recalculate previous estimates.

Where data are not available, inventory compilers moving from a Tier 1 to a Tier 2 approach may assume that there has not been a significant shift in the country from use of one carbonate input to another for lime production. This is likely a reasonable assumption, specifically since limestone typically is the predominant carbonate input.

Inventory compilers should disaggregate lime production data into the three mentioned types: high calcium lime, dolomitic lime, and hydraulic lime. Where country specific data are not available for the entire time series for the proportion of lime consumed, or the proportion of hydrated lime, missing years may be estimated by the Interpolation or Trend Extrapolation Approaches as outlined in Volume 1, Section 5.3, or by assuming that the current year is reflective of the proportion of lime produced in earlier years of the time series.

### 2.3.2 Uncertainty assessment

Uncertainty estimates for lime production result predominantly from uncertainties associated with activity data, and to a lesser extent from uncertainty related to the emission factor. For more information, refer to the uncertainty discussion above for cement production.

TABLE 2.5
DEFAULT UNCERTAINTY VALUES FOR ESTIMATION OF $CO_2$ EMISSIONS FROM LIME PRODUCTION

| Uncertainty | Comment | Tier |
|---|---|---|
| 4-8% | Uncertainty in assuming an average CaO in lime | 1, 2 |
| 2% | Emission factor high calcium lime | 1, 2 |
| 2% | Emission factor dolomitic lime | 1, 2 |
| 15% | Emission factor hydraulic lime | 1, 2 |
| 5% | Correction for hydrated lime | 1, 2 |
|  | Order of magnitude errors possible if non-marketed lime production is not estimated | 1, 2, 3 |
| 1-2% | Uncertainty of plant-level lime production data. Plants generally do not determine output better than this. Assumes complete reporting. | 2 |
| See Table 2.3 | Correction for LKD | 2, 3 |
| 1-3% | Error in assuming 100% carbonate source from limestone (vs. other feeds). | 3 |
| 1-3% | Uncertainty of plant-level weighing of raw materials | 3 |

Source: Based on expert judgment.

#### 2.3.2.1 EMISSION FACTOR UNCERTAINTIES

As outlined above for cement, there is little uncertainty associated with the emission factor component in the Tier 3 approach. In Tier 2 and Tier 1, the stoichiometric ratio is an exact number and therefore the uncertainty of the emission factor is the uncertainty of lime composition, in particular of the share of hydraulic lime (the uncertainty of the emission factor for hydraulic lime is 15 percent and the uncertainty for other lime types is 2 percent). There is uncertainty associated with determining the CaO content and/or the CaO•MgO content of the lime produced.

### 2.3.2.2 ACTIVITY DATA UNCERTAINTIES

The uncertainty for the activity data is likely to be much higher than for the emission factors, based on experience in gathering lime data (see Section 2.3.1.4, Completeness, above). Omission of non-marketed lime production may lead to order of magnitude underestimates. The correction for hydrated lime typically leads to additional uncertainty.

As described above for CKD, there is significant uncertainty associated with quantifying the mass of LKD produced and the degree of calcination (and thus emissions) of LKD. It can be assumed that the uncertainty associated with estimating LKD is at least equal to and likely greater than, the uncertainty associated with CKD.

Where ranges are given for the default uncertainties in Table 2.5, the mid-range should be used unless the upper or lower estimates are more reflective of country-specific circumstances.

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

### 2.3.3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA /QC)

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

#### COMPARISON OF THE EMISSIONS ESTIMATES USING DIFFERENT APPROACHES

Comparisons could be made between emissions estimated following the Tier 2 approach based on lime production and Tier 3 approach based on carbonate input. Similarly, if the bottom-up approach is used to estimate emissions (i.e., collection of plant specific data), then inventory compilers should compare the emissions estimates to the estimate calculated using national or plant-specific lime production data (top-down approach). In cases where a hybrid Tier 1/2 or Tier 2/3 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.

#### ACTIVITY DATA CHECK

Inventory compilers should confirm the correct definitions of the different types of lime produced in the country. Inventory compilers should also carefully consider industries that may produce non-marketed lime to ensure that these data have been included in the activity data for the inventory.

### 2.3.3.2 REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates. Below are general notes that apply to reporting and documentation of emissions and emission reductions from lime production followed by specific information to be reported for the individual tiers.

- If an inventory compiler is reporting on $CO_2$ recovery from sugar refining, precipitated calcium carbonate or water softening under Category 2H, detailed information should be reported on the methods used for calculating emissions recovered. Both emissions and emission reductions should be reported separately; it is not considered *good practice* to report only net emissions from lime production. In addition, documentation should be provided to illustrate that emission reductions from recarbonation are only reported in the year in which recarbonation occurs (see 2.3.1 above).
- Regardless of the method implemented, inventory compilers should document procedures undertaken to ensure that both marketed and non-marketed lime production are reported (see discussion in Section 2.3.1.4, Completeness).

#### TIER 1 METHOD

The Tier 1 approach is methodologically the same as Tier 2 except that default values may be used instead of country-specific information to estimate the various parameters. Documentation for Tier 1, therefore, follows Tier 2 below except a clear indication should be made as to where default values are used.

### TIER 2 METHOD

Tier 2 documentation should include a discussion of the types of lime produced in the country (including hydrated lime) and how that determination was made (collection of sales data, collection of plant specific consumption data, etc.) The procedures used to identify the CaO and/or CaO·MgO content of lime, as well as non-carbonate feeds to lime kiln also should be reported.

### TIER 3 METHOD

Reporting and documentation for Tier 3 for lime production is the same as the Tier 3 method outlined above for cement production, with one minor difference. Instead of collecting information on CKD, data on the quantity and fraction of calcination achieved of LKD should be collected. All underlying information should be documented and reported, it is not considered *good practice* to report just final emissions estimates.

# 2.4 GLASS PRODUCTION

## 2.4.1 Methodological issues

Many kinds of glass articles and compositions are used commercially, but the glass industry can be divided into four main categories: containers, flat (window) glass, fibre glass, and specialty glass.

The great bulk of commercial glass is in the first two categories, and is almost entirely soda-lime glass, consisting of silica ($SiO_2$), soda ($Na_2O$), and lime (CaO), with small amounts of alumina ($Al_2O_3$), and other alkalies and alkaline earths, plus some minor ingredients. Insulation grade fibre glass - a major component of the third category - is similar in composition. Individual manufacturers will have proprietary compositions, but these will be minor variations on the basic composition.

This source category also includes emissions from the production of glass wool, a category of mineral wool, where the production process is similar to glass making. The term mineral wool may also be used to refer to natural rock- and slag-based wool. Where the production of rock wool is emissive these emissions should be reported under IPCC Subcategory 2A5. Emissions related to slag production should be reported in the relevant metallurgical source category. The re-melting of slag to make mineral wool does not involve significant process--related emissions and does not need to be reported.

The major glass raw materials which emit $CO_2$ during the melting process are limestone ($CaCO_3$), dolomite $Ca,Mg(CO_3)_2$ and soda ash ($Na_2CO_3$). Where these materials are mined as carbonate minerals for their use in the glass industry they represent primary $CO_2$ production and should be included in emissions estimates. Where carbonate materials are produced through the carbonation of a hydroxide they do not result in net $CO_2$ emissions and should not be included in the emissions estimate. Minor $CO_2$-emitting glass raw materials are barium carbonate ($BaCO_3$), bone ash ($3CaO_2P_2O_5 + XCaCO_3$), potassium carbonate ($K_2CO_3$) and strontium carbonate ($SrCO_3$). Additionally, powdered anthracite coal or some other organic material may be added to create reducing conditions in the molten glass, and will combine with available oxygen in the glass melt to produce $CO_2$.

The action of these carbonates in the fusion of glass is a complex high-temperature chemical reaction, and is not to be directly compared to the calcination of carbonates to produce quicklime or burnt dolomitic lime. Nevertheless, this fusion (in the region of 1500°C) has the same net effect in terms of $CO_2$ emissions.

In practice, glass makers do not produce glass only from raw materials, but use a certain amount of recycled scrap glass (cullet). Most operations will use as much cullet as they can obtain, sometimes with restrictions for glass quality requirements. The cullet ratio (the fraction of the furnace charge represented by cullet) will be in the range of 0.4 to 0.6 for container applications, which are the bulk of glass production. Insulation fibre glass makers will generally fall below this level, but will use as much cullet as they can purchase.

Cullet comes from two sources: in-house return of glassware broken in process or other glass spillage or retention, and foreign (i.e., external to the plant) cullet from recycling programs or cullet brokerage services. This second source is important in developed economies, but will be less so in developing countries, where recovery of glassware is not popular.

The retention of dissolved $CO_2$ in glass is determined to be relatively insignificant and can be ignored for the purposes of GHG emission estimation.

### 2.4.1.1 CHOICE OF METHOD

#### TIER 1 METHOD

The Tier 1 method should be used (Equation 2.10) where data are not available on glass manufactured by process or the carbonates used in glass manufacturing. Tier 1 applies a default emission factor and cullet ratio to national-level glass production statistics. The uncertainty associated with this method may be considerably higher than the uncertainty associated with the Tier 2 and Tier 3 methods.

**EQUATION 2.10**
**TIER 1: EMISSIONS BASED ON GLASS PRODUCTION**

$$CO_2\ Emissions = M_g \bullet EF \bullet (1 - CR)$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from glass production, tonnes

$M_g$ = mass of glass produced, tonnes

EF = default emission factor for manufacturing of glass, tonnes $CO_2$/tonne glass

CR = cullet ratio for process (either national average or default), fraction

#### TIER 2 METHOD

Tier 2 is a refinement of Tier 1. Instead of collecting national statistics on total glass production, emissions are estimated based on the different glass manufacturing processes undertaken in the country. As discussed below, different glass manufacturing processes (e.g., float glass, container glass, fibre glass, etc) typically use different types and ratios of raw materials. The Tier 2 method applies default emission factors to each glass manufacturing process. The emission estimate must, however, be corrected for the fact that a portion of recycled glass (cullet) may also be supplied to the furnace (Equation 2.11).

**EQUATION 2.11**
**TIER 2: EMISSIONS BASED ON GLASS MANUFACTURING PROCESS**

$$CO_2\ Emissions = \sum_i [M_{g,i} \bullet EF_i \bullet (1 - CR_i)]$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from glass production, tonnes

$M_{g,i}$ = mass of melted glass of type *i* (e.g., float, container, fibre glass, etc.), tonnes

$EF_i$ = emission factor for manufacturing of glass of type *i*, tonnes $CO_2$/tonne glass melted

$CR_i$ = cullet ratio for manufacturing of glass of type *i*, fraction

#### TIER 3 METHOD

The Tier 3 methodology is based on accounting for the carbonate input to the glass melting furnace (Equation 2.12).

**EQUATION 2.12**
**TIER 3: EMISSIONS BASED ON CARBONATE INPUTS**

$$CO_2\ Emissions = \sum_i (M_i \bullet EF_i \bullet F_i)$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from glass production, tonnes

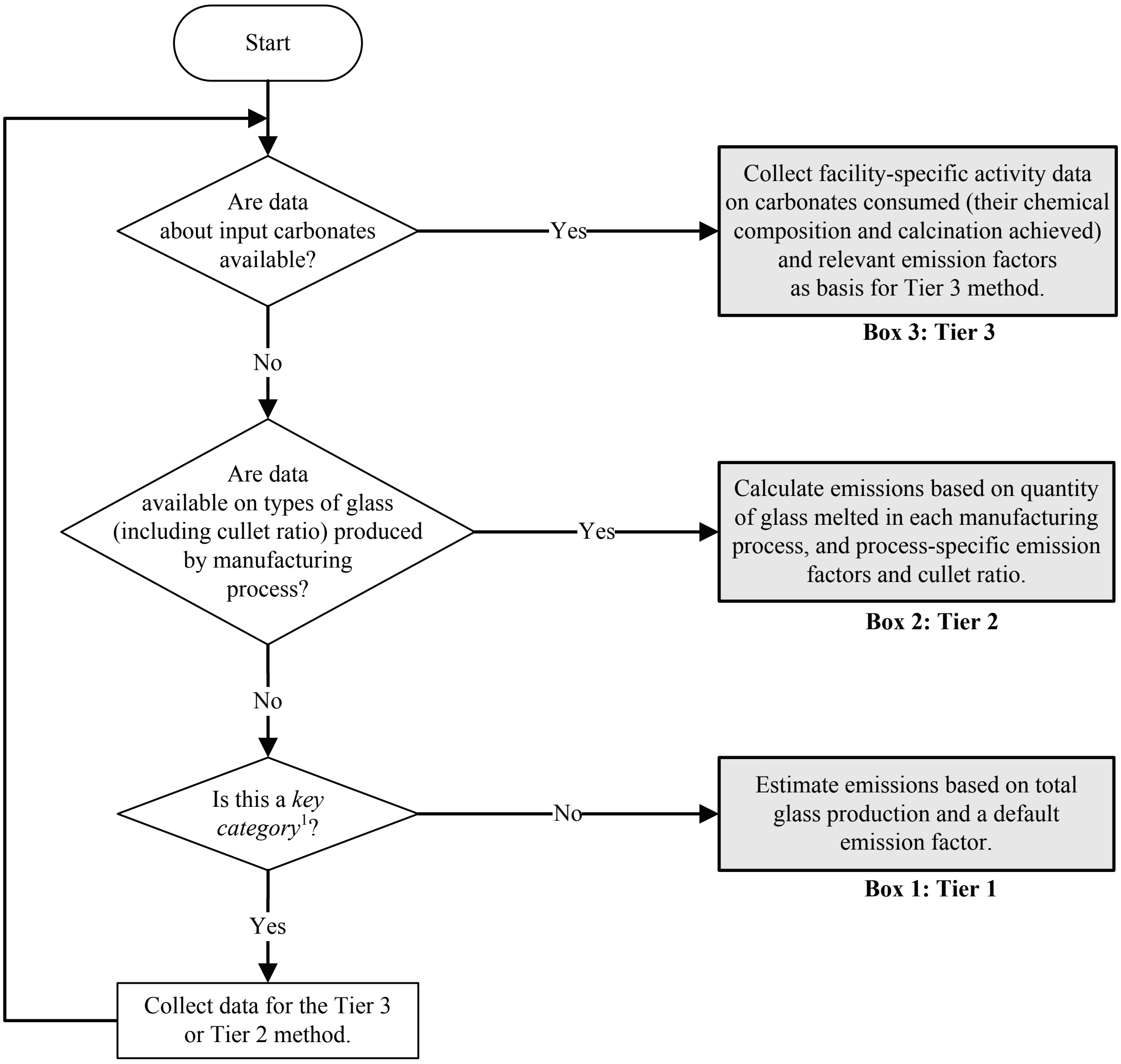
$EF_i$ = emissions factor for the particular carbonate *i*, tonnes $CO_2$/tonne carbonate (see Table 2.1)

$M_i$ = weight or mass of the carbonate *i* consumed (mined), tonnes

$F_i$ = fraction calcination achieved for the carbonate *i*, fraction

Where the fraction calcination achieved for the particulate carbonate is not known, it can be assumed that the fraction calcination is equal to 1.00.

**Figure 2.3 Decision tree for estimation of $CO_2$ emissions from glass 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.

## 2.4.1.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

Tier 1 applies a default emission factor, based on a ‘typical’ raw material mixture, to national glass production data. A ‘typical’ soda-lime batch might consist of sand (56.2 weight percent), feldspar (5.3 percent), dolomite (9.8 percent), limestone (8.6 percent) and soda ash (20.0 percent). Based on this composition, one metric tonne of raw materials yields approximately 0.84 tonnes of glass, losing about 16.7 percent of its weight as volatiles, in this case virtually entirely $CO_2$.

**EQUATION 2.13**
**TIER 1 DEFAULT EMISSION FACTOR FOR GLASS PRODUCTION**

$$EF = 0.167 / 0.84 = 0.20 \text{ tonnes } CO_2 \text{ / tonne glass}$$

### TIER 2 METHOD

The Tier 2 method relies on applying default emission factors and cullet ratios to the various types of glass produced in the country (Table 2.6). Where country specific or even plant specific data are available countries are encouraged to use these data to supplement or replace the defaults provided below. Cullet ratios, in particular, can vary significantly both within a country and across countries.

It is *good practice* to use the mid-point values of the ranges provided unless some other value in the range is known to be more representative of country specific circumstances.

TABLE 2.6
DEFAULT EMISSION FACTORS AND CULLET RATIOS FOR DIFFERENT GLASS TYPES

| Glass Type | $CO_2$ Emission Factor (kg $CO_2$/kg glass) | Cullet Ratio (Typical Range) |
|---|---|---|
| Float | 0.21 | 10% - 25% |
| Container (Flint) | 0.21 | 30% - 60% |
| Container (Amber/Green) | 0.21 | 30% - 80% |
| Fiberglass (E-glass) | 0.19 | 0% - 15% |
| Fiberglass (Insulation) | 0.25 | 10% - 50% |
| Specialty (TV Panel) | 0.18 | 20% - 75% |
| Specialty (TV Funnel) | 0.13 | 20% - 70% |
| Specialty (Tableware) | 0.10 | 20% - 60% |
| Specialty (Lab/Pharma) | 0.03 | 30% - 75% |
| Specialty (Lighting) | 0.20 | 40% - 70% |

Source: Communication with Victor Aume (2004)

### TIER 3 METHOD

The Tier 3 emission factors are based on the actual carbonates consumed in the melting furnace (for the relevant stoichiometric ratios see Table 2.1). The Tier 3 approach requires the full accounting of carbonates (species and sources).

## 2.4.1.3 CHOICE OF ACTIVITY DATA

### TIER 1 METHOD

Activity data for the Tier 1 method includes national statistics for glass production by weight as well a correction for the quantity of cullet used in glass production. Tier 1 assumes a default cullet ratio of 50 percent, therefore national level data on the mass of glass produced can be multiplied by 0.20 • (1 - 0.50) = 0.10 tonnes $CO_2$/tonne glass in order to estimate national emissions. If country specific information is available for the average annual cullet ratio, countries are encouraged to modify the emission factor accordingly [i.e., EF = 0.20 • (1 - country-specific cullet ratio)].

### TIER 2 METHOD

The Tier 2 method requires, at a minimum, the collection of national level data on the quantity of glass melted by manufacturing process. Data for glass often is provided in different units (e.g., tonnes of glass, number of bottles, square meters of glass, etc.) and these should be converted into tonnes. Where possible, data should be collected on a plant-specific basis and aggregated to the national level. Although the Tier 2 method provides default factors for the cullet ratio, if country-specific or plant-specific data are available countries are encouraged to collect these data.

### TIER 3 METHOD

For the Tier 3 method plant-level activity data should be collected on the various types of carbonates consumed for glass production.

### 2.4.1.4 COMPLETENESS

Inventory compilers should consider a number of issues regarding completeness when compiling emission estimates for glass production. First of all, glass is produced from a variety of raw material carbonates. Where emissions are estimated based on carbonate inputs (Tier 3), it is important to ensure that all species and sources of carbonates are included in emission estimates.

Soda ash is a significant input into glass manufacturing in many countries. Inventory compilers are encouraged to ensure that there is no double counting of emissions from soda ash used in glass manufacturing (which should be reported under Category 2A3, Glass Production) and emissions from 'Other Uses of Soda Ash', which should be reported separately below. It is important to consider, however, that there may be a number of smaller facilities (e.g., art glass and specialty glass) that are not accounted for in national statistics. Efforts should be made to ensure complete coverage of the industry.

### 2.4.1.5 DEVELOPING A CONSISTENT TIME SERIES

Glass can be a difficult source for which to acquire activity data because, as noted above, glass production is measured in a variety of units. In order to develop a consistent time series, it is important that the same data sources are used for all years in the Inventory. For additional information for ensuring time series consistency, see Volume 1, Chapter 5.

## 2.4.2 Uncertainty assessment

### 2.4.2.1 EMISSION FACTOR UNCERTAINTIES

Similar to cement and lime, where emissions from glass production are estimated based on the carbonate input (Tier 3), the emission factor uncertainty (1-3 percent) is relatively low because the emission factor is based on a stoichiometric ratio. There may be some uncertainty associated with assuming that there is 100 percent calcination of the carbonate input (1 percent).

Because emissions are estimated based on quantity of melted glass in each manufacturing process and default emission factors, the uncertainty of Tier 2 is higher than Tier 3. The emission factors can be expected to have an uncertainty of +/- 10 percent. As illustrated in Table 2.6, the typical range for the cullet ratio varies among different glass types. For the purposes of uncertainty analysis it can be assumed that the 'typical range' reflects the 95 percent confidence interval.

Uncertainty associated with use of the Tier 1 emission factor and cullet ratio is significantly higher, and may be on the order of +/- 60 percent.

### 2.4.2.2 ACTIVITY DATA UNCERTAINTIES

As with cement and lime production, the uncertainty associated with weighing or proportioning raw materials under the Tier 3 approach is approximately 1-3 percent. While it is possible that some carbonate containing raw materials may be brought into the facility but lost as dust (i.e., never calcined) this amount is assumed negligible.

Glass production data are typically measured fairly accurately (+/-5 percent) for Tier 1 and Tier 2. As mentioned above, inventory compilers should be cautious where activity data are not originally available in mass, but rather as a unit (e.g., bottle) or area (e.g., $m^2$). If activity data have to be converted to mass, this may result in additional uncertainty.

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

### 2.4.3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

If emissions are estimated using a Tier 3 approach these could be compared with the results using a Tier 2 approach to see if the results are of a similar order of magnitude. Similarly, if emissions were estimated from top down data using the Tier 2 method, these results could be compared with a more rigorous Tier 3 approach at a small number of facilities to see if the Tier 2 defaults used reflect national circumstances. The Tier 2 method relies on estimating emissions based on the different types of glass produced. These estimates could be compared with the results of an audit of the various suppliers of raw materials to the glass industry. For example, national estimates could be compared with estimates of the amount of limestone, soda ash and other carbonates that are sold to the glass industry. Such trade data could be elicited from individual suppliers, or from trade associations.

One of the largest sources of uncertainty in the emissions estimate (Tier 1 and Tier 2) for glass production is the cullet ratio. The amount of recycled glass used can vary across facilities in a country and in the same facility over time. The cullet ratio might be a good candidate for more in-depth investigation.

### 2.4.3.2 REPORTING AND DOCUMENTATION

#### TIER 1

For Tier 1, data should be documented and reported to indicate the total quantity of glass produced, and the emission factor applied to estimate emissions (including whether a default or country-specific cullet ratio is used). The process for collecting activity data should be documented (i.e., plant level or national estimates) as should any calculations made to convert glass production to a common unit (e.g., kg).

#### TIER 2

Tier 2 documentation should include the quantity of glass melted in each manufacturing process outlined in Table 2.6, including any calculation necessary to convert different types of glass into the same units (e.g., convert bottles into kilogram). Emission factors by glass type and cullet ratio should be reported, indicating if defaults are used, and whether data were collected on the plant level or at the national level. It is also useful to report whether cullet was internally generated at the facility or is post-consumer cullet (i.e., purchased cullet). This information may be important for identifying, or verifying, mitigation activities that are based on recycling.

#### TIER 3

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 reproduced. Where the Tier 3 method is implemented, inventory compilers should document the species of carbonates consumed and indicate how they ensure that all carbonate inputs are accounted for (see discussion for Tier 3 in Section 2.2.3.2).

# 2.5 OTHER PROCESS USES OF CARBONATES

## 2.5.1 Methodological issues

Limestone ($CaCO_3$), dolomite ($CaMg.(CO_3)_2$) and other carbonates (e.g., $MgCO_3$ and $FeCO_3$) are basic raw materials having commercial applications in a number of industries. In addition to those industries already discussed individually (cement production, lime production and glass production), carbonates also are consumed in metallurgy (e.g., iron and steel), agriculture, construction and environmental pollution control (e.g., flue gas desulphurisation.). As noted in the introduction of this chapter, the calcination of carbonates at high temperatures yields $CO_2$ (Table 2.1). It should be noted that some uses of carbonates, for example, the use of limestone as an aggregate, do not result in the release of $CO_2$ and, therefore, do not need to be included in the national GHG inventory (see Table 2.7).

The following discussion provides the general methodologies for estimating $CO_2$ emissions from the use of carbonates within the mineral industry. These methodologies, however, also are applicable where carbonates are used as fluxes or slagging agents in other source categories. Inventory compilers are suggested, in particular, to consider four broad source categories: (1) ceramics, (2) other uses of soda ash, (3) non-metallurgical magnesia production, and (4) other uses of carbonates.

It is *good practice* to report emissions from the consumption of carbonates in the source category where the carbonates are consumed and the $CO_2$ emitted. So, where limestone is used for the liming of soils, emissions should be reported in the respective source category of the Agriculture, Forestry and Other Land Use (AFOLU) Sector. Where carbonates are used as fluxes or slagging agents (e.g., in iron and steel, chemicals, or for environmental pollution control etc.) emissions should be reported in the respective source categories where the carbonate is consumed. As discussed in Section 2.3.1.1 above, all marketed and non-marketed production of lime should be reported under Lime Production. The specific source categories discussed below (ceramics, other soda ash use and non-metallurgical magnesia production) should be reported within the minerals category. The Other source category should contain estimates of emissions that do not fit into any of the major categories presented in Table 2.7 below.

### CERAMICS

Ceramics include the production of bricks and roof tiles, vitrified clay pipes, refractory products, expanded clay products, wall and floor tiles, table and ornamental ware (household ceramics), sanitary ware, technical ceramics, and inorganic bonded abrasives. Process-related emissions from ceramics result from the calcination of carbonates in the clay, as well as the addition of additives. Similar to the cement and lime production processes, carbonates are heated to high temperatures in a kiln, producing oxides and $CO_2$. Most ceramic products are made from one or more different types of clay (e.g., shales, fire clay and ball clay). The raw materials are collected and finely crushed in successive grinding operations. The ground particles are then fired in a kiln to produce a powder (which may be liquefied). Additives are subsequently added and the ceramic is formed or moulded and 'machined' to smooth rough edges and achieve the desired characteristics of the ceramic. In the case of traditional ceramics, the ceramics are then dried and glazed prior to firing in the kiln. After firing, some ceramics may undergo additional treatment to achieve the final desired quality.

$CO_2$ emissions result from the calcination of the raw material (particularly clay, shale, limestone, dolomite and witherite) and the use of limestone as a flux.

### OTHER USES OF SODA ASH

Soda ash is used in a variety of applications, including, glass production, soaps and detergents, flue gas desulphurisation, chemicals, pulp and paper and other common consumer products. Soda ash production and consumption (including sodium carbonate, $Na_2CO_3$) results in the release of $CO_2$. Emissions from soda ash production are reported in the Chemical Industry, while emissions from use are reported in the respective end use sectors where soda ash is used. Emissions from soda ash used in glass production are already accounted for above. Similarly, where soda ash is used in other source categories such as chemicals, emissions should be reported in that source category.

### NON-METALLURGICAL MAGNESIA PRODUCTION

This source category should include emissions from magnesia (MgO) production that are not included elsewhere. For example, where magnesia is produced for use as a fertiliser, *good practice* is to report those emissions under the appropriate section of Chapter 3, Chemical Industry Emissions.

Magnesite ($MgCO_3$) is one of the key inputs into the production of magnesia, and ultimately fused magnesia. There are three major categories of magnesia products: calcined magnesia, deadburned magnesia (periclase) and fused magnesia. Calcined magnesia is used in many agricultural and industrial applications (e.g., feed supplement to cattle, fertilisers, electrical insulations and flue gas desulphurisation). Deadburned magnesia is used predominantly for refractory applications, while fused magnesia is used in refractory and electrical insulating markets.

Magnesia is produced by calcining $MgCO_3$ which results in the release of $CO_2$ (Table 2.1). Typically, 96-98 percent of the contained $CO_2$ is released in the production of calcined magnesia, with nearly 100 percent of the $CO_2$ released during further heating to produce deadburned magnesia. Production of fused magnesia also results in nearly 100 percent release of the $CO_2$.

### OTHER

Emissions may result from a number of other source categories that are not included above. When allocating emissions to this source category, inventory compilers should be careful to not double count emissions already recorded in other source categories.

### 2.5.1.1 CHOICE OF METHOD

There are two primary methodologies for estimating emissions from the use of carbonate(s) for these source categories. The Tier 1 method assumes that only limestone and dolomite are used as carbonate input in industry, and allows for the use of a default fraction of limestone versus dolomite consumed. Tier 2 is the same as Tier 1 except country specific information on the fraction of limestone versus dolomite consumed must be determined. The Tier 3 method is based on an analysis of all emissive uses of carbonates.

It is possible that Tier 3 could be used for some sub-categories, and a Tier 1 or 2 method used for other categories with limited data availability. Such a hybrid approach is consistent with *good practice.* The selection of method depends on national circumstances.

#### TIER 1 METHOD

The Tier 1 method is based on Equation 2.14.

**EQUATION 2.14**

**TIER 1: EMISSIONS BASED ON MASS OF CARBONATES CONSUMED**

$$CO_2\ Emissions = M_c \bullet (0.85 EF_{ls} + 0.15 EF_d)$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from other process uses of carbonates, tonnes

$M_c$ = mass of carbonate consumed, tonnes

$EF_{ls}$ or $EF_d$ = emission factor for limestone or dolomite calcination, tonnes $CO_2$/tonne carbonate (see Table 2.1)

It is suggested that inventory compilers ensure that data on carbonates reflect pure carbonates and not carbonate rock. If data are only available on carbonate rock, a default purity of 95 percent can be assumed. For clays a default carbonate content of 10 percent can be assumed[4], if no other information is available.

Soda ash is primarily sodium carbonate, not limestone or dolomite. Therefore, the Tier 1 method for soda ash does not require the default fraction of 85%/15%. Emissions are estimated by multiplying the quantity of soda ash consumed on the national level by the default emission factor for sodium carbonate (see Table 2.1).

#### TIER 2 METHOD

Under Tier 2, the amount of $CO_2$ emitted from the use of limestone and dolomite is estimated from a consideration of consumption and the stoichiometry of the chemical processes. Tier 2 uses a similar equation to Tier 1, but Tier 2 requires national data on the quantity of limestone and dolomite consumed in the country (Equation 2.15). It is not *good practice* to use a default for the allocation between these two primary carbonates.

**EQUATION 2.15**

**TIER 2: METHOD FOR OTHER PROCESS USES OF CARBONATES**

$$CO_2\ Emissions = (M_{ls} \bullet EF_{ls}) + (M_d \bullet EF_d)$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from other process uses of carbonates, tonnes

$M_{ls}$ or $M_d$ = mass of limestone or dolomite respectively (consumption), tonnes. (Refer to Equation 2.14 above regarding purity.)

$EF_{ls}$ or $EF_d$ = emission factor for limestone or dolomite calcination respectively, tonnes $CO_2$/tonne carbonate (see Table 2.1)

#### TIER 3 METHOD

The Tier 3 methodology is similar to the approach outlined for cement above, but there is no need to correct for dust or other raw material inputs (Equation 2.16). As noted above, wherever this approach is used, it is important that all carbonate inputs are considered in the analysis.

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[4] EU-BREF (2005) reports a range of carbonate contents for relevant clays used in the ceramics industry ranging from 0 to over 30 percent.

**EQUATION 2.16**

**TIER 3: CARBONATE INPUT APPROACH FOR OTHER PROCESS USES OF CARBONATES**

$$CO_2\ Emissions = \sum_i (M_i \bullet EF_i \bullet F_i)$$

Where:

$CO_2$ Emissions = emissions of $CO_2$ from other process uses of carbonates, tonnes

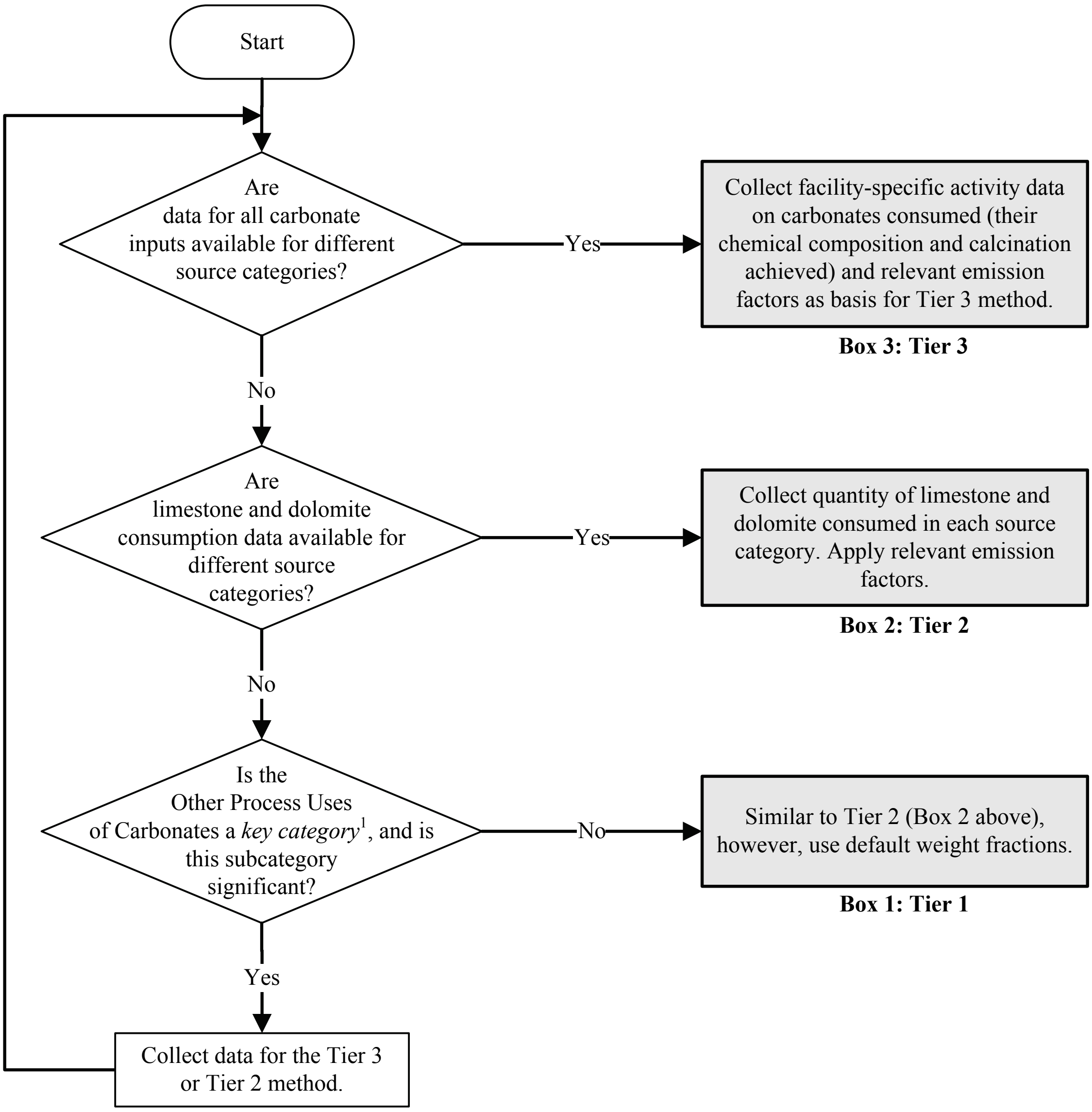
$M_i$ = mass of the carbonate *i* consumed, tonnes (Refer to Equation 2.14 above regarding purity.)

$EF_i$ = emission factor for the carbonate *i*, tonnes $CO_2$/tonne carbonate (see Table 2.1)

$F_i$ = fraction calcination achieved for the particular carbonate *i*, fraction. Where the fraction calcination achieved for the particular carbonate is not known it can be assumed that the fraction calcination is equal to 1.00.

i = one of the carbonate uses

**Figure 2.4 Decision tree for estimation of $CO_2$ emissions from other process uses of carbonates**



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.

### 2.5.1.2 CHOICE OF EMISSION FACTORS

#### TIER 1 AND TIER 2

The emission factor for the Tier 1 and Tier 2 methodologies is based on the mass of $CO_2$ released per mass of carbonate consumed (see Table 2.1.) The distinction between Tier 1 and Tier 2 is in the activity data.

#### TIER 3

The Tier 3 emission factor represents the weighted average of the emission factors of the individual carbonates (see Table 2.1). The Tier 3 approach requires the full accounting of carbonates (species and sources).

### 2.5.1.3 CHOICE OF ACTIVITY DATA

#### TIER 1

In the Tier 1 method, the inventory compiler should collect activity data for total carbonate consumption for emissive uses (see Table 2.7 for uses of carbonates that are emissive.) In the absence of better data, it is consistent with *good practice* for inventory compilers to assume that 85 percent of carbonates consumed are limestone and 15 percent of carbonates consumed are dolomite. For soda ash use, the inventory compiler should collect national or plant level data on the total quantity of soda ash used. For clays used in the ceramics industry, the inventory compiler should collect national production data for bricks and roof tiles, vitrified clay pipes, and refractory products and calculate the amount of clay consumed by multiplying production with a default loss factor of 1.1.

#### TIER 2

It is considered *good practice* to collect activity data to illustrate the total quantity of carbonates consumed in each end use sector. Where specific data are not available to identify the different carbonates consumed in these end use sectors, it is *good practice* to collect national level activity data for limestone and dolomite consumed. Similar to the Tier 1 method, where the fraction of calcination achieved is unknown, it is consistent with *good practice* for the inventory compiler to assume that 100 percent calcination is achieved. Inventory compilers should be cautious not to assume that all limestone and dolomite consumed in the country results in the release of $CO_2$ emissions. For example, limestone and dolomite are often used as aggregates in a number of processes and this use of crushed stone does not result in emissions (Table 2.7).

#### TIER 3

The most accurate method is to collect activity data on carbonate consumption by end use. *Good practice* is to collect plant-specific data of the carbonate(s) consumed for that source category and the fraction of calcination of the carbonate achieved. Carbonate consumption is assumed to be equal to the raw material mined (or dredged), plus raw material imported minus material exported. Where the fraction of calcination achieved is unknown, it is consistent with *good practice* for the inventory compiler to assume that 100 percent calcination is achieved. For clay use in the ceramics industry, the inventory compiler should collect clay consumption data for all relevant ceramics products.

### 2.5.1.4 COMPLETENESS

Completeness is a particular challenge with respect to carbonate-consuming (calcining) industries, because the potential for both underestimation and overestimation exists. As has been noted throughout this chapter, where a method is based on carbonate input, the potential for underestimating the total quantity of carbonates consumed is possible. As such, the Tier 3 method for other process uses of carbonates should only be applied at the plant-level.

The potential also exists for double counting. Inventory compilers should carefully consider how national statistics on limestone, dolomite and other carbonate uses were developed. For example, a data source for the iron and steel industry may contain the total quantity of limestone consumed as a flux, especially to the degree that emissions were part of blast furnace gas or other combustible gas that were included in the fuel combustion emissions from the relevant sector. At a national level, on limestone statistics should be carefully examined to determine whether the data also contains consumption of limestone in the iron and steel industry.

Often national statistics on limestone, dolomite and other carbonate uses contain categories such as ‘other unspecified uses’. Inventory compilers should be cautious that this consumption is not already accounted for in other sources.

The *Guidelines* separately identify two categories (Other Uses of Soda Ash and Non-metallurgical Magnesia Production) that are intermediate products used in a variety of other source categories. Soda ash, in particular, is used in a variety of industries, such as glass production, soaps and detergents. It is suggested that inventory compilers carefully review statistics for those source categories to ensure that no double counting has occurred. For example, where soda ash is used in glass production, emissions should be reported in that category. Where soda ash is used in another industry, emissions should be reported in that industry. Where soda ash is used in another mineral industry or where information is not sufficient to determine where it has been consumed, then emissions should be reported in the Category 2A4b, Other Uses of Soda Ash.

Table 2.7 highlights some questions that inventory compilers may ask themselves to help assure that these emissions are allocated appropriately, and not over-or underestimated.

TABLE 2.7
EMISSIVE AND NON-EMISSIVE USES OF CARBONATES

| Where are Carbonates Consumed? | Is source emissive? | If yes, where should emissions be reported? |
|---|---|---|
| ***Agricultural:*** | | |
| Agricultural limestone | Yes* | AFOLU: 3C2 Liming |
| Poultry grit and mineral food | No | |
| Other agricultural uses | No | |
| ***Chemical and metallurgical:*** | | |
| Cement manufacture | Yes | IPPU: 2A1 Cement Production |
| Lime manufacture | Yes | IPPU: 2A2 Lime Production |
| Dead burning of dolomite | Yes | IPPU: 2A2 Lime Production, where deadburned; outside of lime industry under Other (2A4d). |
| Flux stone | Yes | IPPU: 2C Metal Industry, Industry where consumed; unless counted within Energy (for combustible off-gases sold off-site) |
| Chemical stone | Yes** | Source category where consumed |
| Glass manufacture | Yes | IPPU: 2A3 Glass Production |
| Sulphur oxide removal | Yes* | Source category where consumed |
| Fertilisers | Yes** | IPPU: 2B Chemical Industry |
| ***Ceramics and mineral wool:*** | | |
| Ceramics | Yes | IPPU: Mineral Industry: 2A4a Ceramics |
| Mineral wools | Yes | IPPU: Mineral Industry: 2A3 Glass Production or 2A4d Other, depending on production process. |
| ***Special:*** | | |
| Mine dusting or acid water treatment | Yes* | Source category where consumed |
| Asphalt fillers or extenders | No | |
| Whiting or whiting substitute | No | |
| Other fillers or extenders | No | |
| ***Construction:*** | | |
| Use as a Fine or Coarse Aggregate | No | |

**TABLE 2.7 (CONTINUATION)**
**EMISSIVE AND NON-EMISSIVE USES OF CARBONATES**

| Production | Is source emissive? | If yes, where should emissions be reported? |
|---|---|---|
| ***Other miscellaneous uses:*** | | |
| Refractory stone | No | |
| Acid neutralization | Yes* | Source category where consumed |
| Chemicals | No | |
| Paper manufacture | No | |
| Abrasives | No | |
| Sugar refining | Yes | IPPU: Emissions from lime production at sugar mills should be reported under 2A2 Lime Production; all other emissions in 2A4 Other Process Uses of Carbonates. Removals should be reported under 2H2 Food and Beverages Industry. |
| ***Others*** | Yes*, No | Where Yes, IPPU: 2A4 Other Process Uses of Carbonates |

* Emissions are by an acidification reaction.

** Emissions could be by calcination and/or acidification.

## 2.5.1.5 DEVELOPING A CONSISTENT TIME SERIES

Fundamentally, these *Guidelines* treat the consumption of limestone, dolomite and other carbonate uses differently than earlier *IPCC Guidelines* documents. Previous guidance suggested that, except for the case of limestone and dolomite consumed in cement production, lime production and the liming of agricultural soils, all consumption of limestone and dolomite be reported under the source category Limestone and Dolomite Use.

In the *2006 Guidelines*, emissions from other process uses of carbonates should be reported in the source category where they are consumed, and thereby emissions are reported in the sector where they are emitted. This change could require recalculations to ensure time series consistency for the Other Process Uses of Carbonates source category in the Minerals Industry, and also in the other source categories where the carbonates are consumed.

There are a number of ways that inventory compilers may help ensure time series consistency: It is *good practice* for the inventory compiler to consider the following in accordance with Volume 1, Chapter 5.

- If data are available to complete the Tier 3 (or the Tier 2) method for all years, this should be followed.
- If data are only available for certain years, the intervening years may be estimated by interpolation or extrapolation of the trend lines.
- If data on other process uses of carbonates are available at a disaggregated level for only the most recent year, the inventory compiler may elect to apply the proportion of carbonates consumed in each industry for the most recent year, to production trends for the respective industries, similar to the Surrogate Method outlined in Volume 1, Section 5.3. Inventory compilers should be cautious when using this approach however, and consider if there are national circumstances which may have led to the greater use of fluxes or slagging agents for certain industries over the time period.

## 2.5.2 Uncertainty assessment

### 2.5.2.1 EMISSION FACTOR UNCERTAINTIES

In theory the uncertainty associated with the emission factor for this source category should be relatively low, as the emission factor is the stoichiometric ratio reflecting the amount of $CO_2$ released upon calcination of the carbonate. In practice, there are uncertainties due, in part, to variations in the chemical composition of the limestone and other carbonates. For example, in addition to calcium carbonate, limestone may contain smaller amounts of magnesia, silica and sulphur. Assuming that the activity data are collected correctly, and thus the correct emission factor is applied, there is negligible uncertainty associated with the emission factor. There may be some uncertainty associated with assuming a fractional purity of limestone and dolomite in cases where only carbonate rock data are available (+/- 1-5 percent).

### 2.5.2.2 ACTIVITY DATA UNCERTAINTIES

Activity data uncertainties are greater than the uncertainties associated with emission factors. Assuming that carbonate consumption is allocated to the appropriate consuming sectors/industries, the uncertainty associated with weighing or proportioning the carbonates for any given industry is 1-3 percent. The uncertainty of the overall chemical analysis pertaining to carbonate content and identity also is 1-3 percent. The uncertainty associated with use of the Tier 2 and Tier 1 methods, including the assumption of a default breakdown of limestone versus dolomite of 85%/15%, varies depending on country specific circumstances.

Activity data for limestone and dolomite use may be difficult to collect, as there are a variety of end uses in different industries, some of which are emissive and others not. National statistics may include an end use category of ‘other unspecified uses’ (or an otherwise similar category) and it may be difficult to allocate ‘other unspecified uses’ to the appropriate consuming sector. Where all uses can not be properly identified this will increase uncertainty.

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

### 2.5.3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

#### COMPARISON OF EMISSION ESTIMATES USING DIFFERENT APPROACHES

Emission estimates derived from any Tier can be compared with the other Tiers, even though the Tier 3 approach may be accounting for additional carbonate species not included in the Tier 1 or 2 analyses. Assuming that the same fraction of calcination achieved is used for all Tiers, the emissions estimated using the respective approaches will likely be similar in magnitude, considering that limestone and dolomite likely contribute the greatest percentage of emissions for these sources.

#### ACTIVITY DATA CHECK

As limestone, dolomite and other carbonates are consumed in a variety of industries there may be a number of different data sources available containing carbonate consumption in the respective industries. For example, data for limestone consumption at various facilities in the iron and steel industry could be compared to see if the quantity of flux used in proportion to facility level production is similar.

Also, plant specific information on use of limestone, dolomite and other carbonates as a flux could be compared with industry association statistics. These industry association statistics could in turn be compared with national level statistics on limestone, dolomite and other carbonate consumption.

It is often useful to examine trends in activity data over time to see if there may be large fluctuations year to year. Inventory compilers should be cautious when drawing conclusions based on trends data, as there may be large year to year fluctuations in these statistics.

### 2.5.3.2 REPORTING AND DOCUMENTATION

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 reproduced. As noted above, the most important consideration that inventory compilers should make when reporting emissions from other process uses of carbonates is that emissions should be reported in the source category where the carbonates are consumed.

#### TIER 1 AND TIER 2

Information should be reported on the quantity of limestone and dolomite consumed by each industry. Where the breakdown of carbonates consumed in a particular industry is unknown, and a default allocation of 85 percent limestone and 15 percent dolomite is used, this should be documented.

#### TIER 3

Documentation required for the Tier 3 approach is analogous to the other source categories in this chapter that calculate emissions based on carbonate inputs.

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# CHAPTER 3

# CHEMICAL INDUSTRY EMISSIONS

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# 3 CHEMICAL INDUSTRY EMISSIONS

## 3.1 INTRODUCTION

The following Sections 3.2 through 3.10 give guidance for estimating greenhouse gas emissions that result from the production of various inorganic and organic chemicals for which experience by a number of countries has confirmed significant contributions to global or individual national greenhouse gas emission levels.

- Section 3.2 covers emissions from ammonia production;
- Section 3.3 covers emissions from nitric acid production;
- Section 3.4 covers emissions from adipic acid production;
- Section 3.5 covers emissions from the production of caprolactam, glyoxal, and glyoxylic acid;
- Section 3.6 covers emissions from the production of carbide;
- Section 3.7 deals with emissions from the production of titanium dioxide;
- Section 3.8 deals with emissions from the production of soda ash;
- Section 3.9 covers emissions from key processes in the petrochemical and carbon black production, i.e., methanol, ethylene and propylene, ethylene dichloride, ethylene oxide, acrylonitrile, and carbon black;
- Section 3.10 deals with emissions from fluorochemical production i.e., HFC-23 from the production of HCFC-22 and fugitive and by-product emissions from the production of other fluorinated compounds including hydrofluorocarbons (HFCs), sulphur hexafluoride ($SF_6$) and uranium hexafluoride ($UF_6$).

Care should be exercised to avoid double counting of carbon dioxide ($CO_2$) emissions in both this chapter and in Volume 2 on Energy Sector, or, in omitting $CO_2$ emissions since $CO_2$ emissions resulting from carbon's role as process reactant and as a heat source to drive the chemical reactions involved in the chemical processes can be closely related. Should $CO_2$ capture technology be installed at a chemical plant, the $CO_2$ captured should be deducted in a higher tier emissions calculation. Respective guidance on the capture and subsequent destruction or use of HFC-23 or other fluorochemicals is given in section 3.10. Any methodology taking into account $CO_2$ capture should consider that $CO_2$ emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately, e.g., in the petrochemical industry, inventory compilers should ensure that the same quantities of $CO_2$ are not double counted. In these cases the total amount of $CO_2$ captured should preferably be reported in the corresponding energy combustion and IPPU categories in proportion to the amounts of $CO_2$ generated in these source categories. The default assumption is that there is no $CO_2$ capture and storage (CCS) taking place. For additional information on $CO_2$ capture and storage refer to Volume 3, Section 1.2.2 and for more details to Volume 2, Section 2.3.4.

# 3.2 AMMONIA PRODUCTION

## 3.2.1 Introduction

Ammonia ($NH_3$) is a major industrial chemical and the most important nitrogenous material produced. Ammonia gas is used directly as a fertiliser, in heat treating, paper pulping, nitric acid and nitrates manufacture, nitric acid ester and nitro compound manufacture, explosives of various types, and as a refrigerant. Amines, amides, and miscellaneous other organic compounds, such as urea, are made from ammonia (Austin, 1984; p.303).

Ammonia production requires a source of nitrogen (N) and hydrogen (H). Nitrogen is obtained from air through liquid air distillation or an oxidative process where air is burnt and the residual nitrogen is recovered. Most ammonia is produced from natural gas (chiefly methane ($CH_4$)), although H can be obtained from other hydrocarbons (coal (indirectly), oil), and water (Hocking, 1998; p.317). A small number of plants continue to use fuel oil as the fuel input and H source in the partial oxidation process. The carbon (C) content of the hydrocarbon is eliminated from the process at the primary steam reforming stage and shift conversion stage through conversion to carbon dioxide ($CO_2$) which is the main potential direct greenhouse gas emission. Plants using hydrogen rather than natural gas to produce ammonia do not release $CO_2$ from the synthesis process.

## 3.2.2 Methodological issues

The chemistry to obtain ammonia feedstocks is similar irrespective of the hydrocarbon used – $CH_4$ or other fossil fuels (Hocking, 1998; p.319). Because the industry uses predominantly natural gas, the following outline of the process and sources of greenhouse emissions ($CO_2$) is based on production using natural gas. Anhydrous ammonia produced by catalytic steam reforming of natural gas (mostly $CH_4$) involves the following reactions with carbon dioxide produced as a by-product.

Primary steam reforming:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Secondary air reforming:

$$CH_4 + \text{air} \rightarrow CO + 2H_2 + 2N_2$$

Overall reaction:

$$0.88CH_4 + 1.26\text{Air} + 1.24H_2O \rightarrow 0.88CO_2 + N_2 + 3H_2$$

Ammonia synthesis:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Secondary reformer process gas shift conversion:

$$CO + H_2O \rightarrow CO_2 + H_2$$

(Hocking, 1998; EFMA, 2000a; EIPPCB, 2004a)

The processes that affect $CO_2$ emissions associated with ammonia production are:

- carbon monoxide shift at two temperatures using iron oxide, copper oxide and/or chromium oxide catalyst for conversion to carbon dioxide;
- carbon dioxide absorption by a scrubber solution of hot potassium carbonate, monoethanolamine (MEA), Sulfinol (alkanol amine and tetrahydrothiophene dioxide) or others;
- methanation of residual $CO_2$ to methane with nickel catalysts to purify the synthesis gas.

The production of ammonia represents a significant non-energy industrial source of $CO_2$ emissions. The primary release of $CO_2$ at plants using the natural gas catalytic steam reforming process occurs during regeneration of the $CO_2$ scrubbing solution with lesser emissions resulting from condensate stripping.

Should $CO_2$ capture technology be installed and used at a plant, it is *good practice* to deduct the $CO_2$ captured in a higher tier emissions calculation. The default assumption is that there is no $CO_2$ capture and storage (CCS). In most cases, methodologies that account for $CO_2$ capture should consider that $CO_2$ emissions captured in the process may be both combustion and process-related. However, in the case of ammonia production no distinction is made between fuel and feedstock emissions with all emissions accounted for in the IPPU Sector. Similarly, all $CO_2$ captured should be accounted for in the IPPU Sector. For additional information on $CO_2$ capture and storage refer to Volume 3, Section 1.2.2 and for more details on capture and storage to Volume 2, Section 2.3.4.

### CARBON DIOXIDE REGENERATOR

After absorption of $CO_2$ from the process gas, the saturated scrubbing solutions (e.g., potassium carbonate, MEA, etc.) are regenerated (i.e., for re-use) with steam stripping and/or boiling to release $CO_2$ from the bicarbonates according to the following reactions:

$$\text{Heat} \quad 2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2$$

$$\text{Heat} \quad (C_2H_5ONH_2)_2 + H_2CO_3 \rightarrow 2C_2H_5ONH_2 + H_2O + CO_2$$

The stripping gas, containing $CO_2$ and other impurities, may be directed to a urea plant (where operational), to a liquid carbonic acid plant, or vented to the atmosphere (Environment Canada, 1987).

### CONDENSATE STRIPPER

Cooling the synthesis gas after low temperature shift conversion forms a condensate containing small quantities of $CO_2$ and other process impurities. The condensate is stripped by steam, whereby the components may be vented to the atmosphere, but normally recycled to the process together with the process stream (U.S. EPA, 1985).

## 3.2.2.1 CHOICE OF METHOD

The choice of method will depend on national circumstances as shown in the decision tree, Figure 3.1. Emissions are estimated from the total fuel requirement, or values derived from estimates of the total fuel requirement, used in the production of $NH_3$. The fuel energy requirement is not accounted for separately. Note that values reported in energy units (or volume units) need to be converted to mass units when estimating emissions.

Methods are classified according to the extent of plant-level data that are available. The Tier 1 method is based on default values and national statistics; the Tier 2 method is based on complete plant-level output data distinguished by fuel input type and process type, and default values; and the Tier 3 method is based entirely on plant-level input data.

The Tier 3 method uses plant-level output data and plant-level fuel input per unit of output to derive the total fuel requirement. Similarly, Tier 3 can also use plant-level emission factors per unit of output provided that the source of these factors is plant-level detailed data on the fuel inputs per unit of output.

### TIER 1 METHOD

The Tier 1 method uses ammonia production to derive emissions as follows:

**EQUATION 3.1**

**$CO_2$ EMISSIONS FROM AMMONIA PRODUCTION – TIER 1**

$$E_{CO2} = AP \bullet FR \bullet CCF \bullet COF \bullet 44/12 - R_{CO2}$$

Where:

$E_{CO2}$ = emissions of $CO_2$, kg

AP = ammonia production, tonnes

FR = fuel requirement per unit of output, GJ/tonne ammonia produced

CCF = carbon content factor of the fuel, kg C/GJ

COF = carbon oxidation factor of the fuel, fraction

$R_{CO2}$ = $CO_2$ recovered for downstream use (urea production), kg

Ammonia production and emission factors can be obtained from national statistics and the emission factor can be determined from default values shown in Table 3.1. Where no information is available on the fuel type and/or process type, it is *good practice* to use the highest emission factor shown in Table 3.1. $CO_2$ recovered for downstream use can be estimated from the quantity of urea produced where $CO_2$ is estimated by multiplying urea production by 44/60, the stoichiometric ratio of $CO_2$ to urea. When a deduction is made for $CO_2$ used in urea production it is *good practice* to ensure that emissions from urea use are included elsewhere in the inventory. If data are not available on urea production it is *good practice* to assume that $CO_2$ recovered is zero.

## TIER 2 METHOD

The initial step is to determine the total fuel requirement. For the Tier 2 method the total fuel requirement for each fuel type is estimated as follows:

**EQUATION 3.2**
**TOTAL FUEL REQUIREMENT FOR AMMONIA PRODUCTION – TIER 2**

$$TFR_i = \sum_j \left( AP_{ij} \bullet FR_{ij} \right)$$

Where:

$TFR_i$ = total fuel requirement for fuel type *i*, GJ

$AP_{ij}$ = ammonia production using fuel type *i* in process type *j*, tonnes

$FR_{ij}$ = fuel requirement per unit of output for fuel type *i* in process type *j*, GJ/tonne ammonia produced

Ammonia production, the fuel type and process type can be obtained from producers, and the fuel requirement per unit of output (FR) can be determined from the default values shown in Table 3.1. Emissions are derived according to Equation 3.3:

**EQUATION 3.3**
**$CO_2$ EMISSIONS FROM AMMONIA PRODUCTION – TIER 2 AND 3**

$$E_{CO2} = \sum_i \left( TFR_i \bullet CCF_i \bullet COF_i \bullet 44/12 \right) - R_{CO2}$$

Where:

$E_{CO2}$ = emissions of $CO_2$, kg

$TFR_i$ = total fuel requirement for fuel type *i*, GJ

$CCF_i$ = carbon content factor of the fuel type *i*, kg C/GJ

$COF_i$ = carbon oxidation factor of the fuel type *i*, fraction

$R_{CO2}$ = $CO_2$ recovered for downstream use (urea production, $CO_2$ capture and storage (CCS)), kg

When using the Tier 2 method, the C content of the fuel (CCF) and C oxidation factor (COF) may be obtained from the default values shown in Table 3.1 or country specific Energy Sector information. Data on $CO_2$ recovered for urea production and CCS should be obtained from producers.

## TIER 3 METHOD

The Tier 3 method requires that the fuel requirement be obtained from producers. The total fuel requirement is the sum of the total fuel requirements reported by each $NH_3$ production plant. That is:

**EQUATION 3.4**
**TOTAL FUEL REQUIREMENT FOR AMMONIA PRODUCTION – TIER 3**

$$TFR_i = \sum_n TFR_{in}$$

Where:

$TFR_i$ = total fuel requirement for fuel type *i*, GJ

$TFR_{in}$ = total fuel requirement for fuel type *i* used by plant *n*, GJ

Once data on total fuel requirements are collected and collated, $CO_2$ emissions can be estimated using Equation 3.3. When using the Tier 3 method, it is *good practice* to obtain information on the CCF and COF from producers or to use country specific energy sector information. As with the Tier 2 method, data on $CO_2$ recovered for urea production (if any) and CCS (if undertaken) should be obtained from producers.

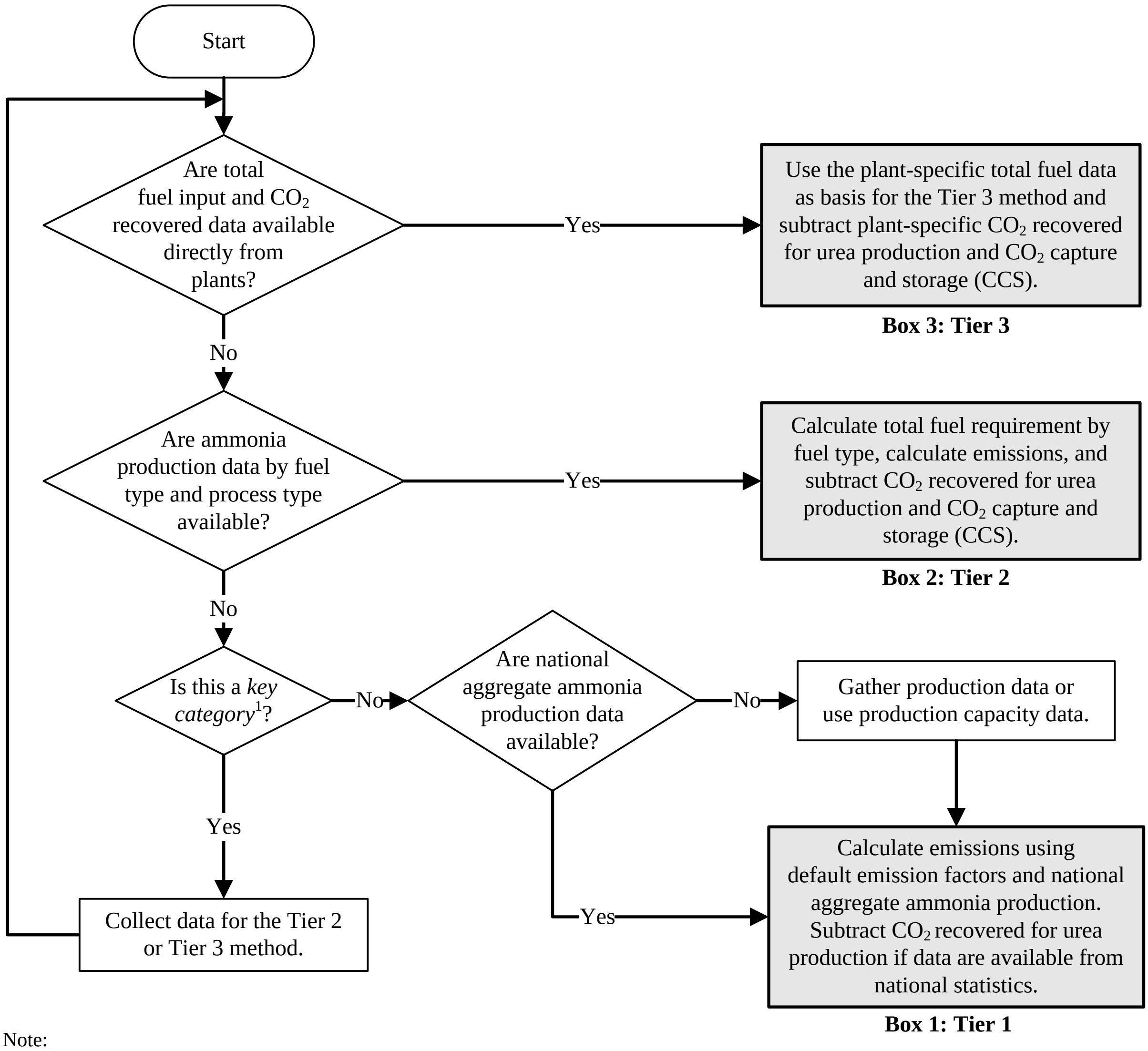
Although data on ammonia production is not used in the calculation under the Tier 3 method it also needs to be collected from producers for reporting purposes.

**BOX 3.1**

**$CO_2$ RECOVERED FOR INDUSTRIAL GAS**

$CO_2$ recovered for industrial gas applications is not accounted for separately as this is a relatively low volume short term use and it is assumed that all industrial gas carbon will be emitted to the atmosphere in the producing country. For example, industrial $CO_2$ used in freezing applications is assumed to be released in the producing country.

**Figure 3.1 Decision tree for estimation of $CO_2$ emissions from ammonia 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.

## 3.2.2.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

If plant-level information is not available, it is *good practice* to use default factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors by production process are provided in Table 3.1, and should be used only in cases where plant-specific data are not available. The default factors are estimates of total fuel requirements per unit of output expressed in energy units. They can be converted to mass units based on C content of the fuel and the C oxidation factor in Volume 2: Energy of these *Guidelines*. These values are also included in Table 3.1 as are emission factors of tonnes of $CO_2$ per tonne of $NH_3$ derived using these values.

For the Tier 1 method it is *good practice* to use the highest total fuel requirement per tonne of ammonia. If no information on fuel type is available, it is *good practice* to use the average value shown in Table 3.1 for partial oxidation.

**TABLE 3.1**
**DEFAULT TOTAL FUEL REQUIREMENTS (FUEL PLUS FEEDSTOCK) AND EMISSION FACTORS FOR AMMONIA PRODUCTION (PER TONNE $NH_3$)**

| **Production Process** | **Total fuel requirement (GJ(NCV)/tonne $NH_3$)**<br>**± Uncertainty (%)** | **Carbon content factor [CCF][1]**<br>**(kg/GJ)** | **Carbon oxidation factor [COF][1]**<br>**(fraction)** | **$CO_2$ emission factor (tonnes $CO_2$ /tonne $NH_3$)** |
|---|---|---|---|---|
| **Modern plants – Europe**<br>Conventional reforming – natural gas | 30.2 (± 6%) | 15.3 | 1 | 1.694 |
| Excess air reforming – natural gas | 29.7 (± 6%) | 15.3 | 1 | 1.666 |
| Autothermal reforming – natural gas | 30.2 (± 6%) | 15.3 | 1 | 1.694 |
| Partial oxidation | 36.0 (± 6%) | 21.0 | 1 | 2.772 |
| **Derived from European average values for specific energy consumption (Mix of modern and older plants)**<br>Average value – natural gas | 37.5 (± 7%) | 15.3 | 1 | 2.104 |
| Average value – partial oxidation | 42.5 (± 7%) | 21.0 | 1 | 3.273 |

NCV – Net Calorific Value.

[1] Values from Energy, Vol. 2, Chapter.1, Tables 1.3 and 1.4..

Source: Adapted from EFMA (2000b; p.21); de Beer, Phylipsen and Bates (2001; p.21); for modern plants default factors can be derived using C content based on natural gas (dry basis) and partial oxidation default factors can be derived using C content based on residual fuel oil.

### TIER 2 METHOD

The total fuel requirement values per unit of output in Table 3.1 can be used in conjunction with data on $NH_3$ production by fuel type and process type, along with either default or country specific data on the C content factor and carbon oxidation factor of the fuels.

### TIER 3 METHOD

Plant-level data on total fuel requirement provide the most rigorous data for calculating $CO_2$ emissions from ammonia production. It is *good practice* to obtain information on the CCF and COF from producers or use country-specific Energy Sector data. The CCF is the key emission factor variable for deriving the quantity of $CO_2$ emissions. Derivation of emissions using plant-level ammonia production depends on an accurate estimate of the fuel requirement per unit of output, along with information on the other variables.

## 3.2.2.3 CHOICE OF ACTIVITY DATA

### TIER 1 METHOD

The Tier 1 method requires data on national production of $NH_3$. If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent) if the inventory compiler can document that utilisation for a year was below capacity. The same capacity utilisation factor should be applied to each year of the time-series.

### TIER 2 METHOD

The Tier 2 method requires plant level data on ammonia production classified by fuel type and production process. In addition, plant level data on $CO_2$ recovered for downstream use or other application are required.

## TIER 3 METHOD

The plant-level activity data required for the Tier 3 approach are total fuel requirement classified by fuel type, $CO_2$ recovered for downstream use or other applications, ammonia production. Although ammonia production is not used in the Tier 3 calculation, collection of all activity data that influence the estimation of emissions allows changes over time and any misreporting of activity data to be identified. Where plant-level fuel requirement per unit of output is used, collection of plant-level production data is required.

### BOX 3.2
### DOUBLE COUNTING

In order to avoid double counting, the total quantities of oil or gas used (fuel plus feedstock) in ammonia production must be subtracted from the quantity reported under energy use in the **Energy Sector**.

In addition, the quantity of $CO_2$ recovered for downstream use in **urea production** must be subtracted from the total quantity of $CO_2$ generated to derive $CO_2$ emitted. Emissions of $CO_2$ from urea use should be accounted for in the corresponding sectors. In particular, emissions from **urea use** as fertiliser should be included in the **Agriculture Forestry and Other Land Use (AFOLU) Sector** (see Volume 4). Emissions from urea use in automobile catalytic converters should be accounted for in the Energy Sector (Volume 2). Emissions from any other chemical products manufactured using $CO_2$ recovered from the process (e.g., emissions from carbonic acid use) are covered by methodology suggested in this section and should not be accounted for in other IPPU sections or in other sectors.

### BOX 3.3
### UREA PRODUCTION

Urea ($CO(NH_2)_2$) (carbonyl amide or carbamide) is an important nitrogenous fertiliser with the highest nitrogen content available in a solid fertiliser. Urea is also used as a protein food supplement for ruminants, in melamine production, as an ingredient in the manufacture of resins, plastics, adhesives, coatings, textile anti-shrink agents, and ion-exchange resins (Austin, 1984; pp.311-312). A developing use is as a reducing agent in selective catalytic reduction of $NO_x$ in exhaust gases originating from diesel or gasoline direct injection engines. Emissions from urea applications should be accounted for in the appropriate application sectors.

Urea production is a downstream process associated with ammonia production plants. The process uses the by-product $CO_2$ stream from an ammonia synthesis plant along with ammonia.

Urea is produced by the reaction of $NH_3$ and $CO_2$ to produce ammonium carbamate which is then dehydrated to urea according to the reactions:

Ammonium carbamate production:

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4$$

Dehydration of ammonium carbamate to urea:

$$NH_2COONH_4 \rightarrow CO(NH_2)_2 + H_2O$$

Assuming complete conversion of $NH_3$ and $CO_2$ to urea, 0.733 tonnes of $CO_2$ are required per tonne of urea produced. Greenhouse gas emissions from modern plants are likely to be small. Excess $NH_3$ and $CO_2$ are contained in the process water which is formed during the reaction. Water treatment is designed to recover these substances from the process water to enable recycling of the gases to the synthesis (EIPPCB, 2004a; p.118). Based on typical inputs for modern plants (EIPPCB, 2004a; p.121), the input values imply that emissions of $CO_2$ range from 2 to 7kg per tonne of urea. For a plant of 1 000 tonnes of urea per day and assuming capacity utilisation of around 90 percent, this would imply annual emissions of $CO_2$ of slightly in excess of 2Gg.

Although emissions from urea production are unlikely to be significant in well-managed modern plants, it is *good practice* to obtain plant-level information on urea production and to account for any significant emissions.

### 3.2.2.4 COMPLETENESS

In countries where only a subset of plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, it may not be possible to report emissions using Tier 3 for all facilities during the transition. Where data for the Tier 3 method are not available for all plants, Tier 2 could be used for the remaining plants. Also, where data for the Tier 2 method are reported by only a subset of plants or where there is a transition from Tier 1 to Tier 2, 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.

Complete coverage for ammonia production requires accounting for all emissions from all sources. $CO_2$ emissions are straightforward. Completeness can be improved by ensuring that emissions of any fugitive $CH_4$ either from the primary reformer stage or catalytic methanation of $CO_2$ process are included. In order to include emissions of $NO_x$, CO and $SO_2$ from the primary reformer stage, see guidance provided in Chapter 7 of Volume 1: General Guidance and Reporting.

### 3.2.2.5 DEVELOPING A CONSISTENT TIME SERIES

$CO_2$ emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available, including plant-specific production data and data for downstream use, for all years in the time series, it will be necessary to consider how current plant data can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.2.3 Uncertainty assessment

### 3.2.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values shown in Table 3.1 are estimates based on data from EFMA (2000a; p.21) and de Beer, Phylipsen and Bates (2001; p.21). In general, default emission factors for gaseous inputs and outputs have higher uncertainties than for solid or liquid inputs and outputs. Mass values for gaseous substances are influenced by temperature and pressure variations and gases are more easily lost through process leaks. It is *good practice* to obtain uncertainty estimates at the plant level, which should be lower than uncertainty values associated with default values. Default emission factor uncertainties reflect variations between plants across different locations.

### 3.2.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. These activity data are likely to be highly accurate (i.e., with uncertainty as low as ±2 percent). This will include uncertainty estimates for fuel use, uncertainty estimates for ammonia production and $CO_2$ recovered. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of ammonia production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±5 percent can be used.

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

### 3.2.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable, if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

### Comparison of emission factors

Inventory compilers should check if the estimated emission factors are within the range of default emission factors provided for the Tier 1 method, and also ensure that the emission factors are consistent with the values derived from analysis of the process chemistry. For example, the $CO_2$ generation rate based on natural gas should not be less than 1.14 tonnes of $CO_2$ per tonne of ammonia produced. If the emission factors are outside of the estimated ranges, it is *good practice* to assess and document the plant-specific conditions that account for the differences.

### Plant-specific data check

The following plant-specific data are required for adequate auditing of emissions estimates:

- Activity data comprising input and output data (input data should be total fuel requirement – fuel energy input plus feedstock input;
- Calculations and estimation method;
- List of assumptions;
- Documentation of any plant-specific measurement method, and measurement results.

If emission measurements from individual plants are collected, inventory compilers should ensure that the measurements were made according to recognised national or international standards. QC procedures in use at the site should be directly referenced and included in the QC plan. If the measurement practices were not consistent with QC standards, the inventory compiler should reconsider the use of these data.

## 3.2.4.2 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, Section 6.11. 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.

Much of the production and process data are considered proprietary by operators, especially where there are only a small number of plants within a country. It is *good practice* to apply appropriate techniques, including aggregation of data, to ensure protection of confidential data. Guidance on managing confidential data is provided in Section 2.2, Volume 1.

# 3.3 NITRIC ACID PRODUCTION

## 3.3.1 Introduction

Nitric acid is used as a raw material mainly in the manufacture of nitrogenous-based fertiliser. Nitric acid may also be used in the production of adipic acid and explosives (e.g., dynamite), for metal etching and in the processing of ferrous metals.

During the production of nitric acid ($HNO_3$), nitrous oxide ($N_2O$) is generated as an unintended by-product of the high temperature catalytic oxidation of ammonia ($NH_3$). The amount of $N_2O$ formed depends, inter alia, on combustion conditions (pressure, temperature), catalyst composition and age, and burner design (EFMA, 2000b; p.15). In addition, some $NO_x$ is produced. Formation of $NO_x$ is most pronounced at start-up and shut-down when the process is least stable (EFMA, 2000b; p.15). $N_2O$ is also generated in other industrial processes that use nitrogen oxides or nitric acid as feedstocks (e.g. the manufacture of caprolactam, glyoxal, and nuclear fuel reprocessing). Nitric acid is a significant source of atmospheric $N_2O$ if not abated and is the major source of $N_2O$ emissions in the chemical industry. While, unlike other emissions from nitric acid production, there are no mature technologies specifically designed for the destruction of $N_2O$ (Perez-Ramirez *et al*., 2003) a number of technologies for $N_2O$ mitigation during nitric acid manufacture have been developed in recent years. Examples include a tail-gas process where both $N_2O$ and NO emissions can be simultaneously reduced (requiring addition of ammonia to the tail-gas), a process-gas option involving direct catalytic decomposition right after the platinum gauzes, and a full-scale catalyst decomposition option.

There are two types of nitric acid plants, single pressure plants and dual pressure plants. In single pressure plants the oxidation and absorption take place at essentially the same pressure, and in dual pressure plants absorption takes place at a higher pressure than the oxidation stage.

## 3.3.2 Methodological issues

Nitric acid production involves three distinct chemical reactions that can be summarised as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Nitrous oxide generation during the production of nitric acid is not well documented. Nitrogen oxidation steps under overall reducing conditions are considered to be potential sources of $N_2O$. Nitric oxide (NO), an intermediate in the production of nitric acid, is also documented to readily decompose to $N_2O$ and nitrogen dioxide ($NO_2$) at high pressures for a temperature range of 30 to 50ºC (Cotton and Wilkinson, 1988).

Perez-Ramirez *et al*. (2003; p.123) specify three intermediate reactions during the oxidation of ammonia that might result in the formation of $N_2O$:

$$NH_3 + O_2 \rightarrow 0.5N_2O + 1.5H_2O$$
$$NH_3 + 4NO \rightarrow 2.5N_2O + 1.5H_2O$$
$$NH_3 + NO + 0.75O_2 \rightarrow N_2O + 1.5H_2O$$

Reactions that lead to the formation of $N_2O$ or $N_2$ are undesirable in that they decrease the conversion efficiency of $NH_3$ and reduce the yield of the desired product, NO (Perez-Ramirez *et al*., 2003; p.124). It is not possible to define a precise relationship between $NH_3$ input and $N_2O$ formation because in general, 'the amount of $N_2O$ formed depends on combustion conditions, catalyst composition and state (age), and burner design' (Perez-Ramirez *et al*., 2003; p.123). Emissions of $N_2O$ depend on the amount generated in the production process and the amount destroyed in any subsequent abatement process. Abatement of $N_2O$ can be intentional, through installation of equipment designed to destroy $N_2O$, or unintentional in systems designed to abate other emissions such as nitrogen oxides ($NO_x$).

Perez-Ramirez *et al*. (2003; p.126) classify abatement approaches as follows and abatement measures associated with each approach are outlined in Table 3.2:

- Primary abatement measures aim at preventing $N_2O$ being formed in the ammonia burner. This involves modification of the ammonia oxidation process and/or catalyst.
- Secondary abatement measures remove $N_2O$ from the valuable intermediate stream, i.e. from the $NO_x$ gases between the ammonia converter and the absorption column. Usually this will mean intervening at the highest temperature, immediately downstream of the ammonia oxidation catalyst.
- Tertiary abatement measures involve treating the tail-gas leaving the absorption column to destroy $N_2O$. The most promising position for $N_2O$ abatement is upstream of the tail-gas expansion turbine.
- Quaternary abatement measures are the pure end-of-pipe solution, where the tail-gas is treated downstream of the expander on its way to the stack.

**TABLE 3.2**
**$N_2O$ ABATEMENT APPROACHES AND ABATEMENT MEASURES**

| Abatement approaches | Abatement measures |
|---|---|
| Primary abatement | • Optimal oxidation process<br>• Modification of platinum-rhodium gauzes<br>• Oxide-based combustion catalysts |
| Secondary abatement | • Homogeneous decomposition in the burner<br>• Catalytic decomposition in the burner (process gas catalytic decomposition)<br>• Catalytic decomposition downstream of the burner (before the absorption column) |
| Tertiary abatement | • Thermal decomposition<br>• Non-selective catalytic reduction (NSCR)<br>• Tail-gas catalytic decomposition<br>• Selective catalytic reduction (SCR) |
| Quaternary abatement | • Non-selective catalytic reduction (NSCR)<br>• Catalytic decomposition<br>• Selective catalytic reduction (SCR) |

Source: Adapted from Perez-Ramirez *et al*. (2003).

The abatement achieved will depend on the technology implemented with tertiary measures stated as, ‘enabling the achievement of high levels of $N_2O$ removal (>99 percent)’ (Perez-Ramirez *et al*., 2003; p.136). Additionally, it is noted that although NSCR is a proven technology for $N_2O$ reduction, the replacement of NSCR systems by SCR systems for $NO_x$ reduction has a negative side-effect on its application for $N_2O$ reduction. Further, ‘NSCR is most likely not a viable option anymore, due to the high fuel consumption levels and high secondary emissions’ (Perez-Ramirez *et al*., 2003; p.137).

Future adoption of technologies will depend on cost-effectiveness and the stringency of any emissions regulation. More cost-effective options are available for new plants than for existing plants. Tail-gas options are appealing since they do not interfere with the process. Direct $N_2O$ decomposition is a very attractive and cost effective option in plants with tail-gas temperatures greater than 723 K. However, two-thirds of the nitric acid plants in Europe have low-temperature tail-gases. To this end, preheating or using reductants (light hydrocarbons or ammonia) is required, making the after-treatment prohibitive. The most elegant and cost-effective option is the in process-gas catalytic decomposition, located in the heart of the plant (the ammonia burner). Concerns with this abatement option are chemical and mechanical stability of the catalyst as well as the possible NO loss. Several catalyst manufacturers and nitric acid producers have addressed this problem and catalysts are in the early stages of commercialisation. Advantageously, and contrary to the tail-gas option, this technology can be retrospectively applied to all existing plants. Further discussion of options is provided in Perez-Ramirez *et al*. (2003).

### 3.3.2.1 CHOICE OF METHOD

The choice of *good practice* method depends on national circumstances. The decision tree in Figure 3.2 describes *good practice* in adapting the methods to national circumstances. Emissions can be estimated from:

- continuous emissions monitoring (CEM) where emissions are directly measured at all times;

- periodic emissions monitoring that is undertaken over a period(s) that is reflective of the usual pattern of operation of the plant to derive an emission factor that is multiplied by output (100 percent $HNO_3$) to derive emissions;
- irregular sampling to derive an emission factor that is multiplied by output (100 percent $HNO_3$) to derive emissions;
- by multiplying a default emission factor by output (100 percent $HNO_3$).

Methods are classified according to the extent of plant-level data that are available. Both Tier 2 and Tier 3 are based on plant-level activity data.

### TIER 1 METHOD

Emissions are estimated as follows:

**EQUATION 3.5**
**$N_2O$ EMISSIONS FROM NITRIC ACID PRODUCTION – TIER 1**

$$E_{N2O} = EF \bullet NAP$$

Where:

$E_{N2O}$ = $N_2O$ emissions, kg

EF = $N_2O$ emission factor (default), kg $N_2O$/tonne nitric acid produced

NAP = nitric acid production, tonnes

When applying the Tier 1 method it is *good practice* to assume that there is no abatement of $N_2O$ emissions and to use the highest default emission factor based on technology type shown in Table 3.3.

### TIER 2 METHOD

There are a large number of nitric acid plants (estimates range from 255 to 600 plants according to Choe *et al.*, 1993; Bockman and Granli, 1994) with substantial variations in the $N_2O$ generation factors among plant types. Consequently, default factors may be needed more often for nitric acid $N_2O$ emissions estimates. Where default values are used to estimate emissions from nitric acid production, it is *good practice* to categorise plants according to type and to use an appropriate $N_2O$ generation factor.

The Tier 2 method uses plant-level production data disaggregated by technology type and default emission factors classified by technology type. Emissions are calculated as follows:

**EQUATION 3.6**
**$N_2O$ EMISSIONS FROM NITRIC ACID PRODUCTION – TIER 2**

$$E_{N2O} = \sum_{i,j} \left[ EF_i \bullet NAP_i \bullet \left(1 - DF_j \bullet ASUF_j\right)\right]$$

Where:

$E_{N2O}$ = emissions of $N_2O$, kg

$EF_i$ = $N_2O$ emission factor for technology type *i*, kg $N_2O$/tonne nitric acid produced

$NAP_i$ = nitric acid production from technology type *i*, tonnes

$DF_j$ = destruction factor for abatement technology type *j*, fraction

$ASUF_j$ = abatement system utilisation factor for abatement technology type *j*, fraction

Note that the default emission factors shown in Table 3.3 include the impact on emissions of abatement technology where relevant. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

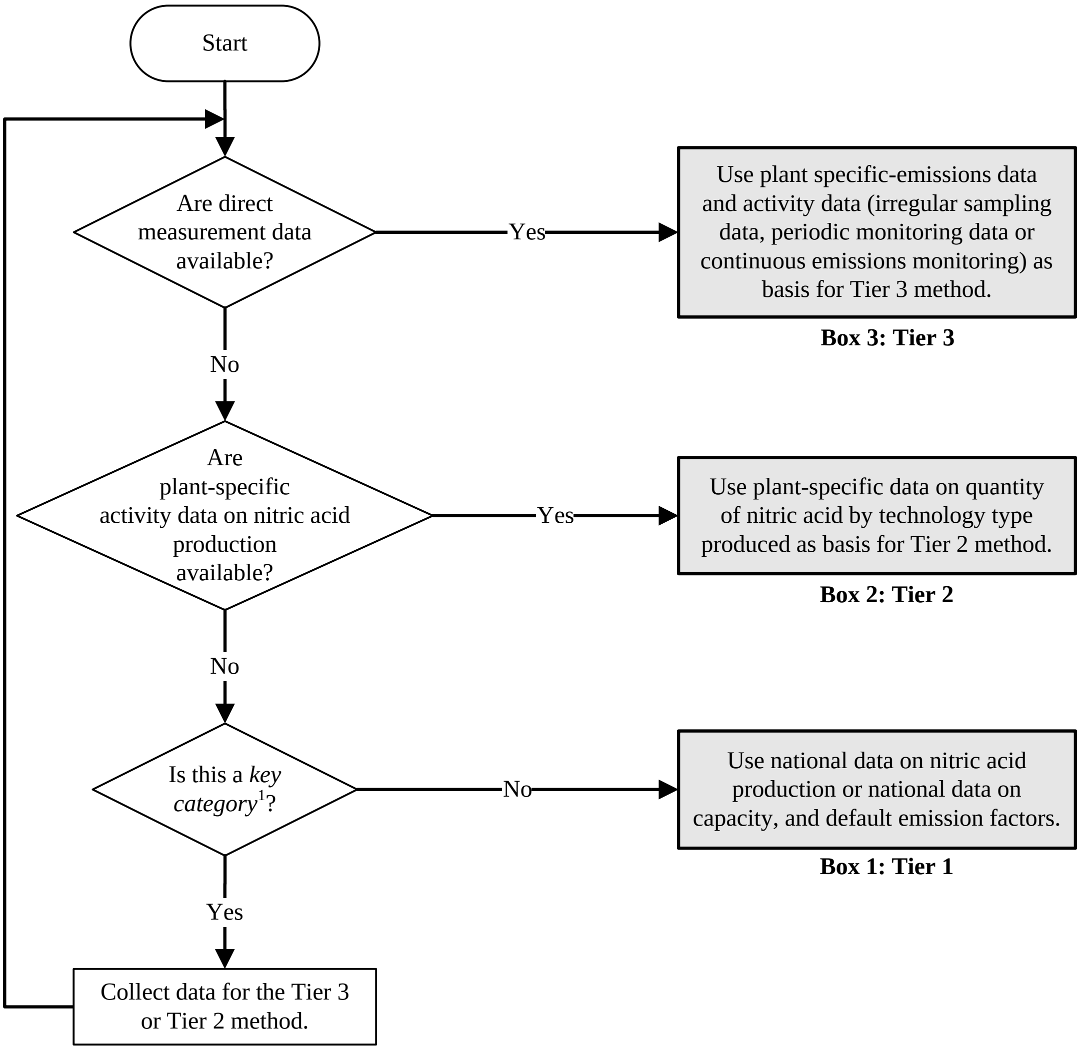
The basic equation for estimating $N_2O$ emissions includes additional terms that recognise the potential future use of $N_2O$ abatement technologies. The $N_2O$ destruction factor has to be multiplied by an abatement system utilisation factor in order to account for any down-time of the emission abatement equipment (i.e., time the equipment is not operating).

### TIER 3 METHOD – DIRECT MEASUREMENT

While the tier 2 approach applies technology specific emission factors reflecting the national technology mix. Tier 3 is based on real measurement data (e.g., CEMS). Plant-level production data disaggregated by technology type and plant level emission factors obtained from direct measurement of emissions. These may be derived from irregular sampling of emissions of $N_2O$ or periodic emissions monitoring of $N_2O$ undertaken over a period(s) that reflects the usual pattern of operation of the plant. Emissions can be derived using Equation 3.6.

Alternatively, the Tier 3 method uses the results of continuous emissions monitoring (CEM), although it is noted that most plants are unlikely to employ CEM due to the resource costs. Where CEM is employed, emissions can be estimated based on the sum of measured $N_2O$ emissions derived from the concentration of $N_2O$ in monitored emissions for each recorded monitoring interval.

**Figure 3.2** **Decision tree for estimation of $N_2O$ emissions from nitric acid 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.

## 3.3.2.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

It is *good practice* to use the highest emission factor based on the technology type shown in Table 3.3 and to assume that there is no abatement of $N_2O$ emissions.

### TIER 2 METHOD

If plant-level factors are not available, it is *good practice* to use default factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors in Table 3.3 should be used only in cases where plant-specific measurements are not available.

Table 3.3 includes emission factors for $N_2O$, and associated uncertainties. The factors listed in Table 3.3 for plants using non-selective catalytic reduction (NSCR), (a $NO_x$ abatement technology that can also be managed to abate $N_2O$), already incorporate the effect of $N_2O$ abatement measures. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

### TIER 3 METHOD

Plant measurements provide the most rigorous data for calculating net emissions (i.e., $N_2O$ generation and destruction factors). Monitoring $N_2O$ emissions from nitric acid production is practical because these are point sources and there are a finite number of production plants. Given currently available technology, instrumentation for sampling and monitoring emission rates do not limit precision or accuracy of the overall measurement. Usually sampling frequency and timing is sufficient to avoid systematic errors and to achieve the desired level of accuracy.

As a general rule, it is *good practice* to conduct sampling and analysis whenever a plant makes any significant process changes that would affect the generation rate of $N_2O$, and sufficiently often otherwise to ensure that operating conditions are constant. In addition, plant operators should be consulted annually to determine the specific destruction technologies employed and confirm their use, since technologies may change over time. Precise measurement of the emissions rate and abatement efficiencies requires measurement of both the exit stream and the uncontrolled stream. Where measurement data are available only on the exit stream, *good practice* is to base emissions on these data. In this case, any available estimates of abatement efficiency should be provided only for information purposes and are not used to calculate emissions.

**TABLE 3.3**
**DEFAULT FACTORS FOR NITRIC ACID PRODUCTION**

| **Production Process** | **$N_2O$ Emission Factor (relating to 100 percent pure acid)** |
|---|---|
| Plants with NSCR[a] (all processes) | 2 kg $N_2O$/tonne nitric acid ±10% |
| Plants with process-integrated or tailgas $N_2O$ destruction | 2.5 kg $N_2O$/tonne nitric acid ±10% |
| Atmospheric pressure plants (low pressure) | 5 kg $N_2O$/tonne nitric acid ±10% |
| Medium pressure combustion plants | 7 kg $N_2O$/tonne nitric acid ±20% |
| High pressure plants | 9 kg $N_2O$/tonne nitric acid ±40% |

[a] Non-Selective Catalytic Reduction (NSCR).

Source: van Balken (2005).

## 3.3.2.3 CHOICE OF ACTIVITY DATA

It is *good practice* to compile production data at a level of detail that allows the use of a Tier 2 or Tier 3 method, where possible. Activity data should be based on 100 percent $HNO_3$, - it is *good practice* to ensure that all production data reported are for 100 percent $HNO_3$.

### TIER 1 METHOD

The Tier 1 method requires data on national production of nitric acid. National nitric acid statistics may omit a substantial proportion of the national total (see details in Section 3.3.2.4 Completeness). If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

### TIER 2 METHOD

The Tier 2 method requires plant-level production data disaggregated by technology type and abatement system type. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Typical plant-level production data is assumed to have an uncertainty of ±2 percent due to the economic value of having accurate information.

#### TIER 3 METHOD

As with the Tier 2 method, plant-level production data disaggregated by technology and abatement system type are required. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Although production data are not used in the estimation of emissions where the estimate is based on CEM, these data should be collected and reported to ensure that changes in variables that influence emissions can be monitored over time. Typical plant-level production data is assumed to have an uncertainty of ±2 percent due to the economic value of having accurate information.

### 3.3.2.4 COMPLETENESS

Nationally compiled nitric acid production statistics could underestimate production. Studies that compare global statistics compiled from national data on nitric acid production with industry estimates of global production suggest that the national statistics account for only 50 to 70 percent of the total (Bouwman *et al*., 1995; Olivier, 1999). This is probably due to nitric acid production that is integrated as part of larger production processes, where the nitric acid never enters into commerce and is not counted in the national statistics. It is *good practice* to account for these sources by methods such as identifying them through national registries of $NO_x$ emissions, another unintended by-product of nitric acid production.

NSCR and SCR systems designed to abate $N_2O$ can give rise to additional emissions of CO, $CO_2$ and hydrocarbons ($CH_4$ and NMVOCs). These emissions will depend on the hydrocarbon reducing agent that is used (methane ($CH_4$), propane ($C_3H_8$), propene ($C_3H_6$), LPG). Emissions can be estimated based on the quantity of reducing agent used and the completeness of combustion. Plant-level information will be required to enable emissions estimation. Over time default values could be developed as more information becomes available, however, at present there are no default values. Methods for estimating these emissions are not included in these *Guidelines,* however, inventory compilers are encouraged to investigate these emission sources and to develop appropriate methodologies.

There will usually be few nitric acid plants in a country, and it is suggested that emissions are calculated from plant specific data. In countries where only a subset of plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, it may not be possible to report emissions using Tier 3 for all facilities during the transition. Where data for the Tier 3 method are not available for all plants, Tier 2 could be used for the remaining plants. Also, where data for the Tier 2 method are reported by only a subset of plants or where there is a transition from Tier 1 to Tier 2, 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.

### 3.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

$N_2O$ emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, it will be necessary to consider how current plant measurements can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.3.3 Uncertainty assessment

### 3.3.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values shown in Table 3.3 are estimates based on expert judgment. In general, default emission factors for gaseous substances have higher uncertainties because mass values for gaseous substances are influenced by temperature and pressure variations and gases are more easily lost through process leaks. The default values for nitric acid production have a relatively high level of uncertainty for two reasons. First, $N_2O$ may be generated in the gauze reactor section of nitric acid production as an unintended reaction by-product (Cook, 1999). Second, the exhaust gas may or may not be treated for $NO_x$ control, and the $NO_x$

abatement system may or may not reduce (or may even increase) the $N_2O$ concentration of the treated gas[1]. It is *good practice* to obtain uncertainty estimates at the plant-level which should be lower than uncertainty values associated with default values.

### 3.3.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of nitric acid production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±2 percent can be used. To reduce uncertainty it is *good practice* to ensure that all activity data are for 100 percent $HNO_3$.

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

### 3.3.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

**Comparison of emissions estimates using different approaches**

If emissions are calculated using data from individual nitric acid plants (bottom-up approach), inventory compilers should compare the estimate to emissions calculated using national production data (top-down approach). They should record the results and investigate any unexplained discrepancies.

Since industrial $N_2O$ source categories are relatively small compared to other anthropogenic and natural sources, it is not feasible to compare emissions with measured trends in atmospheric $N_2O$ concentrations.

**Plant-level data**

Inventory compilers should archive sufficient information to allow an independent review of the time series of emissions beginning in the base year, and to explain trends in emissions when making historical comparisons. This is particularly important in cases where recalculations are necessary, for example, when an inventory compiler changes from using default values to actual values determined at the plant level.

**Revision of direct emission measurements**

If plant-level $N_2O$ measurements are available, inventory compilers should confirm that internationally recognised, standard methods were used. If the measurement practices fail this criterion, then they should evaluate the use of these emissions data. In addition, they should reconsider the uncertainty estimates in light of the QA/QC results.

Inventory compilers should compare plant-based factors to the IPCC defaults to ensure that the plant-specific factors are reasonable. They should explain and document any differences between plant-specific factors and default factors, particularly any differences in plant characteristics that might lead to these differences.

### 3.3.4.2 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, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

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[1] In some cases, processes designed to reduce $NO_x$ emissions may result in additional $N_2O$ generation. Increased $N_2O$ concentrations due to $NO_x$ abatement technology have been measured at various power plants that employ non-catalytic reduction for $NO_x$ (Cook, 1999). From at least one nitric acid plant, it is known that $NO_x$ control resulted in increased $N_2O$ emissions (Burtscher, 1999).

- Description of the method used;
- Number of nitric acid plants;
- Emission factors;
- Production data;
- Production capacity;
- Number of plants using abatement technology;
- Type of abatement technology, destruction efficiency, and utilisation;
- Any other assumptions.

Plant operators should supply this information to the inventory compiler for compilation, and also archive the information at the site. Plant operators should also log and archive the measurement frequencies and instrumental calibration records where actual plant measurements are made.

Where there are only one or two producers in a country, activity data may be considered confidential. In this case, operators and the inventory compiler should determine the level of aggregation at which information can be reported while still protecting confidentiality. Detailed information including instrumentation records should still be archived at the plant level.

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.

# 3.4 ADIPIC ACID PRODUCTION

## 3.4.1 Introduction

Adipic acid is used in the manufacture of a large number of products including synthetic fibres, coatings, plastics, urethane foams, elastomers and synthetic lubricants. The production of Nylon 6.6 accounts for the bulk of adipic acid use. As noted by Hocking (1998; p.657), ‘A large fraction of this consumption is direct, as adipic acid in the production of nylon 6.6, but a substantial fraction of the adipic acid is further processed to give hexamethylene diamine, the other monomer required. A further small fraction of the adipic acid is converted into di-octyl (di-2-ethylhexyl) or di-hexyl esters for use as plasticizers in flexible grades of PVC, etc., or as a high boiling point component of synthetic motor oils’.

## 3.4.2 Methodological issues

Adipic acid is a dicarboxylic acid manufactured from a cyclohexanone/cyclohexanol mixture which is oxidised by nitric acid in the presence of a catalyst to form adipic acid. Nitrous oxide ($N_2O$) is generated as an unintended by-product of the nitric acid oxidation stage:

$$\begin{gathered}(CH_2)_5CO \text{ (Cyclohexanone)} + (CH_2)_5CHOH \text{ (Cyclohexanol)} + wHNO_3 \rightarrow \\ HOOC(CH_2)_4COOH \text{ (Adipic Acid)} + xN_2O + yH_2O\end{gathered}$$

Adipic acid is a significant source of atmospheric $N_2O$ if not abated. Emissions of $N_2O$ depend on the amount generated in the production process and the amount destroyed in any subsequent abatement process. Abatement of $N_2O$ can be intentional through installation of equipment specifically designed to destroy $N_2O$ in adipic acid plants. Adipic acid production also results in the emissions of NMVOC, CO and $NO_x$. Process emissions from the production of adipic acid vary substantially with the level of emission control employed.

### 3.4.2.1 CHOICE OF METHOD

The decision tree in Figure 3.3 describes *good practice* in adapting the methods to national circumstances. Emissions can be estimated from continuous emissions monitoring (CEM) where emissions are directly measured at all times, periodic emissions monitoring that is undertaken over a period(s) that is reflective of the usual pattern of operation of the plant to derive an emission factor that is multiplied by output to derive emissions, irregular sampling to derive an emission factor that is multiplied by output to derive emissions, or by multiplying a default emission factor by output.

Methods are classified according to the extent of plant-level data that are available. Both Tier 2 and Tier 3 require plant-level activity data.

#### TIER 1 METHOD

Emissions are estimated as follows:

**EQUATION 3.7**
**$N_2O$ EMISSIONS FROM ADIPIC ACID PRODUCTION – TIER 1**

$$E_{N2O} = EF \bullet AAP$$

Where:

$E_{N2O}$ = $N_2O$ emissions, kg

EF = $N_2O$ emission factor (default), kg $N_2O$/tonne adipic acid produced

AAP = adipic acid production, tonnes

When applying the Tier 1 method it is *good practice* to assume that there is no abatement of $N_2O$ emissions and to use the highest default emission factor shown in Table 3.4.

### TIER 2 METHOD

The Tier 2 method uses plant-level production data and default emission factors. Where default values are used to estimate emissions, it is *good practice* to categorise plants according to the abatement technology type employed and the utilisation factor of the abatement technology. Emissions are calculated as follows:

**EQUATION 3.8**
**$N_2O$ EMISSIONS FROM ADIPIC ACID PRODUCTION – TIER 2**

$$E_{N2O} = \sum_{i,j} \left[ EF_i \bullet AAP_i \bullet \left( 1 - DF_j \bullet ASUF_j \right) \right]$$

Where:

$E_{N2O}$ = emissions of $N_2O$, kg

$EF_i$ = $N_2O$ emission factor for technology type *i*, kg $N_2O$/tonne adipic acid produced

$AAP_i$ = adipic acid production from technology type *i*, tonnes

$DF_j$ = destruction factor for abatement technology type *j*, fraction

$ASUF_j$ = abatement system utilisation factor for abatement technology type *j*, fraction

The basic equation for estimating $N_2O$ emissions includes additional terms that recognise the use of $N_2O$ abatement technologies. The $N_2O$ destruction factor has to be multiplied by an abatement system utilisation factor in order to account for any down-time of the emission abatement equipment (i.e., time the equipment is not operating).

To achieve the highest accuracy, *good practice* is to apply this equation at the plant-level using $N_2O$ generation and destruction factors developed from plant-specific measurement data. In this case, the national total is equal to the sum of plant totals. Where plant-level information is not available, *good practice* provides default $N_2O$ generation factors and destruction factors as shown in Table 3.4, Default Factors for Adipic Acid Production, based on abatement technologies implemented. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

### TIER 3 METHOD – DIRECT MEASUREMENT

The Tier 3 method uses plant level production data and plant-level emission factors obtained from direct measurement of emissions. These may be derived from irregular sampling of emissions of $N_2O$ or periodic emissions monitoring of $N_2O$ undertaken over a period(s) that reflects the usual pattern of operation of the plant. Emissions can be derived using Equation 3.8. To achieve the highest accuracy, *good practice* is to apply this equation at the plant-level using $N_2O$ generation and destruction factors developed from plant-specific measurement data where relevant. Given the relatively small number of adipic acid plants (about 23 globally, Choe *et al.*, 1993), obtaining plant-specific information requires few additional resources.

Alternatively, the Tier 3 method uses the results of continuous emissions monitoring (CEM), although it is noted that most plants are unlikely to employ CEM due to the resource costs. Where CEM is employed, emissions can be estimated based on the sum of measured $N_2O$ emissions derived from the concentration of $N_2O$ in monitored emissions for each recorded monitoring interval.

## 3.4.2.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

It is *good practice* to use the default emission factor shown in Table 3.4 and to assume that there is no abatement of $N_2O$ emissions.

### TIER 2 METHOD

If plant-level factors are not available, it is *good practice* to use default factors. The Tier 2 method is based on default emission factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors in Table 3.4 should be used only in cases where plant-specific measurements are not available.

Also included in Table 3.4 are default $N_2O$ destruction factors for commonly used abatement technologies, and associated uncertainties. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year. Failure to determine if abatement technologies are being used can result in overestimation of emissions. Determination of the appropriate values requires that plants be classified according to the abatement technology implemented..

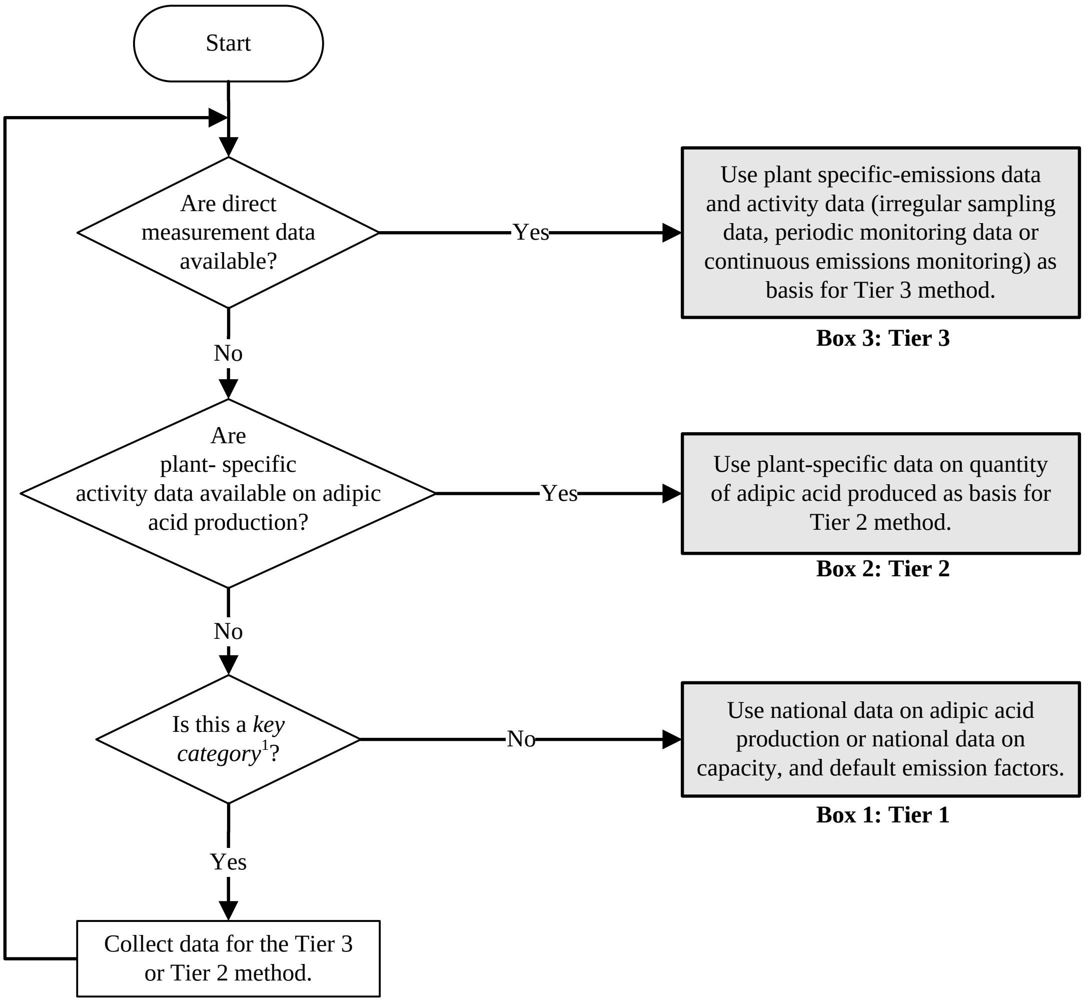
### TIER 3 METHOD

The Tier 3 method requires plant measurements. If the $N_2O$ abatement system is in use, plant measurements provide the most rigorous data for calculating net emissions (i.e., $N_2O$ generation and destruction factors). Monitoring $N_2O$ emissions from adipic acid production is practical because these are point sources and there are a finite number of production plants. Given currently available technology, instrumentation for sampling and monitoring emission rates do not limit precision or accuracy of the overall measurement. Usually sampling frequency and timing is sufficient to avoid systematic errors and to achieve the desired level of accuracy.

Where the $N_2O$ abatement system is not in use, a plant-specific emission factor can be obtained from periodic monitoring of emissions which is multiplied by the production level to estimate plant-level emissions.

As a general rule, it is *good practice* to conduct sampling and analysis whenever a plant makes any significant process changes that would affect the generation rate of $N_2O$, and sufficiently often otherwise to ensure that operating conditions are constant. In addition, plant operators should be consulted annually to determine the specific destruction technologies employed and confirm their use, since technologies may change over time. Precise measurement of the emissions rate and abatement efficiencies requires measurement of both the exit stream and the uncontrolled stream. Where measurement data are available only on the exit stream, *good practice* is to base emissions on these data. In this case, any available estimates of abatement efficiency should be provided only for information purposes and not used to calculate emissions.

**Figure 3.3 Decision tree for estimation of $N_2O$ emissions from adipic acid 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.

**TABLE 3.4**
**DEFAULT FACTORS FOR ADIPIC ACID PRODUCTION**

| **Production Process** | **$N_2O$ Generation Factor**[a,d] | **Uncertainty Estimate** |
|---|---|---|
| Nitric Acid Oxidation | 300 kg/tonne adipic acid (uncontrolled) | ± 10% (based on expert judgement). The range of 300 kg ± 10% encompasses the variability from pure ketone to pure alcohol feedstocks, with most manufacturers somewhere in the middle.[a] |
| **Abatement Technology** | **$N_2O$ Destruction Factor**[b] | **Uncertainty Estimate** |
| Catalytic Destruction | 92.5% | 90-95% (based on expert judgement). Manufacturers known to employ this technology include: BASF (Scott, 1998), and DuPont (Reimer, 1999b). |
| Thermal Destruction | 98.5% | 98-99% (based on expert judgement). Manufacturers known to employ this technology include: Asahi, DuPont, Bayer, and Solutia (Scott, 1998). |
| Recycle to Nitric Acid | 98.5% | 98-99% (based on expert judgement). Manufacturers known to employ this technology include: Alsachemie (Scott, 1998). |
| Recycle to feedstock for Adipic Acid | 94% | 90-98% (based on expert judgement). Solutia implemented this technology around 2002. |
| **Abatement System** | **Utilisation Factor**[d] | **Uncertainty Estimate** |
| Catalytic Destruction | 89% | 80-98% (based on expert judgement)[c]. |
| Thermal Destruction | 97% | 95-99% (based on expert judgement)[c]. |
| Recycle to Nitric Acid | 94% | 90-98% (based on expert judgement)[c]. |
| Recycle to Adipic Acid | 89% | 80-98% (based on expert judgement)[c]. |

[a] With regard to a value from the Japan Environment Agency (1995) (282 kg $N_2O$/tonne adipic acid), it is believed that this manufacturer uses oxidation of pure cyclohexanol (alcohol), instead of a ketone-alcohol mixture (Reimer *et al*., 1999). This is the only plant known to use this method.

[b] The destruction factor (that represents the technology abatement efficiency) should be multiplied by an abatement system utility factor.

[c] Note that these default values are based on expert judgement and not industry-supplied data or plant-specific measurements. In the first 1-5 years of the abatement technology implementation, the utilisation factor tends to be at the lower end of the range. Lower utility of the equipment typically results because of the need to learn how to operate the abatement system and because more maintenance problems occur during the initial phase. After 1-5 years, the operating experience improves and the utilisation factor would tend to be at the high end of the range.

Source:
[d] Thiemans and Trogler (1991).
[e] Reimer (1999b).

### 3.4.2.3 CHOICE OF ACTIVITY DATA

It is *good practice* to compile production data at a level of detail that allows the use of a Tier 2 or Tier 3 method.

#### TIER 1 METHOD

The Tier 1 method requires data on national production of adipic acid. If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

#### TIER 2 METHOD

The Tier 2 method requires plant-level production data disaggregated by abatement technology type. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Typical plant-level production data is accurate to ±2 percent due to the economic value of having accurate information.

#### TIER 3 METHOD

As with the Tier 2 method, plant-level production data disaggregated by abatement technology type are required when emissions estimates are derived using data from irregular or periodic sampling of emissions. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Although production is not used in the estimation of emissions where the estimate is based on CEM, these data should be collected and reported to ensure that changes in variables that influence emissions can be monitored over time. Typical plant-level production data is accurate to ±2 percent due to the economic value of having accurate information.

### 3.4.2.4 COMPLETENESS

Complete coverage for the adipic acid source category is straightforward because of the small number of readily identifiable plants.

### 3.4.2.5 DEVELOPING A CONSISTENT TIME SERIES

$N_2O$ emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, it will be necessary to consider how current plant measurements can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.4.3 Uncertainty assessment

### 3.4.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values shown in Table 3.4 are estimates based on expert judgement. In general, adipic acid default emission factors are relatively certain because they are derived from the stoichiometry of an intended chemical reaction (nitric acid oxidation) and $N_2O$-specific abatement systems. The uncertainty in the emission factor for adipic acid represents a variability in $N_2O$ generation due to differences in the composition of the cyclohexanone and cyclohexanol feedstock (i.e. ketone and alcohol) that are used by different manufacturers. Higher ketone content results in increased $N_2O$ generation, whereas higher alcohol content results in less $N_2O$ generation (Reimer, 1999a). Dependent on the process, based on nitric acid ($HNO_3$) consumption an individual plant should be able to determine the production of $N_2O$ within 1 percent. Uncertainties for the default values are shown in Table 3.4.

### 3.4.3.2 ACTIVITY DATA UNCERTAINTIES

Potential $N_2O$ emissions per metric tonne produced are far greater for adipic acid production than for other industrial sources of $N_2O$. Measurements obtained from a properly maintained and calibrated monitoring system can determine emissions using Equation 3.8 to within ±5 percent at the 95 percent confidence level. Given the small number of adipic acid plants, the uncertainty in national production data (Tier 1) is the same as for plant-level data, namely, ±2 percent.

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

### 3.4.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1 and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this source category are outlined below.

### Comparison of emissions estimates using different approaches

If emissions are calculated using data from individual adipic acid plants (bottom-up approach), inventory compilers should compare the estimate to emissions calculated using national production data (top-down approach). They should record the results and investigate any unexplained discrepancies.

Since industrial $N_2O$ source categories are relatively small compared to other anthropogenic and natural sources, it is not feasible to compare emissions with measured trends in atmospheric $N_2O$ concentrations.

### Plant-level data

Inventory compilers should archive sufficient information to allow an independent review of the time series of emissions beginning in the base year, and to explain trends in emissions when making historical comparisons. This is particularly important in cases where recalculations are necessary, for example, when an inventory compiler changes from using default values to actual values determined at the plant level.

### Revision of direct emission measurements

If plant-level $N_2O$ measurements are available, it is suggested that inventory compilers confirm that internationally recognised, standard methods were used. If the measurement practices fail this criterion, then they should evaluate the use of these emissions data. In addition, they should reconsider the uncertainty estimates in light of the QA/QC results.

Inventory compilers are encouraged to compare plant-based factors to the IPCC defaults to ensure that the plant-specific factors are reasonable. They should explain and document any differences between plant-specific factors and default factors, particularly any differences in plant characteristics that might lead to these differences.

## 3.4.4.2 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, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

- Description of the method used;
- Number of adipic acid plants;
- Emission factors;
- Production data;
- Production capacity;
- Number of plants using abatement technology;
- Type of abatement technology, destruction efficiency, and utilisation;
- Any other assumptions.

Plant operators should supply this information to the inventory compiler for compilation, and also archive the information at the site. Plant operators should also log and archive the measurement frequencies and instrumental calibration records where actual plant measurements are made.

Where there are only one or two producers in a country, as could often be the case for adipic acid production, activity data may be considered confidential. In this case, operators and the inventory compiler should determine the level of aggregation at which information can be reported while still protecting confidentiality. Detailed information including instrumentation records should still be archived at the plant level.

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.

# 3.5 CAPROLACTAM, GLYOXAL AND GLYOXYLIC ACID PRODUCTION

## 3.5.1 Introduction

This section addresses the production of three chemicals - caprolactam, glyoxal, and glyoxylic acid - that are potentially important sources of nitrous oxide ($N_2O$) emissions in the countries in which the chemicals are produced. The methodology for caprolactam is discussed in detail and is suitable for application to estimation of emissions from glyoxal and glyoxylic acid. In Section 3.5.3, the production processes for glyoxal and glyoxylic acid that give rise to emissions of $N_2O$ are outlined. Default generation factors, destruction factors, and emission factors are provided based on information from Clariant (France) (Babusiaux, 2005).

## 3.5.2 Caprolactam

Almost all of the annual production of caprolactam ($C_6H_{11}NO$) is consumed as the monomer for nylon-6 fibres and plastics (Kirk-Othmer, 1999; p.310), with a substantial proportion of the fibre used in carpet manufacturing. All commercial processes for the manufacture of caprolactam are based on either toluene or benzene.

### 3.5.2.1 METHODOLOGICAL ISSUES

Where caprolactam is produced from benzene, the main process, the benzene is hydrogenated to cyclohexane which is then oxidised to produce cyclohexanone ($C_6H_{10}O$). The classical route (Raschig process) and basic reaction equations for production from cyclohexanone are (Reimschuessel, 1977; p.83: Lowenheim and Moran, 1975; p. 201):

Oxidation of $NH_3$ to $NO/NO_2$
↓
$NH_3$ reacted with $CO_2/H_2O$ to yield ammonium carbonate $(NH_4)_2CO_3$
↓
$(NH_4)_2CO_3$ reacted with $NO/NO_2$ (from $NH_3$ oxidation) to yield ammonium nitrite ($NH_4NO_2$)
↓
$NH_3$ reacted with $SO_2/H_2O$ to yield ammonium bisulphite ($NH_4HSO_3$)
↓
$NH_4NO_2$ and $NH_4HSO_3$ reacted to yield hydroxylamine disulphonate ($NOH(SO_3NH_4)_2$)
↓
$NOH(SO_3NH_4)_2$ hydrolised to yield hydroxylamine sulphate ($(NH_2OH)_2.H_2SO_4$) and ammonium sulphate ($(NH_4)_2SO_4$)
↓
Cyclohexanone reaction:

$$C_6H_{10}O + \frac{1}{2}(NH_2OH)_2.H_2SO_4\ (+NH_3 \text{ and } H_2SO_4) \rightarrow C_6H_{10}NOH + (NH_4)_2SO_4 + H_2O$$

Beckmann rearrangement:

$$C_6H_{10}NOH\ (+H_2SO_4 \text{ and } SO_2) \rightarrow C_6H_{11}NO.H_2SO_4\ (+4NH_3 \text{ and } H_2O) \rightarrow C_6H_{11}NO + 2(NH_4)_2SO_4$$

Lowenheim and Moran (1975; p. 202) summarise the Raschig production process as follows. Caprolactam is produced via Beckmann rearrangement (conversion of a ketone oxime into an amide, usually using sulphuric acid as a catalyst) by the addition of hydroxylamine sulphate to cyclohexanone. Hydroxylamine sulphate is produced from ammonium nitrate and sulphur dioxide. Ammonia gas and air are fed to a converter where ammonia is converted to hydroxylamine disulphonate by contacting it with ammonium carbonate and sulphur dioxide in series. Ammonium carbonate is produced by dissolving ammonia and carbon dioxide in water, and sulphur dioxide by burning sulphur. The disulphonate is hydrolysed to hydroxylamine sulphate and ammonium sulphate. The addition of hydroxylamine sulphate to cyclohexanone produces cyclohexanone oxime which is converted to caprolactam by the Beckmann rearrangement.

Production of caprolactam can give rise to emissions of nitrous oxide ($N_2O$) from the ammonia oxidation step, emissions of $CO_2$ from the ammonium carbonate step, emissions of sulphur dioxide ($SO_2$) from the ammonium bisulphite step, and emissions of NMVOCs. Emissions of $CO_2$, $SO_2$ and NMVOCs from the conventional process are unlikely to be significant in well-managed plants. The main greenhouse gas to be accounted for from caprolactam production is $N_2O$. Modified caprolactam production processes are primarily concerned with elimination of the high volumes of ammonium sulphate that are produced as a by-product of the conventional process (Reimschuessel, 1977; p.84). $NH_3$ oxidation remains an integral part of all processes to obtain the $NO/NO_2$ required.

## CHOICE OF METHOD

Estimation of emissions of $N_2O$ from caprolactam production can be treated as analogous to estimation of emissions of $N_2O$ from nitric acid production. Both production processes involve an initial step of $NH_3$ oxidation which is the source of $N_2O$ formation and emissions.

The choice of *good practice* method depends on national circumstances. The decision tree in Figure 3.4 describes *good practice* in adapting the methods to national circumstances. Emissions can be estimated from continuous emissions monitoring (CEM) where emissions are directly measured at all times, periodic emissions monitoring that is undertaken over a period(s) that is reflective of the usual pattern of operation of the plant to derive an emission factor that is multiplied by output to derive emissions, irregular sampling to derive an emission factor that is multiplied by output to derive emissions, or by multiplying a default emission factor by output.

Methods are classified according to the extent of plant-level data that are available. Both Tier 2 and Tier 3 are require plant-level activity data.

### Tier 1 method

Emissions are estimated as follows:

**EQUATION 3.9**
**$N_2O$ EMISSIONS FROM CAPROLACTAM PRODUCTION – TIER 1**

$$E_{N2O} = EF \bullet CP$$

Where:

$E_{N2O}$ = $N_2O$ emissions, kg

EF = $N_2O$ emission factor (default), kg $N_2O$/tonne caprolactam produced

CP = caprolactam production, tonnes

When applying the Tier 1 method it is *good practice* to assume that there is no abatement of $N_2O$ emissions and to use the highest default emission factor shown in Table 3.5.

### Tier 2 method

Information on emissions arising from caprolactam production and control technologies is limited. Where plant-level information is not available, *good practice* provides default $N_2O$ generation factors as shown in Table 3.5. The default factors are based on $N_2O$ emissions from nitric acid plants because there is no information on caprolactam plants and the initial reaction step of oxidation of ammonia is similar for both processes. *Good practice* encourages the development of factors specific to caprolactam plants.

The number of caprolactam plants is relatively small (approximately 42 plants with around 19 plants using DSM (Stamicarbon) technology). It is unlikely that there are substantial variations in the $N_2O$ generation factors between plants. Where default values are used to estimate emissions from caprolactam production, it is *good practice* to ascertain the extent to which plant emissions vary according to type and to use an appropriate $N_2O$ generation factor.

The Tier 2 method uses plant-level production data disaggregated by technology type and default emission factors classified by technology type. Emissions are calculated as follows:

**EQUATION 3.10**
**$N_2O$ EMISSIONS FROM CAPROLACTAM PRODUCTION – TIER 2**

$$E_{N2O} = \sum_{i,j} \left[ EF_i \bullet CP_i \bullet \left(1 - DF_j \bullet ASUF_j\right)\right]$$

Where:

$E_{N2O}$ = emissions of $N_2O$, kg

$EF_i$ = $N_2O$ emission factor for technology type *i*, kg $N_2O$/tonne caprolactam produced

$CP_i$ = caprolactam production from technology type *i*, tonnes

$DF_j$ = destruction factor for abatement technology type *j*, fraction

$ASUF_j$ = abatement system utilisation factor for abatement technology type *j*, fraction

The basic equation for estimating $N_2O$ emissions includes additional terms that recognise current and the potential future use of $N_2O$ abatement technologies. The $N_2O$ destruction factor has to be multiplied by an abatement system utilisation factor in order to account for any down-time of the emission abatement equipment (i.e. time the equipment is not operating).

Where plant-level information is not available, *good practice* provides default $N_2O$ generation factors as shown in Table 3.5, Default Factors for Caprolactam Production, based on plant types classified by age. To achieve the highest accuracy, *good practice* is to apply Equation 3.10 at the plant-level taking into account $N_2O$ generation and destruction factors developed from plant-specific measurement data. In this case, the national total is equal to the sum of plant totals.

### Tier 3 method – direct measurement

The Tier 3 method uses plant level production data and plant-level emission factors obtained from direct measurement of emissions. These may be derived from irregular sampling of emissions of $N_2O$ or periodic emissions monitoring of $N_2O$ undertaken over a period(s) that reflects the usual pattern of operation of the plant. Emissions can be derived using Equation 3.10.

Alternatively, the Tier 3 method uses the results of continuous emissions monitoring (CEM), although it is noted that most plants are unlikely to employ CEM due to the resource costs. Where CEM is employed, emissions can be estimated based on the sum of measured $N_2O$ emissions derived from the concentration of $N_2O$ in monitored emissions for each recorded monitoring interval.

## CHOICE OF EMISSION FACTORS

### Tier 1 method

It is *good practice* to use the emission factor shown in Table 3.5 and to assume that there is no abatement of $N_2O$ emissions.

### Tier 2 method

If plant-level factors are not available, it is *good practice* to use default factors. The Tier 2 method uses a default factor. Default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant’s emission rate is unknown. This is especially true for caprolactam production where the value is based on high pressure nitric acid plants. Default factor in Table 3.5 should be used only in cases where plant-specific measurements are not available.

### Tier 3 method

Plant measurements provide the most rigorous data for calculating net emissions (i.e., $N_2O$ generation and destruction factors). Monitoring $N_2O$ emissions from caprolactam production is practical because these are point sources and there are a finite number of production plants. Given currently available technology, instrumentation for sampling and monitoring emission rates do not limit precision or accuracy of the overall measurement. Usually sampling frequency and timing is sufficient to avoid systematic errors and to achieve the desired level of accuracy.

As a general rule, it is *good practice* to conduct sampling and analysis whenever a plant makes any significant process changes that would affect the generation rate of $N_2O$, and sufficiently often otherwise to ensure that operating conditions are constant. In addition, plant operators should be consulted annually to determine the specific destruction technologies employed and confirm their use, since technologies may change over time. Precise measurement of the emissions rate and abatement efficiencies requires measurement of both the exit stream and the uncontrolled stream. Where measurement data are available only on the exit stream, *good practice* is to base emissions on these data. In this case, any available estimates of abatement efficiency should be provided only for information purposes and not used to calculate emissions.

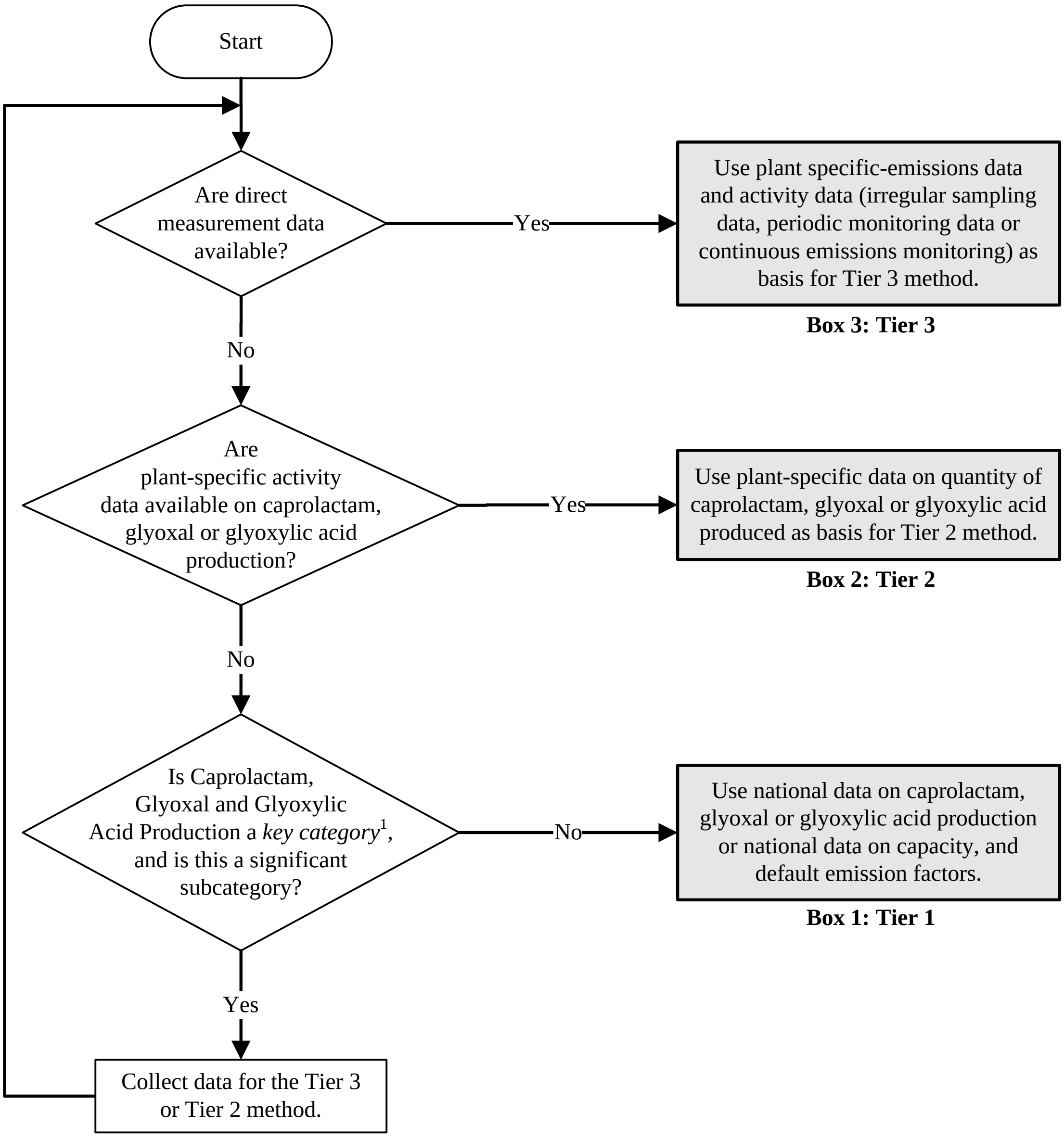
**TABLE 3.5**
**DEFAULT FACTOR FOR CAPROLACTAM PRODUCTION**

| Production Process | $N_2O$ Emission Factor (kg $N_2O$/tonne caprolactam) | Uncertainty |
|---|---|---|
| Raschig | 9.0[a] | ± 40% |

[a] Based on high pressure plants for nitric acid production.

Source: Default Factors for Nitric Acid Production. (See Table 3.3 in this chapter.)

**Figure 3.4** **Decision tree for estimation of $N_2O$ emissions from caprolactam, glyoxal or glyoxylic acid 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.

### CHOICE OF ACTIVITY DATA

It is *good practice* to compile production data at a level of detail that allows the use of Tier 2 or Tier 3 method.

#### Tier 1 method

The Tier 1 method requires data on national production of caprolactam. If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 20 percent (i.e., a range of 60-100 percent).

#### Tier 2 method

The Tier 2 method requires plant-level production data disaggregated by the age the plant. If additional information on technology type and abatement technology is available, it is *good practice* to collect this information and disaggregate production data according to the information obtained. That is, it is *good practice* to gather activity (production) data at a level of detail consistent with that of generation and destruction data. Where plant-level emission factors are used, *good practice* is to collect plant-level production data. Typical plant-level production data are accurate to ±2 percent due to the economic value of having accurate information.

#### Tier 3 method

The Tier 3 method require plant-level production data disaggregated by technology type when emissions estimates are derived using data from irregular or periodic sampling of emissions. It is *good practice* to collect activity (production) data at a level of detail consistent with that of any generation and destruction data. Although production is not used in the estimation of emissions where the estimate is based on CEM, these data should be collected and reported to ensure that changes in variables that influence emissions can be monitored over time. Typical plant-level production data are accurate to ±2 percent due to the economic value of having accurate information.

### COMPLETENESS

Complete coverage requires accounting for all plants and emissions of all direct greenhouse gases. In addition to $N_2O$, there may be non-combustion emissions of $CO_2$, $NO_x$, NMVOCs and $SO_2$. In order to include emissions of the indirect greenhouse gases ($NO_x$, NMVOCs and $SO_2$), see guidance provided in Chapter 7 of Volume 1: General Guidance and Reporting. Plant-level information will be required to enable emissions estimation. Over time default values could be developed as more information becomes available.

There will be few caprolactam plants in a country, and it is suggested that emissions are calculated from plant specific data.

### DEVELOPING A CONSISTENT TIME SERIES

$N_2O$ emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, it will be necessary to consider how current plant measurements can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.5.2.2 UNCERTAINTY ASSESSMENT

### EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default value shown in Table 3.5 is an estimate based on default values for nitric acid plants. In general, default emission factors for gaseous substances have higher uncertainties because mass values for gaseous substances are influenced by temperature and pressure variations and gases are more easily lost through process leaks. The default values for caprolactam production have a relatively high level of uncertainty due to the limited information available. It is *good practice* to obtain uncertainty estimates at the plant-level which should be lower than uncertainty values associated with default values.

### ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of nitric acid production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±2 percent can be used.

### 3.5.2.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

#### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of emissions estimates using different approaches

If emissions are calculated using data from individual caprolactam plants (bottom-up approach), inventory compilers should compare the estimate to emissions calculated using national production data (top-down approach). They should record the results and investigate any unexplained discrepancies.

Since industrial $N_2O$ source categories are relatively small compared to other anthropogenic and natural sources, it is not feasible to compare emissions with measured trends in atmospheric $N_2O$ concentrations.

#### Plant-level data

Inventory compilers should archive sufficient information to allow an independent review of the time series of emissions beginning in the base year, and to explain trends in emissions when making historical comparisons. This is particularly important in cases where recalculations are necessary, for example, when an inventory compiler changes from using default values to actual values determined at the plant level.

#### Revision of direct emission measurements

If plant-level $N_2O$ measurements are available, inventory compilers should confirm that internationally recognised, standard methods were used. If the measurement practices fail this criterion, then they should evaluate the use of these emissions data. In addition, they should reconsider the uncertainty estimates in light of the QA/QC results.

Inventory compilers should compare plant-based factors to the IPCC defaults to ensure that the plant-specific factors are reasonable. They should explain and document any differences between plant-specific factors and default factors, particularly any differences in plant characteristics that might lead to these differences.

#### 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, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

- Description of the method used;
- Number of caprolactam plants;
- Emission factors;
- Production data;
- Production capacity;
- Number of plants using abatement technology;
- Type of abatement technology, destruction efficiency, and utilisation;
- Any other assumptions.

Plant operators should supply this information to the inventory compiler for compilation, and also archive the information at the site. Plant operators should also log and archive the measurement frequencies and instrumental calibration records where actual plant measurements are made.

Where there are only one or two producers in a country as will be the case for caprolactam producers, activity data may be considered confidential. In this case, operators and the inventory compiler should determine the level of aggregation at which information can be reported while still protecting confidentiality. Detailed information including instrumentation records should still be archived at the plant level.

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.

## 3.5.3 Glyoxal and glyoxylic acid production

Glyoxal (ethanedial) ($C_2H_2O_2$) is produced from oxidation of acetaldehyde (ethanal) ($C_2H_4O$) with concentrated nitric acid ($HNO_3$). Glyoxal can also be produced from catalytic oxidation of ethylene glycol (ethanediol) ($CH_2OHCH_2OH$). Glyoxal is used as a crosslinking agent for vinyl acetate/acrylic resins, disinfectant, gelatine hardening agent, textile finishing agent (permanent-press cotton, rayon fabrics), wet-resistance additive (paper coatings) (Ashford, 1994; p.454).

Glyoxylic acid is produced by nitric acid oxidation of glyoxal. Glyoxylic acid is used for the production of synthetic aromas, agrochemicals and pharmaceutical intermediates (Babusiaux, 2005; p.1).

The basic reaction equation for the production of glyoxal from acetaldehyde is:

$$\boxed{2C_2H_4O \text{ (Acetaldehyde)} + 2HNO_3 \rightarrow 2C_2H_2O_2 \text{ (Glyoxal)} + N_2O + H_2O}$$

The stoichiometric relationship indicates that complete reaction will result in 0.543 tonnes of $N_2O$ per tonne of glyoxal. Under commercial conditions, the yield of $N_2O$ per tonne of glyoxal is approximately 0.52 tonnes (Babusiaux, 2005; p.1).

Glyoxylic acid production is a batch process where nitric acid is reduced to NO and $N_2O$ with NO recovered as $HNO_3$ in the process. $N_2O$ arises in the production process through a secondary reaction where glyoxal is converted to oxalic acid $(COOH)_2$.

Default factors for glyoxal and glyoxylic acid production are shown in Table 3.6. Emissions can be estimated using the same approach as described in the foregoing for caprolactam. To use default destruction factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

**TABLE 3.6**
**DEFAULT FACTORS FOR GLYOXAL AND GLYOXYLIC ACID PRODUCTION**

| **Product** | **$N_2O$ Generation Factor (tonnes $N_2O$/tonne)** | **$N_2O$ Destruction Rate (%)** | **$N_2O$ Emission Factor (tonnes $N_2O$/tonne)** | **Uncertainty (%)** |
|---|---|---|---|---|
| Glyoxal | 0.52 | 80 | 0.10 | ±10 |
| Glyoxylic acid | 0.10 | 80 | 0.02 | ±10 |

Source: Babusiaux (2005)

# 3.6 CARBIDE PRODUCTION

## 3.6.1 Introduction

Greenhouse gas emissions are associated with production of silicon carbide (SiC) and calcium carbide ($CaC_2$). The production of carbide can result in emissions of carbon dioxide ($CO_2$), methane ($CH_4$), carbon monoxide (CO) and sulphur dioxide ($SO_2$). Silicon carbide is a significant artificial abrasive. It is produced from silica sand or quartz and petroleum coke. Calcium carbide is used in the production of acetylene, in the manufacture of cyanamide (a minor historical use), and as a reductant in electric arc steel furnaces. It is made from two carbon-containing raw materials: calcium carbonate (limestone) and petroleum coke.

Use of carbon-containing raw materials in the production processes result in emissions of $CO_2$ and CO. The presence of hydrogen-containing volatile compounds and sulphur (S) in the petroleum coke may cause formation and emission to the atmosphere of $CH_4$ and $SO_2$.

## 3.6.2 Methodological issues

### $CO_2$ AND $CH_4$ FROM SILICON CARBIDE PRODUCTION

Silicon carbide is produced from silica sand or quartz and petroleum coke, which is used as a carbon source, according to the reactions (Austin, 1984; p. 262):

$$\boxed{\begin{array}{c} SiO_2 + 2C \rightarrow Si + 2CO \\ Si + C \rightarrow SiC \end{array}}$$

The formula describing the overall reaction is given below but in practice it does not proceed in the stoichiometric proportions indicated:

$$\boxed{SiO_2 + 3C \rightarrow SiC + 2CO \ (+ O_2 \rightarrow 2CO_2)}$$

In the production process, silica sand and carbon are mixed in an approximate molar ratio of 1:3. Some carbon, about 35 percent, is contained in the product and the rest is converted to $CO_2$ in excess oxygen and released to the atmosphere as a process by-product.

The petroleum coke used in this process may contain volatile compounds, which will form methane. Some methane will escape to the atmosphere, particularly during start-up.

### $CO_2$ FROM CALCIUM CARBIDE PRODUCTION

Calcium carbide ($CaC_2$) is made by heating calcium carbonate (limestone) and subsequently reducing CaO with carbon e.g., petroleum coke. Both steps lead to emissions of $CO_2$. Around 67 percent of the carbon from petroleum coke will be contained in the product.

The basic reactions are:

$$\boxed{\begin{array}{c} CaCO_3 \rightarrow CaO + CO_2 \\ CaO + 3C \rightarrow CaC_2 + CO \ (+ \tfrac{1}{2} O_2 \rightarrow CO_2) \end{array}}$$

The CO gas will be used as an energy source in most plants.

**BOX 3.4**
**DOUBLE COUNTING**

To avoid double counting, $CO_2$ emission from combusting CO gas generated in the process of $CaC_2$ production should be accounted in the **IPPU Sector**, and should not be included in the **Energy Sector**. Petroleum coke used in the production process should be deducted from the **Energy Sector** as a non-energy use of petroleum coke.

The most important application of calcium carbide is producing acetylene ($C_2H_2$) by reacting $CaC_2$ with water. A substantial use of acetylene is welding applications. Acetylene is also used in chemical synthesis for the production of acetaldehyde, acetic acid, acetic anhydride, and as a feedstock to manufacture ‘acetylene black’, a form of carbon black. Frequently, acetylene is not produced within the same plant that produces $CaC_2$ and this needs to be taken into account when applying higher tier methods to estimating $CO_2$ emissions from $CaC_2$ use.

Use of acetylene in chemical synthesis and production of acetylene black results in carbon contained in the products reducing the total emissions of $CO_2$ that are related to $CaC_2$ use. Acetylene may be produced from partial oxidation of natural gas as well as from $CaC_2$. The approach to accounting for acetylene in these uses is outlined in Section 3.9 of this volume.

Production and use of acetylene for welding applications is summarised by reaction:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\ (+\ 2.5O_2 \rightarrow 2CO_2 + H_2O)$$

Where acetylene is used in welding applications, emissions can be derived from the quantity of $CaC_2$ used in the production of this acetylene on the assumption that the acetylene will be used in a relatively short period of time after production.

**BOX 3.5**
**ALLOCATION OF EMISSIONS FROM CaO PRODUCTION**

CaO (lime) might be produced in-house or at a plant other than the carbide plant. In either case, the emissions from the CaO step should be reported as emissions from lime production (Section 2.3 of this volume) and only the emissions from reaction of CaO with petroleum coke and use of the product to produce acetylene for welding applications should be reported as emissions from calcium carbide.

### 3.6.2.1 CHOICE OF METHOD

Methods are classified according the extent of plant-level data that are available. The Tier 1 method is based on default values and national statistics. Tier 2 is based on plant-level data on production and use of $CaC_2$ in acetylene production for welding applications. The Tier 3 method is based on plant-level data on petroleum coke input (including the carbon content factor (CCF) and carbon oxidation factor (COF) if available; alternatively, country specific Energy Sector values may be used), use of $CaC_2$ in acetylene production for welding applications, and plant-level emission factors where relevant.

Both Tier 2 and Tier 3 are based on plant-level activity data. The choice of method to estimate emissions of $CO_2$ and $CH_4$ depends on national circumstances as shown in Figure 3.5.

#### CO$_2$ AND CH$_4$ FROM CARBIDE PRODUCTION

#### Tier 1 method

Emissions from carbide production can be estimated from activity data (AD) on petroleum coke consumption or carbide production, calcium carbide used in the production of acetylene used in welding applications, and default emission factors. Where AD on petroleum coke consumption are used the CCF and COF of the petroleum coke can be obtained from Volume 2, Chapter 1 and the result must be multiplied by 44/12 to convert C to $CO_2$. The basic equation for estimating emissions is:

**EQUATION 3.11**
**EMISSIONS FROM CARBIDE PRODUCTION**

$$E_{CO2} = AD \bullet EF$$

Where:

$E_{CO2}$ = emissions of $CO_2$, tonnes

AD = activity data on petroleum coke consumption or carbide production, tonnes raw material used or tonnes carbide produced

EF = $CO_2$ emission factor. There are two options as follows:
When carbide production is used as activity data, EF should be average $CO_2$ emissions per unit of output for carbide production, tonnes $CO_2$/tonne carbide production.
When petroleum coke consumption is used as activity data, EF should be CCF (carbon content

factor) multiplied by COF (carbon oxidation factor) multiplied by 44/12 and adjusted to account for the C contained in the product, tonnes $CO_2$/tonne material used

Adjustment factor for SiC = 0.35 $\Rightarrow$ Emission factor = 0.65 • CCF • COF • 44/12;

Adjustment factor for $CaC_2$ = 0.67 $\Rightarrow$ Emission factor = 0.33 • CCF • COF • 44/12.

Equation 3.11 can also be used to estimate $CH_4$ emissions, where EF is the appropriate emission factor for $CH_4$.

Estimation of emissions from $CaC_2$ needs to include emissions of $CO_2$ indirectly attributable to $CaC_2$ that is used in acetylene production. Equation 3.11 can be applied where AD is the amount of $CaC_2$ used and EF is the emission factor associated with this use. Under the Tier 1 method it is *good practice* to assume that all $CaC_2$ used in acetylene production gives rise to $CO_2$ emissions.

### Tier 2 method

The Tier 2 method uses plant-level data on production of carbide and the amount of C contained in the product. For $CaC_2$, data on the use of $CaC_2$ for the production of acetylene used in welding applications is also required. Emissions from production and use can be estimated with Equation 3.11 using default emission factors. Where acetylene is produced from $CaC_2$ at another location and the quantity of $CaC_2$ used for this purpose is not known, it is *good practice* to document this fact.

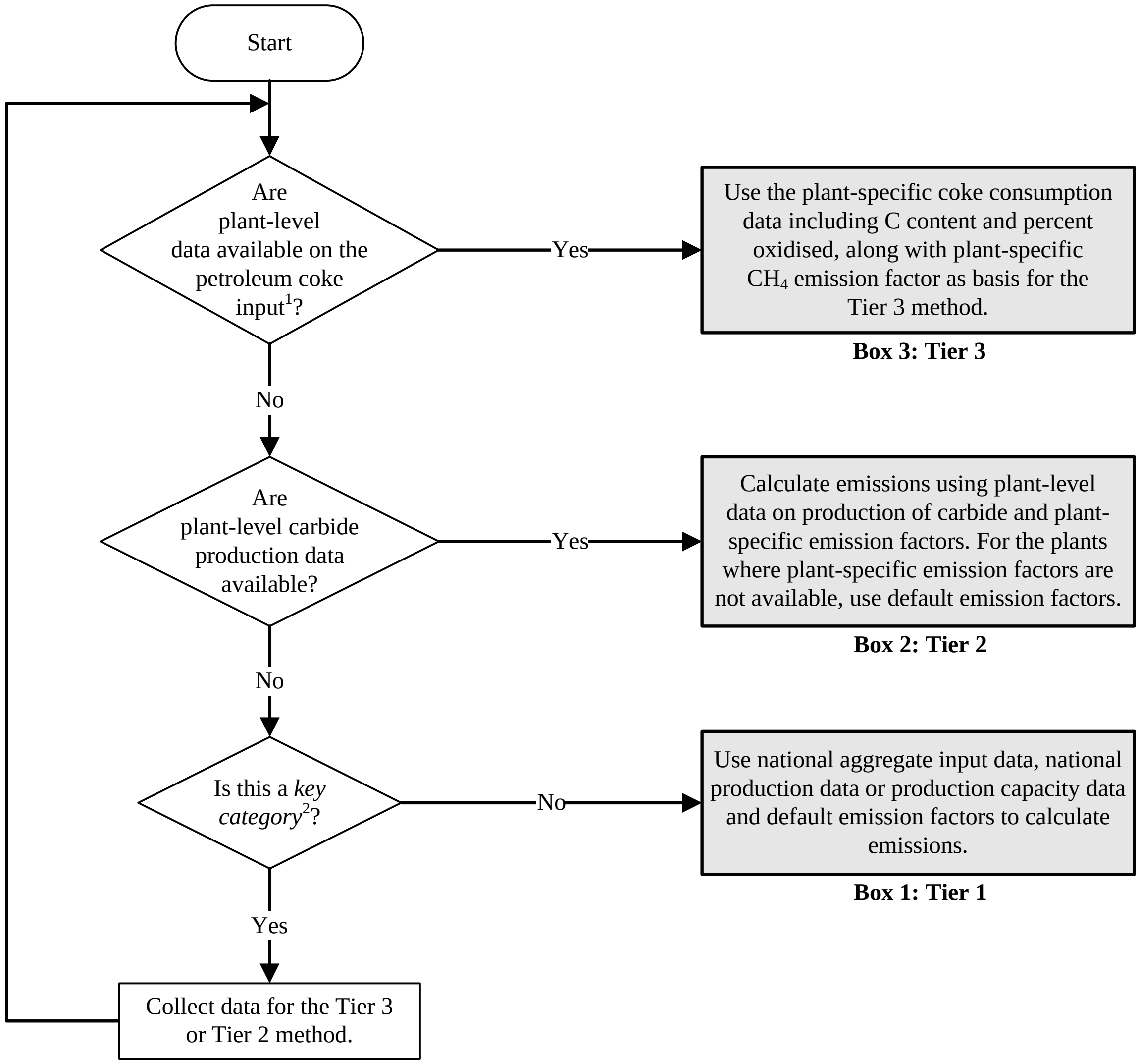
### Tier 3 method

The Tier 3 method requires plant-level data on the petroleum coke input along with the CCF and COF if available; alternatively, country specific Energy Sector values for CCF and COF may be used. Plant-level data on the amount of C contained in the product are also required.

In the case of $CaC_2$, data on the use of $CaC_2$ for the production of acetylene used in welding applications are required, as are plant-level emission factors. Where acetylene is produced from $CaC_2$ at another location and the quantity of $CaC_2$ used for this purpose is not known, it is *good practice* to document this fact. In addition, plant-level emission factors for $CH_4$ need to be collected. Equation 3.11 can be applied to estimate emissions for each plant and total national emissions are the sum of these estimates.

Production data are not used in the calculation but should be collected for reporting purposes. Where acetylene production data cannot be disaggregated by use, national inventory compilers using the Tier 3 method are encouraged to account for any emissions at the point where they arise; for example, emissions from acetylene use in welding applications should be accounted for at the point of use of acetylene using a country specific emission factor. A similar approach should be followed for other uses of acetylene.

**Figure 3.5** **Decision tree for estimation of $CO_2$ and $CH_4$ emissions from carbide production**



Note:
1. "Input data" means raw material consumption data.
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.

## 3.6.2.2 CHOICE OF EMISSION FACTORS

### Tier 1 method

The Tier 1 method uses default values for CCF, COF and C contained in the product where petroleum coke is used in the estimation. Alternatively, where carbide production is used, the method uses default emission factors shown in Tables 3.7 and 3.8 where relevant. In both cases, the default factor for $CaC_2$ use is applied.

### Tier 2 method

As for the Tier 1 method, the Tier 2 method uses default emission factor values except for the amount of C contained in the product, where plant-level data are required.

### Tier 3 method

The Tier 3 method requires plant-level data for all variables except for CCF and COF of the petroleum coke where country specific Energy Sector values may be used. This includes plant-level emission factors for lime if it is produced in-house and plant-level emission factors for $CaC_2$ used to produce acetylene for welding applications.

### $CO_2$ from silicon carbide production

More carbon is needed in the silicon carbide production process than calculated from a stoichiometric reaction. The excess carbon is oxidised during the process, little is left as ash (Raaness, 1991). Typical default values for Norwegian plants for carbon content in coke are 97 percent and for carbon contained in product, 35 percent. This implies a typical emission factor of 2.3 tonnes $CO_2$/tonne petroleum coke used (IPCC, 1997), or 2.62 tonnes $CO_2$/tonne carbide produced.

### $CH_4$ from silicon carbide production

Measurements at Norwegian plants suggest emission factors of 10.2 kg $CH_4$/tonne petroleum coke or 11.6 kg $CH_4$/tonne carbide produced (IPCC, 1997).

**TABLE 3.7**
**DEFAULT FACTORS FOR $CO_2$ AND $CH_4$ EMISSIONS FROM SILICON CARBIDE PRODUCTION**

| Process | Emission Factor (tonnes $CO_2$/tonne raw material used) | Emission Factor (kg $CH_4$/tonne raw material used) | Emission Factor (tonnes $CO_2$/tonne carbide produced) | Emission Factor (kg $CH_4$/tonne carbide produced) |
|---|---|---|---|---|
| Silicon carbide production | 2.30 | 10.2 | 2.62 | 11.6 |

Source: *Revised 1996 IPCC National Greenhouse Gas Inventories,* Vol.3, p.2.21 (IPCC, 1997)

### $CO_2$ from calcium carbide production

Emission factors may be derived from the use of raw materials (petroleum coke) and from carbide production using a mass-balance approach. Limestone used in carbide manufacture contains about 98 percent $CaCO_3$ and is accounted for elsewhere. 1 750 kg limestone (or 950 kg CaO), 640 kg of petroleum coke and 20 kg carbon electrodes are required to produce 1 tonne of carbide.

The default emission factors for estimating emissions are included in Table 3.8.

**TABLE 3.8**
**EMISSION FACTORS FOR $CO_2$ EMISSION FROM CALCIUM CARBIDE PRODUCTION AND USE**

| Process | Default Emission Factor (tonnes $CO_2$/tonne raw material used) | Default Emission Factor (tonnes $CO_2$/tonne carbide produced) |
|---|---|---|
| Petroleum coke use | 1.70 | 1.090 |
| Use of product | not relevant | 1.100 |

Source: *Revised 1996 IPCC National Greenhouse Gas Inventories,* Vol.3, p.2.22 (IPCC, 1997)

The theoretical emission factor calculated from a stoichiometric reaction is lower for the petroleum coke step than that shown in the table. Excess carbon is oxidised in the process and the suggested emission factors were calculated from the actual use of raw materials in a Norwegian plant. The emission factor for acetylene use is calculated from the actual (not stoichiometric) carbon content of carbide.

The $CO_2$ emissions may be lowered by utilising the gas when producing dicyanodiamide from carbide (Olsen, 1991).

## 3.6.2.3 CHOICE OF ACTIVITY DATA

### Tier 1 method

The Tier 1 method requires data on petroleum coke used in carbide production or national production of carbide. These data may be obtained from national statistics or from industrial and trade organizations representing carbide and petroleum coke producers.

### Tier 2 method

Activity data required for the Tier 2 method comprise plant-level data on carbide produced and the amount of $CaC_2$ used in the production of acetylene for welding applications.

**Tier 3 method**

The Tier 3 method requires plant-level activity data for all variables including the petroleum coke input and $CaC_2$ used to produce acetylene for welding applications.

The Tier 2 methods require the collection of activity data from individual plants or companies. In Tier 1 the activity data provided by national statistics or by industrial and trade organizations associated with carbide and petroleum coke production should be used. However, if sufficient plant-specific or company-specific data are available, they may be used to estimate emissions.

### 3.6.2.4 COMPLETENESS

Carbide production plants are generally known in each country. As a result, carbide production data may be available in national statistical databases, or could be collected, even if these data have not been published in national statistics. The petroleum coke consumption data may be obtained directly from carbide production plants, or from coke producers and traders. Activity data and emissions estimation is complicated by the fact that acetylene produced from $CaC_2$ is not necessarily produced at the same plant that produces the $CaC_2$. This needs to be accounted for when using the higher tier methods, with emissions originating from the use of $CaC_2$ accounted at the point where the emissions occur; for example, in the case of acetylene used in welding applications, where the acetylene is produced at a different location to the $CaC_2$ emissions should be accounted for at the point of production of the acetylene on the assumption that it will be used in a short time after production.

Application of the Tier 2 and 3 methods assumes the bottom-up (plant by plant) estimation of emissions and plant-level data collection. In countries where only a subset of plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, it may not be possible to report emissions using Tier 3 for all facilities during the transition.  Where data for the Tier 3 method are not available for all plants, Tier 2 could be used for the remaining plants. Also, where data for the Tier 2 method are reported by only a subset of plants or where there is a transition from Tier 1 to Tier 2, 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.

### 3.6.2.5 DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to estimate emissions from carbide production using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, it is *good practice* is to recalculate these gaps according to the guidance provided in Volume 1, Chapter 5.

## 3.6.3 Uncertainty assessment

### 3.6.3.1 EMISSION FACTOR UNCERTAINTIES

In general, the default $CO_2$ emission factors are relatively uncertain because industrial-scale carbide production processes differ from the stoichiometry of theoretical chemical reactions. The uncertainty in the emission factors for $CH_4$ is due to the possible variations in the hydrogen-containing volatile compounds in the raw material (petroleum coke) that are used by different manufacturers and due to the possible variations in production process parameters. Where uncertainty values are not available from other sources, a default value of ±10 percent can be used.

It is *good practice* to obtain uncertainty estimates at the plant level which should be lower than uncertainties associated with default values.

### 3.6.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained directly from plants, uncertainty estimates can be obtained from producers. This will include uncertainty estimates for petroleum coke and limestone used and for carbide production data. Data that are obtained from national statistical agencies or from industrial and trade organizations usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistic agencies collect carbide production data from production facilities, uncertainties in national statistics are not expected to differ from uncertainties estimated from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±5 percent can be used.

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

### 3.6.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emission estimates. More extensive quality control checks and quality assurance procedures may be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance given in Volume 1, specific procedures of relevance to this source category are outlined below.

**Comparison of emission estimates using different approaches**

If the Tier 2 (plant-specific) method is used, then inventory compilers should compare the emission estimates to the estimates calculated using national level activity data (Tier 1). The inventory compilers are also encouraged to compare the emission estimates calculated using different modifications of the same methods.

The results of such comparison should be recorded for internal documentation, including explanation for any discrepancies.

**Review of emission factors**

Inventory compilers should compare aggregated national emission factors with the IPCC default emission factors in order to determine if the national factor is reasonable relative to the IPCC default. The same procedure (i.e., comparison with the IPCC default) should be applied to plant specific emission factors. Differences between national or plant specific factors and default factors should be explained and documented, particularly if they are representative of different circumstances.

**Plant-specific data check**

For plant-specific data, inventory compilers should review inconsistencies between plants to establish whether they reflect errors, different measurement techniques, or result from real differences in raw materials, operational conditions or technology.

Inventory compilers should ensure that activity data and emission factors are developed in accordance with internationally recognized and proven measurement methods. If any emission measurements from individual plants are collected inventory compilers should ensure that the measurements were made according to the recognised national or international standards. If the measurement practices fall this criterion, then the use of this emission factors and activity data should be carefully evaluated, uncertainty estimations reconsidered and qualifications documented.

**Expert review**

Inventory compilers are encouraged to include key industrial and trade organizations associated with carbide and petroleum coke production in a review process. This process should begin on the early stage of the inventory development to provide input to the development and review of methods and data acquisition.

Third party reviews may be also useful for this source category, particularly in relation of initial data collection, transcription, calculation and documentation.

### 3.6.4.2 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, Section 6.11. Recalculation of previous years emissions also should be documented and archived.

# 3.7 TITANIUM DIOXIDE PRODUCTION

## 3.7.1 Introduction

Titanium dioxide ($TiO_2$) is one of the most commonly used white pigments. The main use is in paint manufacture followed by paper, plastics, rubber, ceramics, fabrics, floor covering, printing ink, and other miscellaneous uses (Austin, 1984; Lowenheim and Moran, 1975). Given production of around 4 million tonnes of $TiO_2$, and the substantial use of the chloride route, carbon dioxide ($CO_2$) emissions are likely to be significant and need to be accounted for in greenhouse gas inventories. Global production by the chloride route has increase approximately eight fold since 1970 whilst sulphate route production has been relatively stable (Kirk-Othmer, 1999; p. 2017). Note that in the discussion, titanium dioxide products are referred to generically as titanium dioxide unless there is a need to make a distinction between the products. The discussion applies to titanium slag, synthetic rutile (>90 percent $TiO_2$) and rutile $TiO_2$.

## 3.7.2 Methodological issues

$TiO_2$ is produced as anatase $TiO_2$ and rutile $TiO_2$. The forms of $TiO_2$ differ in terms of the crystalline structure and purity of the final product. Anatase $TiO_2$ may be produced by digesting ilmenite (essentially ferrous titanate ($FeO.TiO_2$)) with sulphuric acid, the sulphate process, or from titanium slag. Basic reaction equations for the acid digestion route are (Lowenheim and Moran, 1975; p. 814):

$$FeTiO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiO.SO_4 + 2H_2O$$

$$TiO.SO_4 + 2H_2O \rightarrow TiO_2.H_2O + H_2SO_4$$

$$TiO_2.H_2O + \text{heat} \rightarrow TiO_2 + H_2O$$

The sulphate route process does not give rise to process greenhouse gas emissions that are of significance.

There are three processes that are used in the production of $TiO_2$ that lead to process greenhouse gas emissions: titanium slag production in electric furnaces, synthetic rutile production using the Becher process, and rutile $TiO_2$ production via the chloride route.

Titanium slag used for production of anatase $TiO_2$ is produced from electric furnace smelting of ilmenite. Where titanium slag is used the acid reduction step is not required as the electric furnace smelting reduces the ferric iron contained as an impurity in ilmenite. Rutile $TiO_2$ may be produced by further processing of the anatase $TiO_2$. Process emissions arise from the reductant used in the process.

Production of synthetic rutile can give rise to $CO_2$ emissions where the Becher process is used. This process reduces the iron oxide in ilmenite to metallic iron and then reoxidises it to iron oxide, and in the process separates out the titanium dioxide as synthetic rutile of about 91 to 93 percent purity (Chemlink, 1997). Black coal is used as the reductant and the $CO_2$ emissions arising should be treated as industrial process emissions.
The main route for the production of rutile $TiO_2$ is the chloride route. Rutile $TiO_2$ is produced through the carbothermal chlorination of rutile ore or synthetic rutile to produce titanium tetrachloride ($TiCl_4$) and oxidation of the $TiCl_4$ vapours to $TiO_2$ according to the following reactions (Kirk-Othmer, 1999; p.2017):

$$2TiO_2 + 4Cl_2 + 3C \rightarrow 2TiCl_4 + 2CO + CO_2$$

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

Based on stoichiometry and assuming complete conversion of the input C to $CO_2$ through further conversion of CO in excess air, the $CO_2$ emission factor cannot be less than 0.826 tonnes of $CO_2$ per tonne of $TiO_2$ (based on 1.5 moles of $CO_2$ per mole of $TiO_2$).

### 3.7.2.1 CHOICE OF METHOD

The general approach for calculating $CO_2$ emissions from titanium dioxide production is the same irrespective of the product because the emissions are based on the quantity of reducing agent or carbothermal input. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 3.6. Process emissions of carbon dioxide in $TiO_2$ production take place primarily as a result of anode carbon oxidisation in the production of titanium slag, coal oxidisation in the process of producing synthetic rutile using the Becher process, and petroleum coke oxidisation in the process of producing rutile $TiO_2$ via the chloride route.

Methods are classified according to the extent of plant-level data that are available.

### TIER 1 METHOD

The Tier 1 method uses a default emission factor per unit of output multiplied by activity data obtained from national statistics. The basic equation for estimating $CO_2$ emissions is:

**EQUATION 3.12**
**$CO_2$ EMISSIONS FROM TITANIUM SLAG, SYNTHETIC RUTILE AND RUTILE $TiO_2$ PRODUCTION – TIER 1**

$$E_{CO2} = \sum_i \left(AD_i \bullet EF_i\right)$$

Where:

$E_{CO2}$ = emissions of $CO_2$, tonnes

$AD_i$ = production of titanium slag, synthetic rutile or rutile $TiO_2$ (product *i*), tonnes

$EF_i$ = $CO_2$ emissions per unit of production of titanium slag, synthetic rutile or rutile $TiO_2$ (product *i*), tonnes $CO_2$/tonne product

### TIER 2 METHOD

Emissions can be calculated from the consumption of the reducing agent for electrode carbon (titanium slag), and coal (synthetic rutile) in the Becher process, and the carbothermal input (petroleum coke) for rutile $TiO_2$ from the chloride rout process. The Tier 2 method uses plant-level data on the quantities of reducing agent and carbothermal input to derive emissions as follows:

**EQUATION 3.13**
**$CO_2$ EMISSIONS FROM TITANIUM SLAG, SYNTHETIC RUTILE AND RUTILE $TiO_2$ PRODUCTION – TIER 2**

$$E_{CO2} = \sum_i \left(AD_i \bullet CCF_i \bullet COF_i \bullet 44/12\right)$$

Where:

$E_{CO2}$ = emissions of $CO_2$, kg

$AD_i$ = amount of reducing agent or carbothermal input *i*, GJ

$CCF_i$ = carbon content factor of reducing agent or carbothermal input *i*, kg C/GJ

$COF_i$ = carbon oxidation factor for reducing agent or carbothermal input *i*, fraction

To achieve the highest accuracy, *good practice* is to apply Equation 3.13 at the plant-level with all data inputs obtained from plant operators.

Where plant-level information is not available, *good practice* provides default $CO_2$ emission factors for synthetic rutile and rutile $TiO_2$ as shown in Table 3.9. A default factor for titanium slag is not available because of the small number of plants.

**BOX 3.6**
**DOUBLE COUNTING**

In order to avoid double counting, the quantities of electrode carbon, coal used as a reductant, and petroleum coke used in the chloride route process, must be subtracted from the quantity reported under energy and non-energy use in the **Energy Sector**.

## 3.7.2.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

If plant-level information is not available, it is *good practice* to use default factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors by product are provided in Table 3.9, and should be used only in cases where plant-specific data are not available. The default factors are based on estimates of reductant or carbothermal input per unit of output assuming complete conversion of the C content to $CO_2$.

### TIER 2 METHOD

Plant-level data provides the most rigorous data for calculating $CO_2$ emissions from titanium dioxide production. For the Tier 3 method, C content of the reductant and carbothermal inputs along with the proportion of C oxidised are the key emission factor variables for deriving the quantity of $CO_2$ emitted.

**TABLE 3.9**
**DEFAULT FACTORS FOR TITANIUM DIOXIDE PRODUCTION (TONNES $CO_2$ PER TONNE PRODUCT)**

| **Product** | **Emission factor and respective uncertainty (tonnes $CO_2$/tonne product)** |
|---|---|
| Titanium slag[1] | Not available |
| Synthetic rutile[2] | 1.43 (± 10%) |
| Rutile titanium dioxide (chloride route)[3] | 1.34 (± 15%) |

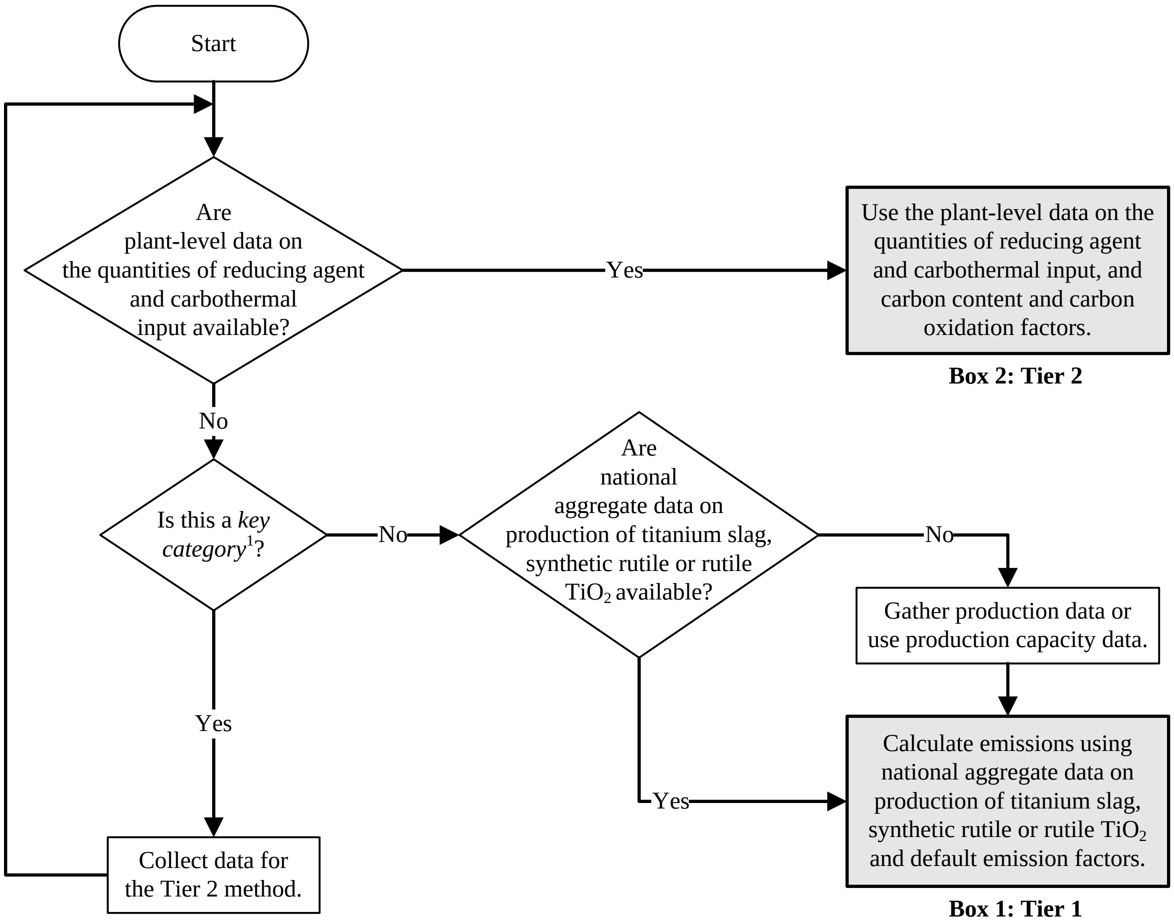
Source:

[1] A default emission factor is not available because there are two plants only, Richards Bay in South Africa, and Allard Lake in Canada, and data are confidential. It is *good practice* for the respective countries to include plant specific estimates of emissions in their national greenhouse gas inventories.

[2] Derived from data provided by Iluka Resources.

[3] Adapted from EIPPCB (2004a; p.99).

**Figure 3.6 Decision tree for estimation of $CO_2$ emissions from titanium dioxide 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.

### 3.7.2.3 CHOICE OF ACTIVITY DATA

It is *good practice* to compile activity data at a level of detail that allows the use of the Tier 2 method. When applying the methods it is essential that a clear distinction is made between the products to avoid multiplying the incorrect emission factor by activity data.

#### TIER 1 METHOD

The Tier 1 method requires data on national production of titanium slag, synthetic rutile and rutile $TiO_2$. If national-level activity data are not available, information on production capacity can be used with emissions estimated using a default emission factor. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

#### TIER 2 METHOD

The plant-level activity data required for the Tier 2 method are total reductant use, total carbon electrode consumption, and total carbothermal input. It is *good practice* to also collect data on total titanium slag production, total synthetic rutile production, and total rutile $TiO_2$ production. Collection of production data enables comparisons of inputs per unit of outputs over time and provides a sound basis for ensuring time series consistency. Where plant-level emission factors are used, *good practice* is to collect plant-level production data. Typical plant-level activity data is assumed to be accurate to ±2 percent due to the economic value of having accurate information. If plant-level data are not available, nationally compiled production data may be used.

### 3.7.2.4 COMPLETENESS

Complete coverage for titanium dioxide production requires accounting for all emissions from all sources including titanium slag, synthetic rutile and rutile $TiO_2$. $CO_2$ emissions are the main process emissions. In order to include emissions of $NO_x$, CO and $SO_2$ from this source category, see guidance provided in Chapter 7 of Volume 1: General Guidance and Reporting.

### 3.7.2.5 DEVELOPING A CONSISTENT TIME SERIES

$CO_2$ emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available, including plant-specific production data, for all years in the time series, it will be necessary to consider how current plant data can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.7.3 Uncertainty assessment

### 3.7.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values are estimates based on expert judgement. It is *good practice* to obtain uncertainty estimates at the plant level which should be lower than uncertainty values associated with default values.

### 3.7.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. This will include uncertainty estimates for reductant use, carbothermal inputs, and production data. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of titanium dioxide production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±5 percent can be used.

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

## 3.7.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable, if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

### Comparison of emission factors

Inventory compilers should check if the estimated emission factors are within the range of default emission factors provided for the Tier 1 method, and also ensure that the emission factors are consistent with the values derived from analysis of the process chemistry. For example, the $CO_2$ generation rate for rutile $TiO_2$ from the chloride route process should not be less than 0.826 tonnes of $CO_2$ per tonne of rutile $TiO_2$ produced. If the emission factors are outside of the estimated ranges, it is *good practice* to assess and document the plant-specific conditions that account for the differences.

If emission measurements from individual plants are collected, inventory compilers should ensure that the measurements were made according to recognised national or international standards. QC procedures in use at the site should be directly referenced and included in the QC plan. If the measurement practices were not consistent with QC standards, the inventory compiler should reconsider the use of these data.

## 3.7.4.2 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, Section 6.11. 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.

### Plant-specific data check

The following plant-specific data is required for adequate auditing of emissions estimates:

- Activity data comprising electrode carbon consumption (titanium slag), coal reductant use (synthetic rutile), carbothermal input (rutile $TiO_2$), titanium slag production, synthetic rutile production, and rutile $TiO_2$ production;
- Emission factor data including the carbon content of the reductant (carbon electrode and coal) and carbothermal input (petroleum coke), and the proportion oxidised in the process;
- Calculations and estimation method;
- List of assumptions;
- Documentation of any plant-specific measurement method, and measurement results.

In general production and process data are considered proprietary by operators, especially where there are only a small number of plants within a country. It is *good practice* to apply appropriate techniques, including aggregation of data, to ensure protection of confidential data.

# 3.8 SODA ASH PRODUCTION

## 3.8.1 Introduction

Soda ash (sodium carbonate, $Na_2CO_3$) is a white crystalline solid that is used as a raw material in a large number of industries including glass manufacture, soap and detergents, pulp and paper production and water treatment. Carbon dioxide ($CO_2$) is emitted from the use of soda ash and these emissions are accounted for as a source under the relevant using industry as discussed in Volume 3, Chapter 2. $CO_2$ is also emitted during production with the quantity emitted dependent on the industrial process used to manufacture soda ash.

Emissions of $CO_2$ from the production of soda ash vary substantially with the manufacturing process. Four different processes may be used commercially to produce soda ash. Three of these processes, monohydrate, sodium sesquicarbonate (trona) and direct carbonation, are referred to as natural processes. The fourth, the Solvay process, is classified as a synthetic process. Calcium carbonate (limestone) is used as a source of $CO_2$ in the Solvay process. Other uses of limestone and other carbonates are discussed in Volume 3, Chapter 2.

## 3.8.2 Natural soda ash production

About 25 percent of the world production is produced from natural sodium carbonate-bearing deposits referred to as natural processes. During the production process, Trona (the principal ore from which natural soda ash is made) is calcined in a rotary kiln and chemically transformed into a crude soda ash. Carbon dioxide and water are generated as by-products of this process. Carbon dioxide emissions can be estimated based on the following chemical reaction:

$$2Na_2CO_3.NaHCO_3.2H_2O\ (\text{Trona}) \rightarrow 3Na_2CO_3\ (\text{Soda Ash}) + 5H_2O + CO_2$$

### 3.8.2.1 METHODOLOGICAL ISSUES

#### CHOICE OF METHOD

The choice of method will depend on national circumstances. Emissions can be estimated using an output-based approach (emissions per unit of output), or an input-based approach (emissions per unit of input). However, it is *good practice* to use the input-based method where data are available.

Methods are classified according to the extent of plant-level data that are available. The Tier 1 method is based on default values and national statistics, and the Tier 2 method is based on complete plant-level input or output data and plant specific emission factors. If there is monitoring and direct measurement of $CO_2$ emissions this would be equivalent to a Tier 3 method.

#### Tier 1 method

Natural soda ash production emits $CO_2$ through the thermal decomposition (calcination) of the Trona ($Na_2CO_3.NaHCO_3.2H_2O$) to produce soda ash. According to the chemical reaction presented above, it takes 10.27 tonnes of Trona to produce 1 tonne of carbon dioxide. Hence, for natural soda ash production using Trona, emissions of carbon dioxide can be calculated from the Trona input or natural soda ash output by the following formula:

**EQUATION 3.14**
**$CO_2$ EMISSIONS FROM NATURAL SODA ASH PRODUCTION – TIER 1**

$$E_{CO2} = AD \bullet EF$$

Where:

$E_{CO2}$ = emissions of $CO_2$, tonnes

AD = quantity of Trona used or soda ash produced, tonnes of Trona used or tonnes natural soda ash produced

EF = emission factor per unit of Trona input or natural soda ash output, tonnes $CO_2$/tonne of Trona or tonnes $CO_2$/tonne natural soda ash produced: $EF_{Trona}$ = 0.097 tonnes $CO_2$/tonne of Trona, $EF_{Soda\ Ash}$ = 0.138 tonnes $CO_2$/tonnes natural soda ash produced.

It is *good practice* to assess the available national statistics for completeness. The choice of *good practice* methods depends on national circumstances, as shown in Figure 3.7: Decision Tree for Estimation of $CO_2$ Emissions from Natural Soda Ash Production. If no data are available for the purity of the Trona input, it is *good practice* to assume it is 90 percent and adjust the emission factor shown in Equation 3.14.

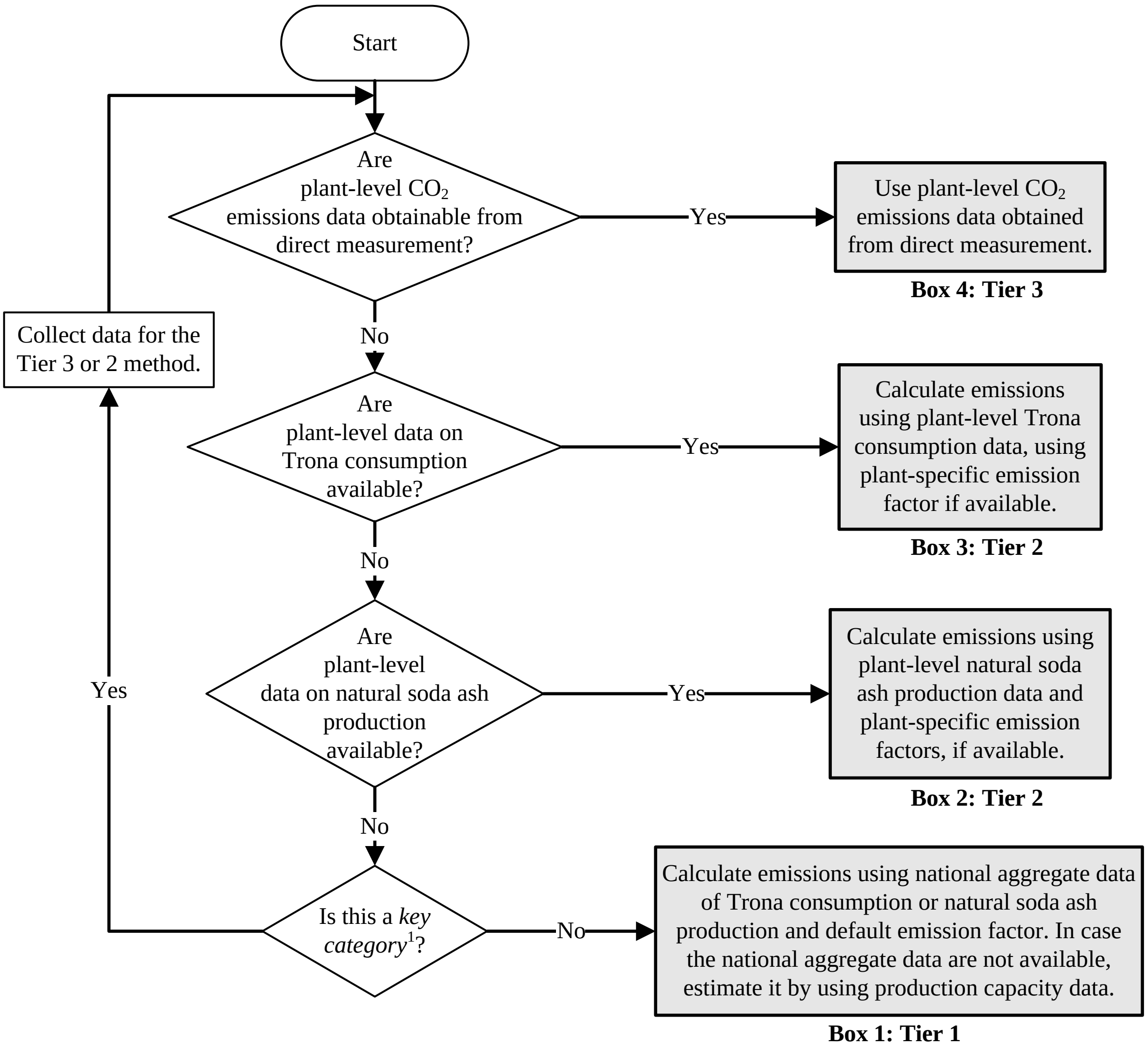
### Tier 2 method

To use the Tier 2 method, it is necessary to gather complete data on Trona consumption or natural soda ash production for each of the plants within the country along with plant-specific emission factors for the Trona input or soda ash output. The $CO_2$ emissions for each plant can be calculated using either variation of Equation 3.14. For plants where plant-specific emission factors are not available, the default emission factors provided in Equation 3.14 can be used. Total $CO_2$ emissions are the sum of the emissions from all plants.

### Tier 3 method

The Tier 3 method uses plant-level $CO_2$ emissions data obtained from direct measurement. Total emissions are the sum of emissions from all plants.

**Figure 3.7 Decision tree for estimation of $CO_2$ emissions from natural soda ash 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.

### CHOICE OF EMISSION FACTORS

#### Tier 1 method

The Tier method uses the default emission factors presented in Equation 3.14. The default emission factors are derived from the stoichiometric ratio between soda ash produced and purified sodium sesquicarbonate obtained from Trona. They are based on the main natural production process that is used at present, where soda ash is produced by calcination of purified sodium sesquicarbonate.

#### Tier 2 method

The Tier 2 method requires plant-level emission factors per unit of Trona input or per unit of natural soda ash output. Plant-level emission factors should reflect the fractional purities of the Trona input and natural soda ash output and it is *good practice* to ensure that these are taken into account in the derivation of plant-level emission factors.

### CHOICE OF ACTIVITY DATA

It is *good practice* to compile activity data at a level of detail that allows the use of the Tier 2 method. When applying the methods it is essential that a clear distinction is made between the products to avoid multiplying the incorrect emission factor by activity data.

#### Tier 1 method

The Tier 1 method requires data on national consumption of Trona or national production of natural soda ash. If national-level activity data are not available, information on production capacity can be used with emissions estimated using a default emission factor. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

#### Tier 2 method

Activity data should be collected at the plant-level to use the Tier 2 method. The most important data are the amount of Trona used for soda ash production and the amount of natural soda ash produced at each plant. Although soda ash production is not used in the calculation if emissions are derived from Trona input, it is *good practice* to collect and report these data to enable comparisons of inputs per unit of outputs over time and provide a sound basis for ensuring time series consistency.

### COMPLETENESS

Completeness of the activity data (e.g., Trona utilisation) is a crucial attribute of *good practice*. Therefore, it is *good practice* to assess the available national statistics for completeness. If data are available at the plant-level, it is *good practice* to aggregate these data and check the result with the data available at a national level. This practice enables assessment of whether any significant soda ash producer is omitted, and ensures that all production processes within the country have been considered. If data at the plant-level are not available, it is *good practice* to use production capacity data along with national statistics to estimate the emissions for completeness purposes.

### DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to calculate emissions from soda ash using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, *good practice* is to recalculate these gaps according to the guidance provided in Volume 1, Chapter 5.

## 3.8.2.2 UNCERTAINTY ASSESSMENT

### EMISSION FACTOR UNCERTAINTIES

The stoichiometric ratio is an exact number and assuming 100 percent purity of the input or output, the uncertainty of the default emission factor is negligible. However, the default factors do not take into account the fractional purities of either the Trona input or soda ash output and, in both cases, are expected to result in consistent over-estimation of emissions. As noted earlier, if no data are available for the purity of the Trona input, it is *good practice* to assume it is 90 percent and adjust the emission factor shown in Equation 3.14. It is *good practice* to develop uncertainty estimates based on plant-level data.

### ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. This will include uncertainty estimates for Trona used and natural soda ash used. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of soda ash production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±5 percent can be used.

### 3.8.2.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

#### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of the emissions estimates using different approaches

If the bottom-up approach is used, then inventory compilers should compare the emissions estimates to the estimate calculated using the top-down approach. The results of such comparisons should be recorded for internal documentation, including explanations for any discrepancies.

#### REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume1, Section 6.11. 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 data sources, and all the information needed to reproduce the estimate.

Besides the emissions, *good practice* is to report the activity data used in the calculation (Trona utilisation) and the corresponding emission factors along with all assumptions used in the derivation.

To preserve an internally consistent emission time series, whenever national methods change, *good practice* is to recalculate the entire time series. If confidentiality is an issue for any type of production, estimates may be aggregated to the minimum extent possible to maintain confidentiality.

In addition, inventory compilers should document the QA/QC procedures.

## 3.8.3 Solvay soda ash production

About 75 percent of the world production of soda ash is synthetic ash made from sodium chloride. In the Solvay process, sodium chloride brine, limestone, metallurgical coke and ammonia are the raw materials used in a series of reactions leading to the production of soda ash. Ammonia, however, is recycled and only a small amount is lost. The series of reactions involved in the Solvay process may be described as follows:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2NaCl + 2H_2O + 2NH_3 + 2CO_2 \rightarrow 2NaHCO_3 + 2NH_4Cl$$

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + CO_2 + H_2O$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The net overall reaction may be summarised as:

$$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$$

From the series of reactions presented above, $CO_2$ is generated in two pyrolysis processes. The $CO_2$ generated is captured, compressed and directed to Solvay precipitating towers for consumption in a mixture of brine (aqueous NaCl) and ammonia. Although $CO_2$ is generated as a by-product, the $CO_2$ is recovered and recycled for use in the carbonation stage and in theory the process is neutral, i.e., $CO_2$ generation equals uptake.

In practice, some $CO_2$ is emitted to the atmosphere during production by the Solvay process because more $CO_2$ is produced than is stoichiometrically required. The excess $CO_2$ arises from calcining the limestone with metallurgical grade coke. The limestone is combined with the coke at approximately 7 percent of limestone by weight.

The estimation of the $CO_2$ emissions from a stand alone soda ash plant should be based on an overall balance of $CO_2$ around the whole chemical process. For inventory purposes, a simplified version of the balance may be used assuming that the $CO_2$ emissions result from the stoichiometric oxidation of the coke carbon. The Solvay ammonia soda ash production process is a chemical industry activity and emissions should be reported under the Industrial Processes and Product Use (IPPU) Sector.

**BOX 3.7**
**DOUBLE COUNTING**

In order to avoid double counting, $CO_2$ emissions generated in the process of soda ash production should be accounted in the **IPPU Sector**, and should not be included in the **Energy Sector**. Coke used in the production process should be deducted from the **Energy Sector** as a non-energy use of coke.

### 3.8.3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

The allocation of emissions from the use of metallurgical grade coke in the Solvay process to the **Energy Sector** means that a methodology for estimating these emissions is not provided in the **Industrial Processes and Product Use Sector**. However, data on soda ash production from the Solvay process should be collected and collated to ensure that all data on soda ash production by process are available for recording, reporting, archiving and reconciliation with national statistics on soda ash use.

#### QUALITY ASSURANCE/ QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume1, Section 6.11. 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 data sources, and all the information needed to reproduce the estimate.

# 3.9 PETROCHEMICAL AND CARBON BLACK PRODUCTION

## 3.9.1 Introduction

The petrochemical industry uses fossil fuels (e.g., natural gas) or petroleum refinery products (e.g., naphtha) as feedstocks. This section provides guidance for estimating emissions from the production of methanol, ethylene and propylene[2], ethylene dichloride, ethylene oxide, and acrylonitrile. These petrochemicals are addressed in detail because their global production volume and associated greenhouse gas emissions are relatively large. However, the chemicals included are not intended to represent the entire petrochemical process industry. There are a number of other petrochemical processes that emit small amounts of greenhouse gases for which specific guidance is not provided (e.g., styrene production).

This section also provides guidance for production of carbon black. Carbon black is not considered to be a petrochemical; however, the carbon black production process uses petrochemical feedstocks. Emissions from carbon black production are smaller than for petrochemical processes but may be significant for certain countries.

Examples of feedstock to product production chains for methanol, ethylene and propylene, ethylene dichloride, ethylene oxide, acrylonitrile, and carbon black are included in the Annex to Section 3.9.

### Allocation and Reporting

Within the petrochemical industry and carbon black industry, primary fossil fuels (natural gas, petroleum, coal) are used for non-fuel purposes in the production of petrochemicals and carbon black. The use of these primary fossil fuels may involve combustion of part of the hydrocarbon content for heat raising and the production of secondary fuels (e.g., off gases).

Combustion emissions from fuels obtained from the feedstocks should be allocated to the source category in the IPPU Sector. However, where the fuels are not used within the source category but are transferred out of the process for combustion elsewhere (e.g., for district heating purposes) the emissions should be reported in the appropriate Energy Sector source category. The industries are included in the source category Chemical Industry (2B1 – 2B10), see Figure 1.1, Industrial Process and Product Use Source Categories in Chapter 1 of this volume. Further discussion of the non-energy use of fuels is included in Chapters 1 and 5 of this volume.

Note that national energy statistics may include total combustion of fossil fuels (including natural gas, oil, and coal,) and also secondary fuels (such as industrial process off gases) for energy production. It is important to investigate if fuels used in petrochemical industries are included in national energy statistics. If this is the case, emissions from petrochemical processes should be subtracted from the calculated energy sector emissions to avoid double counting. This is particularly relevant for ethylene and methanol, where primary fuel (e.g., natural gas, ethane, propane) feedstock consumption may be reported in national energy statistics.

Should carbon dioxide ($CO_2$) capture technology be installed and used at a plant, it is *good practice* to deduct the $CO_2$ captured in a higher tier emissions calculation. The default assumption is that there is no $CO_2$ capture and storage (CCS) taking place. Any methodology taking into account $CO_2$ capture should consider that $CO_2$ emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately, inventory compilers should ensure that the same quantities of $CO_2$ are not double counted. In these cases the total amount of $CO_2$ captured should preferably be reported in the corresponding energy combustion and IPPU source categories in proportion to the amounts of $CO_2$ generated in these source categories. For additional information on $CO_2$ capture and storage refer to Volume 3, Section 1.2.2 and for more details on capture and storage to Volume 2, Section 2.3.4.

Petrochemical processes may utilise $CO_2$ captured elsewhere as a feedstock, and $CO_2$ may also be captured from petrochemical processes. This may create potential double counting issues. For example, some methanol plants may utilise by-product $CO_2$ captured from other industrial processes as a feedstock for methanol production. To avoid double counting the $CO_2$ captured should not be reported as $CO_2$ emissions from the process from which the $CO_2$ is captured.

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[2] Note that there is no separate inventory methodology for propylene. Propylene is assumed to be a co-product of ethylene production.

## METHANOL

Worldwide almost all methanol is made by way of steam reforming of natural gas. The steam reforming and shift reaction produce ‘synthesis gas’ comprised of $CO_2$, carbon monoxide (CO), and hydrogen ($H_2$). The natural gas to methanol production process produces methanol and by-product $CO_2$, CO, and $H_2$ from the synthesis gas. There are several alternative processes for producing methanol from natural gas or other feedstocks. These include conventional reforming process, combined reforming and partial oxidation process. An example of a feedstock to product process flow diagram for methanol production is provided in an Annex to Section 3.9 (Annex 3.9A). Process descriptions for methanol production are included in Box 3.8 below.

### BOX 3.8
### METHANOL PROCESS DESCRIPTIONS

**Conventional Reforming Process**

The Conventional Reforming Process for methanol production involves steam reforming (which may include either a single reformer unit or both a primary reformer unit and a secondary reformer unit) and methanol synthesis. The overall equations for the Conventional Reforming Process are:

| Steam Reforming | Shift Reaction | Methanol Production |
|---|---|---|
| $CH_4 + H_2O \rightarrow CO + 3\ H_2$ | $CO + H_2O \rightarrow CO_2 + H_2$ | $CO + 2\ H_2 \rightarrow CH_3OH$ |
| $C_nH_m + nH_2O \rightarrow nCO + (m/2 + n)\ H_2$ | | $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ |

| Reforming/Shift Reaction | Methanol Production |
|---|---|
| $2\ CH_4 + 3\ H_2O \rightarrow CO + CO_2 + 7\ H_2$ | $CO + CO_2 + 7\ H_2 \rightarrow 2\ CH_3OH + 2\ H_2 + H_2O$ |

The surplus hydrogen from this process and methanol process purge gas containing methane ($CH_4$) and non-methane volatile organic compounds (NMVOC) are recovered and burned for energy recovery, generally within the methanol production process, to produce process steam and/or electricity for the process. The Conventional Reforming Process may utilise $CO_2$ captured from other industrial processes as a supplemental feedstock to the methanol production process.

**Combined Reforming Process**

The Combined Reforming Process combines the Conventional Steam Reforming process with a Catalytic Partial Oxidation process. The Partial Oxidation chemical equations are:

| Methanol Steam Reforming Reaction | Feedstock Oxidation Reaction |
|---|---|
| $CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2 \rightarrow CH_3OH$ | $CH_4 + O_2 \rightarrow CO_2 + 2\ H_2$ |

The Combined Reforming Process produces a synthesis gas that contains a more balanced ratio of hydrogen to carbon monoxide (CO) and $CO_2$ than does the Conventional Reforming Process, and does not produce a hydrogen gas stream for energy recovery. The Combined Reforming Process produces a purge gas containing $CH_4$ that is burned for energy recovery within the methanol process.

**Other Production Processes**

Methanol may also be produced from the partial oxidation of oil, coal, or petrochemical feedstocks, or by gasification of coal to synthesis gas, however; these feedstocks and processes currently represent only a small amount of worldwide methanol production.

## ETHYLENE

Worldwide almost all ethylene is made by way of steam cracking of petrochemical feedstocks. Ethylene may be produced from steam cracking of petrochemical feedstocks in a petrochemical plant, and may also be produced from cracking and other processes operated at petroleum refineries. Steam cracking for ethylene production also produces secondary products including propylene and butadiene. A process description for steam cracking process for ethylene production is provided in Box 3.9 below.

**BOX 3.9**
**ETHYLENE PROCESS DESCRIPTION**

**Steam Cracking**

The fundamental chemical equation for ethylene production is as follows:

Ethane Dehydrogenation to Ethylene

$C_2H_6 \rightarrow C_2H_4 + H_2$

The types and mix of feedstock used in steam cracking for ethylene production varies by region, and include ethane, propane, butane, naphtha, gas oil, and other petrochemical feedstocks. In the United States, most ethylene is produced from steam cracking of ethane, while in Europe, Korea, and Japan most ethylene is produced from steam cracking of naphtha.

Steam cracking of petrochemical feedstocks to produce ethylene also produces other high value (saleable) petrochemical products, including propylene, butadiene, and aromatic compounds. Most propylene worldwide is produced as a by-product of ethylene production, recovered either from steam crackers or from fluid catalytic cracking units at petroleum refineries. Steam crackers using naphtha feedstock are the largest source of propylene. There are other process technologies that are used to produce propylene including catalytic dehydrogenation of propane. Note that the emissions estimation methods in this section apply only to production of ethylene and propylene in steam crackers and do not apply to other process technologies used to produce ethylene or propylene. The steam cracking process also produces by-product hydrogen and methane and C4+ hydrocarbons that are generally burned for energy recovery within the process.

(Houdek, 2005: Figure 1 on Page 3, Page 4)

## ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER

Worldwide almost all ethylene dichloride (1, 2 dichloroethane) is made by way of direct chlorination or oxychlorination of ethylene, or by a combination of the two processes (referred to as the ‘balanced process.’) An example of a feedstock to product process flow diagram for ethylene dichloride production is provided in an Annex to Section 3.9 (Annex 3.9A). Process descriptions for ethylene dichloride and vinyl chloride monomer production are provided in Box 3.10 below. Note that the chemical compound ‘ethylene dichloride’ is also referred to as 1,2-dichloroethane. The chemical compound ‘dichloroethylene,’ also referred to as 1, 2-dichloroethene, is a different compound.

**BOX 3.10**
**ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER PROCESS DESCRIPTIONS**

**Direct Chlorination and Oxychlorination Processes**

The direct chlorination process involves gas-phase reaction of ethylene with chlorine to produce ethylene dichloride. The oxychlorination process involves gas-phase reaction of ethylene with hydrochloric acid and oxygen to produce ethylene dichloride and water. The ethylene dichloride is then cracked to produce vinyl chloride monomer and hydrochloric acid. The oxychlorination process produces a process off gas containing by-product $CO_2$ produced from the direct oxidation of the ethylene feedstock.

The fundamental chemical equations for the direct chlorination and oxychlorination processes are as follows:

| Direct chlorination | Oxychlorination reaction | Ethylene dichloride>vinyl chloride |
|---|---|---|
| $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ | $C_2H_4 + \frac{1}{2} O_2 + 2\ HCl \rightarrow C_2H_4Cl_2 + H_2O$<br>$[C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O]$ | $2\ C_2H_4Cl_2 \rightarrow 2\ CH_2CHCl + 2\ HCl$ |

### BOX 3.10 (CONTINUATION)
### ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER PROCESS DESCRIPTIONS

**Balanced Process**

The combination of the direct chlorination process to produce ethylene dichloride and the ethylene dichloride cracking process to produce vinyl chloride monomer produces a surplus of hydrogen chloride. The oxychlorination process provides a sink for the hydrogen chloride. Therefore, ethylene dichloride/vinyl chloride monomer production facilities may operate a ‘balanced process’ in which both the direct chlorination process and the oxychlorination process are combined. The ‘balanced process’ also produces process vent gas containing by-product $CO_2$ from the direct oxidation of the ethylene feedstock.

The fundamental chemical equations for the ‘balanced process’ for producing vinyl chloride monomer from ethylene are as follows:

| Ethylene Dichloride-Vinyl Chloride Monomer Reaction | Feedstock Oxidation Reaction |
|---|---|
| $2\ C_2H_4 + Cl_2 + ½\ O_2 \rightarrow 2\ CH_2CHCl + H_2O$ | $[C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O]$ |

The direct chlorination process and the oxychlorination process for ethylene dichloride production are not 100 percent efficient in the utilisation of the ethylene feedstock. On the order of three percent of the ethylene feedstock is not converted to ethylene dichloride but is converted either to $CO_2$ (by direct oxidation in the oxychlorination process) or to other chlorinated hydrocarbons (in either the oxychlorination process or the direct chlorination process.) Process off gas containing other chlorinated hydrocarbons is generally treated prior to discharge to the atmosphere. The chlorinated hydrocarbons are converted to $CO_2$ in a thermal incineration process or a catalytic incineration process. Most ethylene dichloride/vinyl chloride monomer plants recover energy from the incinerator off gases and process off gases.

## ETHYLENE OXIDE

Ethylene oxide ($C_2H_4O$) is manufactured by reacting ethylene with oxygen over a catalyst. The by-product $CO_2$ from the direct oxidation of the ethylene feedstock is removed from the process vent stream using a recycled carbonate solution, and the recovered $CO_2$ may be vented to the atmosphere or recovered for further utilisation (e.g., food production.) The oxygen may be supplied to the process through either air or through pure oxygen separated from air. An example of a feedstock to product process flow diagram for ethylene oxide production is provided in an Annex to Section 3.9 (Annex 3.9A). A process description for ethylene oxide production is provided in Box 3.11 below.

### BOX 3.11
### ETHYLENE OXIDE PROCESS DESCRIPTION

The fundamental chemical equations for the production of ethylene oxide from ethylene and the production of monoethylene glycol are as follows:

| Ethylene Oxide Reaction | Feedstock Oxidation Reaction | Monoethylene Glycol Production |
|---|---|---|
| $C_2H_4 + ½\ O_2 \rightarrow C_2H_4O$ | $C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$ | $C_2H_4O + H_2O \rightarrow HO\text{-}\ C_2H_4\ \text{-}\ OH$ |

The ratio of the ethylene oxide reaction and the by-product reaction defines the selectivity of the ethylene oxide process, in terms of tonnes of ethylene consumed per tonne of ethylene oxide produced. The combined ethylene oxide reaction and by-product $CO_2$ reaction is exothermic and generates heat, which is recovered to produce steam for the process. The ethylene oxide process also produces other liquid and off-gas by-products (e.g., ethane) that may be burned for energy recovery within the process. The amount of $CO_2$ and other by-products produced from the process and the amount of steam produced from the process is dependent upon the selectivity of the process.

Ethylene oxide is used as a feedstock in the manufacture of glycols, glycol ethers, alcohols, and amines. Worldwide approximately 70 percent of ethylene oxide produced is used in the manufacture of glycols, including monoethylene glycol.

## ACRYLONTRILE

Worldwide more than 90 percent of acrylonitrile (vinyl cyanide) is made by way of direct ammoxidation of propylene with ammonia ($NH_3$) and oxygen over a catalyst. This process is referred to as the SOHIO process, after the Standard Oil Company of Ohio (SOHIO). Acrylonitrile can also be manufactured by ammoxidation of propane or directly from reaction of propane with hydrogen peroxide. The propane-peroxide direct process has recently been commercialised by British Petroleum (BP) and other manufacturers. (DOE, 2000) However, process data were not readily available for production of acrylonitrile from propane feedstocks. Therefore no emission estimation methodology is provided for this process. An example of a feedstock to product process flow diagram for acrylonitrile production from propylene is provided in an Annex to Section 3.9 (Annex 3.9A). Process descriptions for acrylonitrile production are provided in Box 3.12 below.

### BOX 3.12
### ACRYLONITRILE PROCESS DESCRIPTION

**SOHIO Process**

The SOHIO process involves a fluidized bed reaction of chemical-grade propylene, ammonia, and oxygen over a catalyst. The catalyst is a mixture of heavy metal oxides (including bismuth and molybdenum). The process produces acrylonitrile as its primary product and acetonitrile (methyl cyanide) and hydrogen cyanide (HCN) as secondary products. The process yield of the primary product acrylonitrile depends in part on the type of catalyst used and the process configuration. The ammoxidation process also produces by-product $CO_2$, CO, and water from the direct oxidation of the propylene feedstock, and produces other hydrocarbons from side reactions in the ammoxidation process.

The acetonitrile and hydrogen cyanide are separated from the acrylonitrile by absorption, and the hydrogen cyanide may be used in manufacturing other products on site or sold as product. Hydrogen cyanide that is not used or sold may be burned for energy recovery or flared. The acetonitrile may be also recovered for sale as a product, but more often the acetonitrile is burned for energy recovery or flared. The off gas from the main absorber vent containing $CO_2$, CO, nitrogen, water, unreacted propylene, and other hydrocarbons, may be flared or treated in a thermal or catalytic oxidation unit, with or without energy recovery.

Heavy bottoms liquids from the acetonitrile – hydrogen cyanide - acrylonitrile absorption separations process may also be burned for energy recovery or recycled. Acrylonitrile and other non-methane hydrocarbons are also released from miscellaneous process vents, including storage tanks. These miscellaneous process vents may be flared or captured and burned for energy recovery.

The fundamental chemical equations for the production of acrylonitrile by ammoxidation are as follows:

| | |
|---|---|
| Acrylonitrile Reaction<br>$CH_2{=}CHCH_3 + 1.5\ O_2 + NH_3 \rightarrow CH_2{=}CHCN + 3\ H_2O$ | Hydrogen Cyanide Reaction<br>$CH_2{=}CHCH_3 + 3\ O_2 + 3\ NH_3 \rightarrow 3\ HCN + 6\ H_2O$ |
| Acetonitrile Reaction<br>$CH_2{=}CHCH_3 + 1.5\ O_2 + 1.5\ NH_3 \rightarrow 1.5\ CH_3CN + 3\ H_2O$ | Feedstock Oxidation<br>$C_3H_6 + 4.5\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$<br>$C_3H_6 + 3\ O_2 \rightarrow 3\ CO + 3\ H_2O$ |

The ammoxidation of propylene to acrylonitrile is not 100 percent efficient in utilisation of the propylene feedstock. On the order of 70 percent of the propylene feedstock is converted to acrylonitrile. On the order of 85 percent of the propylene feedstock is converted to either the primary product acrylonitrile or secondary products acetonitrile or hydrogen cyanide. The remainder of the propylene feedstock is either converted directly to $CO_2$ by direct oxidation of the feedstock in the ammoxidation process or converted to other hydrocarbons through side reactions in the ammoxidation process.

## CARBON BLACK

Worldwide almost all carbon black is produced from petroleum-based or coal-based feedstocks using the ‘furnace black’ process. Process descriptions for carbon black production are provided in Box 3.13 below.

The furnace black process is a partial combustion process where a portion of the carbon black feedstock is combusted to provide energy to the process. Carbon black may also be produced using other petroleum-feedstock or coal-based feedstock partial oxidation processes, including the ‘channel black’ process and ‘lamp black’ process, or may be produced directly by the partial oxidation of natural gas or aromatic oils (‘channel black process’). Carbon black may also be produced by the thermal cracking of acetylene-containing feedstocks (‘acetylene black process’) or by the thermal cracking of other hydrocarbons (‘thermal black process’.) Approximately 95 percent of worldwide carbon black production is by way of the furnace black process; the remaining 5 percent being produced by way of other processes.

Approximately 90 percent of carbon black produced worldwide is used in the tire and rubber industry (referred to as ‘rubber black.’) and the remainder is used in pigment applications (e.g., inks) and other applications (e.g., carbon dry cell batteries.) Carbon black may be produced using a furnace black process, thermal black process, acetylene carbon black process, channel black process and lamp black process. These processes are further described in Box 3.13 below. An example of a feedstock to product process flow diagram for carbon black production using the furnace black process is provided in an Annex to Section 3.9 (Annex 3.9A).

### BOX 3.13
### CARBON BLACK PRODUCTION PROCESS DESCRIPTIONS

**Furnace Black Process**

The furnace black process produces carbon black from ‘carbon black feedstock’ (also referred to as ‘carbon black oil’) which is a heavy aromatic oil that may be derived either as a by-product of the petroleum refining process or the metallurgical (coal) coke production process. For either petroleum-derived or coal-derived feedstock, the carbon black feedstock, the ‘primary feedstock,’ is injected into a furnace heated by a ‘secondary feedstock’ (generally natural gas or oil). Both the natural gas secondary feedstock and a portion of the carbon black feedstock are oxidized to provide heat to the production process that pyrolyzes the remaining carbon black feedstock to carbon black. The vent gas from the furnace black process contains $CO_2$, CO, sulphur compounds, $CH_4$, and NMVOCs. A portion of the tail gas is generally burned for energy recovery to heat the downstream carbon black product dryers. The remaining tail gas may also be burned for energy recovery, flared, or vented uncontrolled to the atmosphere.

**Thermal Black Process**

Carbon black is produced in the thermal black process by thermal decomposition of gaseous hydrocarbons or atomized petroleum oils in the absence of air in a pair of production furnaces. The carbon black feedstock is introduced into a preheated furnace that is heated by a secondary feedstock, usually natural gas, and by the off gas from the carbon black production process. One of the pair of furnaces is being preheated by the secondary feedstock while the other furnace is receiving carbon black feedstock. Yield from this process is approximately 45 percent of total carbon input to the process (or 40 percent with respect to the total carbon black feedstock used) and energy utilisation is approximately 280 MJ/kg carbon black produced.

**Acetylene Black Process**

Carbon black produced from acetylene or acetylene-containing light hydrocarbons by feeding the feedstock to a preheated reactor where the acetylene decomposes to carbon black in an exothermic process. Total worldwide production of acetylene black is only approximately 40 000 metric tons per year. The carbon black yield from this process is approximately 95-99 percent of theoretical yield. Acetylene black is approximately 99.7 percent carbon.

**Other Production Processes**

The channel black process involves partial oxidation of vaporised carbon black feedstock that is burned in a furnace with a carrier gas (which may be coke oven gas, hydrogen, or methane). The carbon black yield for this process may be 60 percent of total carbon input for production of rubber-grade carbon black or 10-30 percent of total carbon input for pigment-grade carbon black.

The lamp black process involves open burning of carbon black feedstock in shallow pans. Data are not readily available concerning feedstock yield and energy consumption for the lamp black process. This process represents an insignificant percentage of worldwide carbon black production.

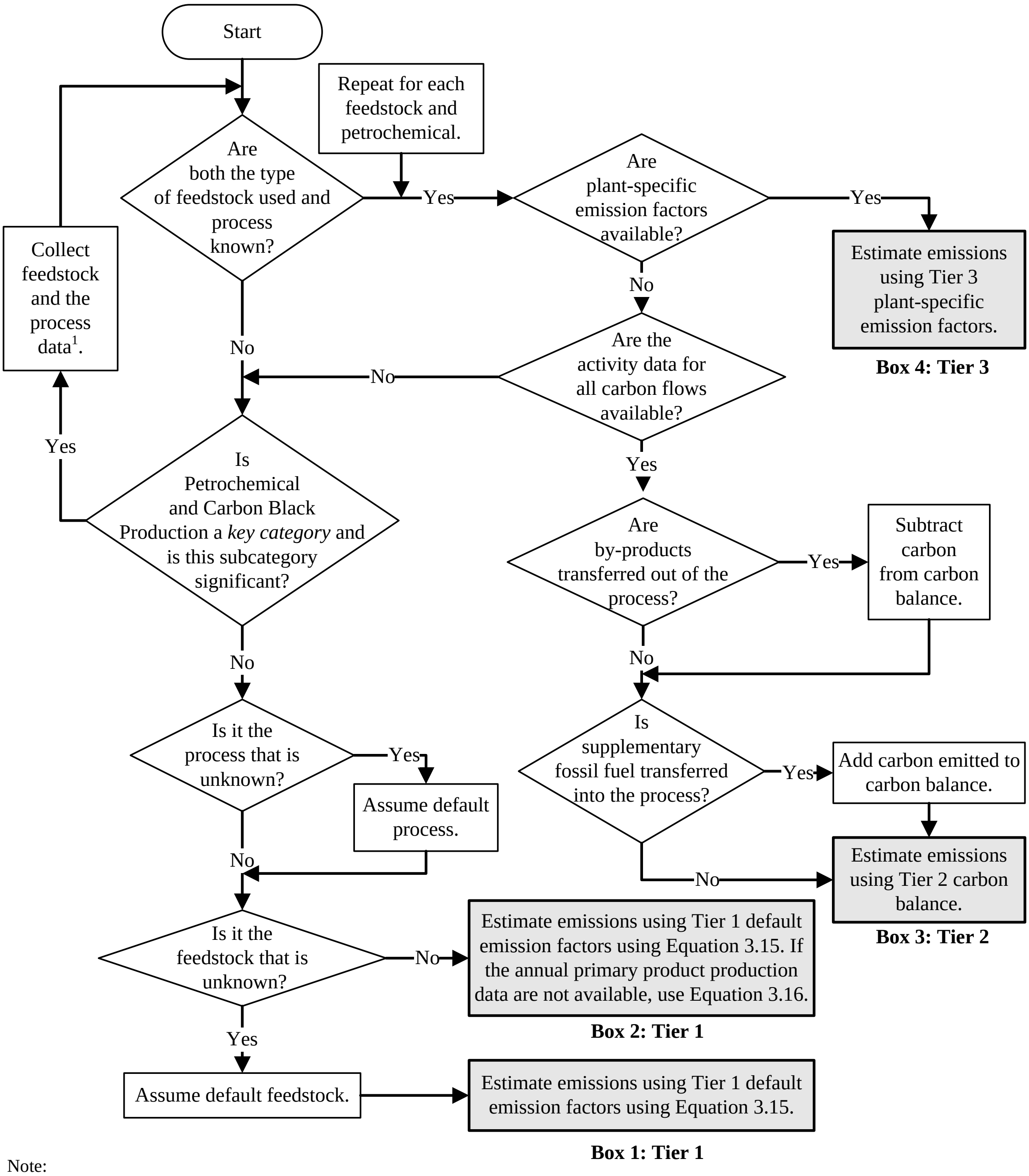
(Kirk Othmer, 1992)

## 3.9.2 Methodological issues

### 3.9.2.1 CHOICE OF METHOD

The emissions from petrochemical and carbon black production vary both with the process used and the feedstock used. The choice of method should thus be repeated for each product, process and feedstock used. Three methodological tiers are provided depending on the availability of data. The choice of method depends on national circumstances and is given by the decision trees in Figure 3.8 and Figure 3.9.

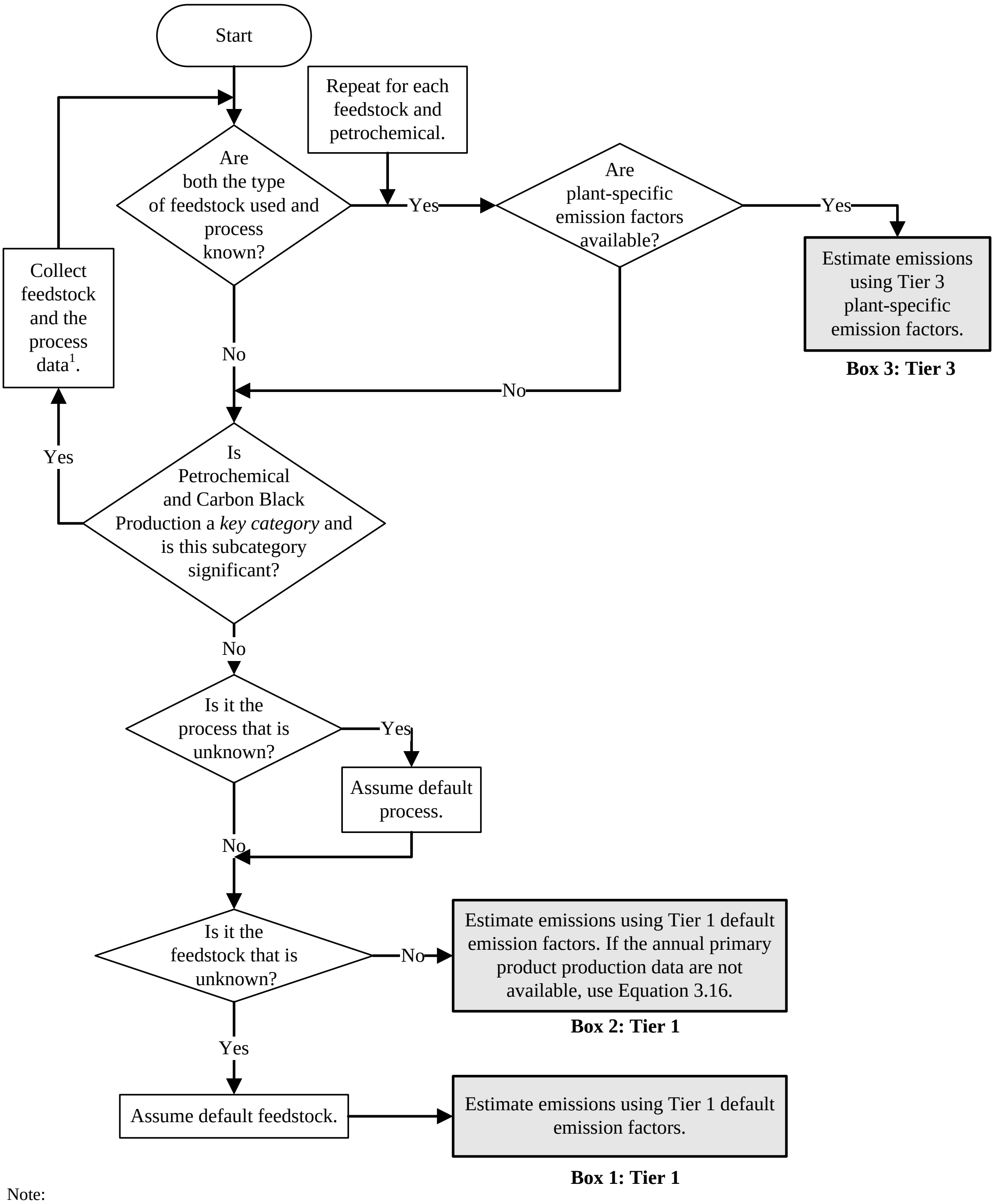
**Figure 3.8 Decision tree for estimation of $CO_2$ emissions from petrochemical industry and carbon black industry**



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.

**Figure 3.9 Decision tree for estimation of $CH_4$ emissions from petrochemical industry and carbon black industry**



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.
2. Note that there is no Tier 2 method for estimating $CH_4$ emissions. The Tier 2 method is a total feedstock carbon mass balance method that is applicable to estimating total carbon ($CO_2$) emissions but not applicable to estimating $CH_4$ emissions.

The Tier 3 methodology can be used to estimate plant-level $CO_2$ emissions and $CH_4$ emissions. The Tier 3 method depends upon the availability of plant-specific data for the petrochemical process. The Tier 2 methodology is a mass balance approach that is applicable to estimating $CO_2$ emissions but is not applicable to estimating $CH_4$ emissions. When using the Tier 2 methodology, both carbon flows of primary and secondary feedstocks to the process are included in the mass balance calculation. Carbon flows of primary fuels to the process may involve combustion of part of the hydrocarbon content for heat raising and the production of secondary fuels (e.g., off gases). In order to apply the Tier 2 methodology the flows of primary and secondary feedstocks to the process and the flows of primary and secondary products must be characterised, and the flows of by-products burned for energy recovery within the process and flows of by-products transferred out of the process must be characterised.

## CARBON DIOXIDE

The decision tree for choice of method for $CO_2$ emissions is shown in Figure 3.8. The Tier 1, Tier 2, and Tier 3 methods are described in this section.

### Tier 1 product-based emission factor method

The Tier 1 emission factor methodology is applied to estimate $CO_2$ emissions from the petrochemical process in cases where neither plant specific data nor activity data for carbon flows are available for the petrochemical process. The Tier 1 emission factor method does not require activity data for the consumption of each carbon-containing feedstock to the petrochemical production process. It requires only activity data for the amount of product produced. The Tier 1 methodology does not consider the carbon content of emissions of carbon monoxide or NMVOC that may be generated by the petrochemical processes. The equations in this section for petrochemical production processes also apply to carbon black production.

The Tier 1 method calculates emissions from petrochemical processes on the basis of activity data for production of each petrochemical and the process-specific emission factor for each petrochemical, as shown in the Equation 3.15 for production of each primary petrochemical product (e.g., methanol, ethylene, ethylene dichloride, ethylene oxide, acrylonitrile) and carbon black.

**EQUATION 3.15**
**TIER 1 $CO_2$ EMISSION CALCULATION**

$$ECO2_i = PP_i \bullet EF_i \bullet GAF / 100$$

Where:

$ECO2_i$ = $CO_2$ emissions from production of petrochemical *i*, tonnes

$PP_i$ = annual production of petrochemical *i*, tonnes

$EF_i$ = $CO_2$ emission factor for petrochemical *i*, tonnes $CO_2$/tonne product produced

GAF = Geographic Adjustment Factor (for Tier 1 $CO_2$ emission factors for ethylene production, See Table 3.15), percent

Tier 1 $CO_2$ emission factors for ethylene production (discussed in Section 3.9.2.2) have been developed based on data for ethylene steam crackers operating in Western Europe. Geographic Adjustment Factors are applied to the Tier 1 emission factor to account for regional variability in steam cracker operating efficiency. Geographic Adjustment Factors are only applicable to ethylene production.

If activity data for annual primary product production are not available, primary product production may be estimated from feedstock consumption, as shown in the Equation 3.16:

**EQUATION 3.16**
**PRIMARY PRODUCT PRODUCTION ESTIMATE CALCULATION**

$$PP_i = \sum_k \left( FA_{i,k} \bullet SPP_{i,k} \right)$$

Where:

$PP_i$ = annual production of petrochemical *i*, tonnes

$FA_{i,k}$ = annual consumption of feedstock *k* consumed for production of petrochemical (i), tonnes

$SPP_{i,k}$ = specific primary product production factor for petrochemical *i* and feedstock *k* ,tonnes primary product/tonne feedstock consumed

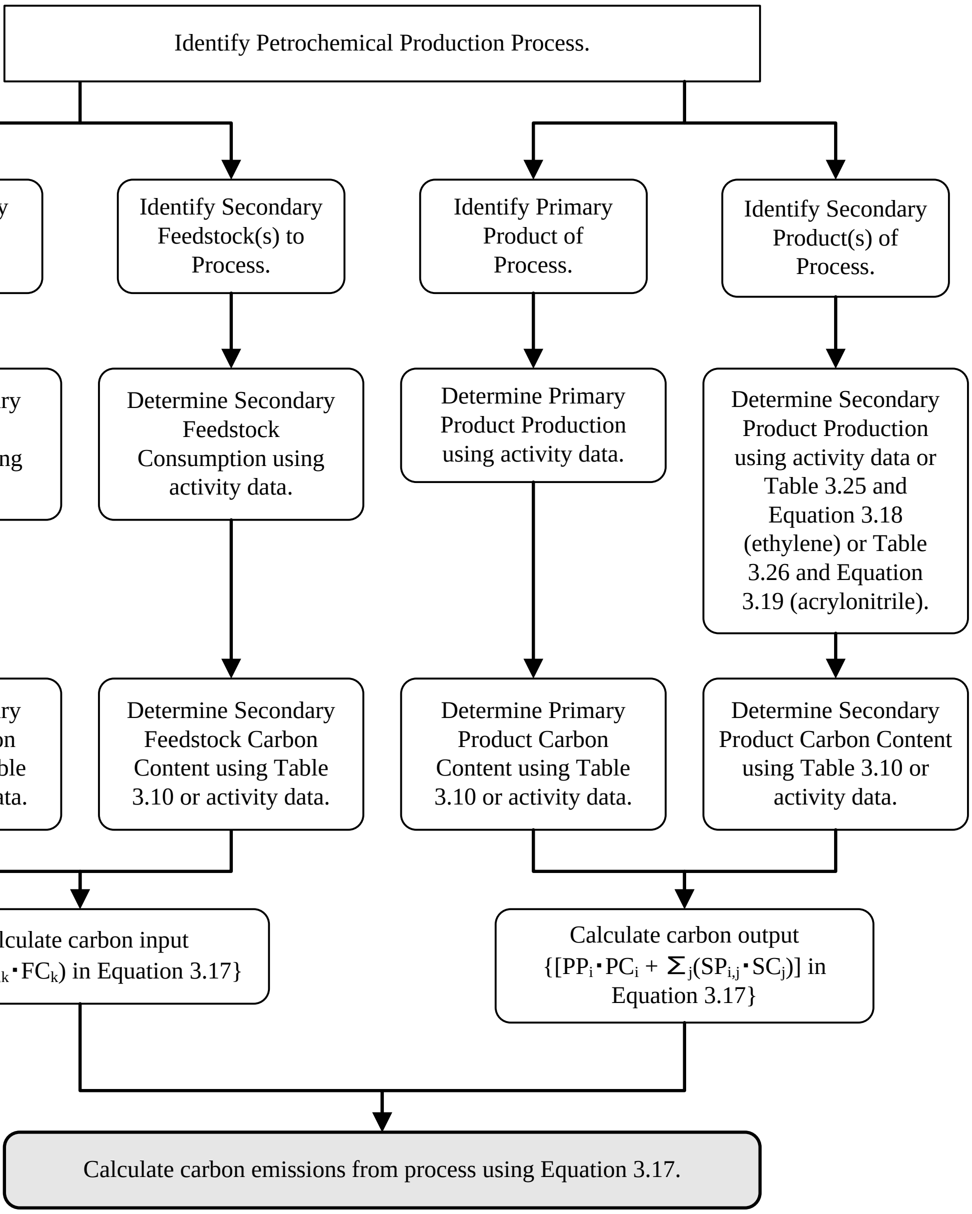
Either Equation 3.15 or both Equation 3.15 and Equation 3.16 would be applied separately to each of the known feedstocks for each petrochemical process. The Tier 1 emissions estimate shown in Box 1 of Figure 3.8 would utilise Equation 3.15, while the Tier 1 emissions estimate shown in Box 2 of Figure 3.8 would use either

Equation 3.15 or both Equation 3.16 and Equation 3.15. Equation 3.15 would be utilised alone in cases where annual primary product production data are available for the petrochemical process. In cases where annual primary product production data are not available but feedstock consumption data are available for the petrochemical process, Equation 3.16 would be utilised to estimate the annual production of primary products, and the annual primary product production estimated using Equation 3.16 would then be applied in Equation 3.15 to estimate the emissions.

### Tier 2 total feedstock carbon balance method

The Tier 2 method is a feedstock-specific and process-specific carbon balance approach. This approach is applicable in cases where activity data are available for both feedstock consumption and primary and secondary product production and disposition. Activity data for all carbon flows are required to implement the Tier 2 methodology. Examples of process flow diagrams that illustrate feedstock and product flows for the methanol, ethylene dichloride, ethylene oxide, acrylonitrile, and carbon black production processes are included in an Annex to Section 3.9. The number of potential feedstocks and products for ethylene production from the steam cracking process is such that the process is better illustrated by a feedstock-product matrix rather than by a process flow diagram. The feedstock-product matrix for ethylene production is included in Table 3.25 in Section 3.9.2.3. A flow diagram of the Tier 2 method is shown in Figure 3.10.

**Figure 3.10 Tier 2 carbon mass balance flow diagram**



The Tier 2 method calculates the difference between the total amount of carbon entering into the production process as primary and secondary feedstock and the amount of carbon leaving the production process as petrochemical products. The difference in carbon content of the primary and secondary feedstocks and the carbon content of the primary and secondary products produced by and recovered from the process is calculated as $CO_2$. The Tier 2 mass balance methodology is based on the assumption that all of the carbon input to the process is converted either into primary and secondary products or into $CO_2$. This means that any of the carbon input to the process that is converted into CO, $CH_4$, or NMVOC are assumed to be $CO_2$ emissions for the purposes of the mass balance calculation.

The overall mass balance equation for the Tier 2 methodology is Equation 3.17.

**EQUATION 3.17**
**OVERALL TIER 2 MASS BALANCE EQUATION**

$$ECO2_i = \left\{ \sum_k \left( FA_{i,k} \bullet FC_k \right) - \left[ PP_i \bullet PC_i + \sum_j \left( SP_{i,j} \bullet SC_j \right) \right] \right\} \bullet 44/12$$

Where:

$ECO2_i$ = $CO_2$ emissions from production of petrochemical *i*, tonnes

$FA_{i,k}$ = annual consumption of feedstock *k* for production of petrochemical *i*, tonnes

$FC_k$ = carbon content of feedstock *k*, tonnes C/tonne feedstock

$PP_i$ = annual production of primary petrochemical product *i*, tonnes

$PC_i$ = carbon content of primary petrochemical product *i*, tonnes C/tonne product

$SP_{i,j}$ = annual amount of secondary product *j* produced from production process for petrochemical *i*, tonnes
[The value of $SP_{i,j}$ is zero for the methanol, ethylene dichloride, ethylene oxide, and carbon black processes because there are no secondary products produced from these processes. For ethylene production and acrylonitrile production, see secondary product production Equations 3.18 and 3.19 below to calculate values for $SP_{i,j}$.]

$SC_j$ = carbon content of secondary product *j*, tonnes C/tonne product

For ethylene production and acrylonitrile production there are both primary and secondary products produced by the process. If activity data are not available for the amount of secondary products produced by these processes, the amount of secondary products produced may be estimated by applying default values to the primary feedstock consumption, as shown in Equations 3.18 and 3.19:

**EQUATION 3.18**
**ESTIMATE SECONDARY PRODUCT PRODUCTION FROM PRIMARY PRODUCT [ETHYLENE] PRODUCTION**

$$SP_{Ethylene,j} = \sum_k \left( FA_{Ethylene,k} \bullet SSP_{j,k} \right)$$

Where:

$SP_{Ethylene,j}$ = annual production of secondary product *j* from ethylene production, tonnes

$FA_{Ethylene\ k}$ = annual consumption of feedstock *k* consumed for ethylene production, tonnes

$SSP_{j,k}$ = specific secondary product production factor for secondary product *j* and feedstock *k*, tonnes secondary product/tonne feedstock consumed

**EQUATION 3.19**
**ESTIMATE SECONDARY PRODUCT PRODUCTION FROM PRIMARY PRODUCT [ACRYLONITRILE] PRODUCTION**

$$SP_{Acrylonitrile,j} = \sum_k \left( FP_{Acrylonitrile,k} \bullet SSP_{j,k} \right)$$

Where:

$SP_{Acrylonitrile,j}$ = annual production of secondary product *j* from acrylonitrile production, tonnes

$FP_{Acrylonitrile,k}$ = annual production of acrylonitrile from feedstock *k*, tonnes

$SSP_{j,k}$ = specific secondary product production factor for secondary product *j* and feedstock *k*, tonnes secondary product/tonne acrylonitrile produced

Note: It is anticipated that in most cases only a single feedstock (propylene) would be used for acrylonitrile production.

### *Feedstock and product carbon contents*

Carbon contents of feedstocks and products of petrochemical production processes are listed in Table 3.10, in units of tonnes of carbon per tonne of feedstock or product. Carbon contents of pure substances (e.g., methanol) are calculated from the chemical formula. Carbon contents of other feedstocks and products (e.g., carbon black feedstock, carbon black) are estimated from literature sources. Representative carbon contents of fossil fuels (e.g., natural gas, naphtha) can be found in Table 1.3 in Chapter 1 of Volume 2: Energy; however, carbon contents for fossil fuels will vary by country and region and are best obtained from national energy statistics or fossil fuel product specifications or national standards.

## Tier 3 direct estimate of plant-specific emissions

The most rigorous *good practice* method is to use plant specific data to calculate $CO_2$ emissions from the petrochemical production process. In order to apply the Tier 3 method, plant-specific data and/or plant-specific measurements are required. The emissions from the petrochemical production process include $CO_2$ emitted from fuel or process by-products combusted to provide heat or thermal energy to the production process, $CO_2$ emitted from process vents, and $CO_2$ emitted from flared waste gases. These emissions are calculated using Equations 3.20 through 3.22.

Overall $CO_2$ emissions from the petrochemical production process are calculated using Equation 3.20

**EQUATION 3.20**
**TIER 3 $CO_2$ EMISSIONS CALCULATION EQUATION**

$$ECO2_i = E_{Combustion,i} + E_{Process\ Vent,i} + E_{Flare,i}$$

Where:

$ECO2_i$ = $CO_2$ emissions from production of petrochemical *i*, tonnes

$E_{Combustion,i}$ = $CO_2$ emitted from fuel or process by-products combusted to provide heat or thermal energy to the production process for petrochemical *i*, tonnes

$E_{Process\ Vent,i}$ = $CO_2$ emitted from process vents during production of petrochemical *i*, tonnes

$E_{Flare,i}$ = $CO_2$ emitted from flared waste gases during production of petrochemical *i*, tonnes

$E_{combustion}$ and $E_{flare}$ are given by Equations 3.21 and 3.22 where plant specific or national net calorific value data should be used. The emission factor is given by the carbon content of the fuel, the combustion oxidation factor and a constant (44/12) converting the result from carbon to $CO_2$. If the emission factor is not known a default value may be found in Table 1.4 in Chapter 1 of Volume 2: Energy. Net calorific values are included in Table 1.2 in Chapter 1 of Volume 2: Energy. Carbon contents are included in Table 1.3 in Chapter 1 of Volume 2: Energy. For the process vents, inventory compilers should measure/estimate emissions of $CO_2$ directly and thus no further equation is provided.

**EQUATION 3.21**
**FUEL COMBUSTION TIER 3 $CO_2$ EMISSIONS CALCULATION**

$$E_{Combustion,i} = \sum_k \left( FA_{i,k} \bullet NCV_k \bullet EF_k \right)$$

Where:

$FA_{i,k}$ = amount of fuel *k* consumed for production of petrochemical *i*, tonnes

$NCV_k$ = net calorific value of fuel *k*, TJ/tonne
(Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$ = $CO_2$ emission factor of fuel *k*, tonnes $CO_2$/TJ
(Note: In Table 1.4 in Chapter 1 of Volume 2, $CO_2$ emission factors are expressed in kg/TJ)

**EQUATION 3.22**
**FLARE GAS TIER 3 $CO_2$ EMISSIONS CALCULATION**

$$E_{Flare,i} = \sum_k \left( FG_{i,k} \bullet NCV_k \bullet EF_k \right)$$

Where:

$FG_{i,k}$ = amount of gas *k* flared during production of petrochemical *i*, tonnes

$NCV_k$ = net calorific value of flared gas *k*, TJ/tonne
(Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$ = $CO_2$ emission factor of flared gas *k*, tonnes $CO_2$/TJ
(Note: In Table 1.4 in Chapter 1 of Volume 2, $CO_2$ emission factors are expressed in kg/TJ)

**TABLE 3.10**
**SPECIFIC CARBON CONTENT OF PETROCHEMICAL FEEDSTOCKS AND PRODUCTS**

| Substance | Carbon (tonne carbon per tonne feedstock or product) |
|---|---|
| Acetonitrile | 0.5852 |
| Acrylonitrile | 0.6664 |
| Butadiene | 0.888 |
| Carbon black | 0.970 |
| Carbon Black Feedstock | 0.900 |
| Ethane | 0.856 |
| Ethylene | 0.856 |
| Ethylene dichloride | 0.245 |
| Ethylene glycol | 0.387 |
| Ethylene oxide | 0.545 |
| Hydrogen Cyanide | 0.4444 |
| Methanol | 0.375 |
| Methane | 0.749 |
| Propane | 0.817 |
| Propylene | 0.8563 |
| Vinyl Chloride Monomer | 0.384 |

Note: Carbon content values for natural gas and naphtha vary by country and region. Net calorific values (NCV) for natural gas, naphtha, and other primary fuels that may be used as petrochemical feedstocks are included in Table 1.2 in Chapter 1 of Volume 2: Energy. Feedstock carbon contents are included in Table 1.3 in Chapter 1 of Volume 2: Energy.

## METHANE

The decision tree for choice of method for $CH_4$ emissions is shown in Figure 3.9. The Tier 1 and Tier 3 methods for $CH_4$ are described in this section. There is no Tier 2 method applicable to $CH_4$ emissions.

### Tier 1 product-based emission factor method

$CH_4$ emissions from petrochemical processes may be fugitive emissions and/or process vent emissions. Fugitive emissions are emitted from flanges, valves, and other process equipment. Emissions from process vent sources include incomplete combustion of waste gas in flare and energy recovery systems. $CH_4$ emissions using the Tier 1 method may be calculated using Equation 3.23 for fugitive $CH_4$ emissions and Equation 3.24 for process vent emissions and Equation 3.25 for total $CH_4$ emissions. If annual primary product production data are not available but feedstock consumption data are available for the petrochemical process, Equation 3.16 would be utilised to estimate the annual production of primary products, and the annual primary product production estimated using Equation 3.16 would then be applied in Equations 3.23 and 3.24 to estimate the emissions.

**EQUATION 3.23**

**TIER 1 $CH_4$ FUGITIVE EMISSION CALCULATION**

$$ECH4_{Fugitive,i} = PP_i \bullet EFf_i$$

**EQUATION 3.24**

**TIER 1 $CH_4$ PROCESS VENT EMISSION CALCULATION**

$$ECH4_{Process\,Vent,i} = PP_i \bullet EFp_i$$

**EQUATION 3.25**

**TIER 1 $CH_4$ TOTAL EMISSIONS CALCULATION**

$$ECH4_{Total,i} = ECH4_{Fugitive,i} + ECH4_{Process\,Vent,i}$$

Where:

$ECH4_{Total,i}$ = total emissions of $CH_4$ from production of petrochemical *i*, kg

$ECH4_{Fugitive,i}$ = fugitive emissions of $CH_4$ from production of petrochemical *i*, kg

$ECH4_{Process\ Vent,i}$ = process vent emissions of $CH_4$ from production of petrochemical *i*, kg

$PP_i$ = annual production of petrochemical *i*, tonnes

$EFf_i$ = $CH_4$ fugitive emission factor for petrochemical *i*, kg $CH_4$/tonne product

$EFp_i$ = $CH_4$ process vent emission factor for petrochemical *i*, kg $CH_4$/tonne product

### Tier 2 total feedstock carbon balance method

The total feedstock carbon mass balance method is not applicable to estimation of $CH_4$ emissions. The total carbon mass balance method estimates the total carbon emissions from the process but does not directly provide an estimate of the amount of the total carbon emissions that is emitted as $CO_2$, $CH_4$, CO, or NMVOC.

### Tier 3 direct estimate of plant-specific emissions

The Tier 3 method is based on continuous or periodic plant-specific measurements. The emissions from the petrochemical production process include $CH_4$ emitted from fuel or process by-products combusted to provide heat or thermal energy to the production process, $CH_4$ emitted from process vents, and $CH_4$ emitted from flared waste gases. If methane is vented directly to the atmosphere this will dominate the emissions. $CH_4$ emissions from process vents may also be combusted in a flare or energy recovery device. Measurement of atmospheric concentration of VOCs directly above the plants or in the plume is the preferred activity data for estimating fugitive $CH_4$ emissions; however, such data may not be available. The atmospheric measurements are generally expensive and will most often not be continuous measurements but rather a discrete and periodic measurement program to obtain data to be used as basis for the development of plant specific emission factors. The results of such measurement programs would then be related to other plant process parameters to enable estimation of emissions between measurement periods.

Direct measurement of VOC and $CH_4$ concentrations in plant exhaust gas streams and direct measurement of fugitive VOC and $CH_4$ emissions from plant valves, fittings, and related equipment using a comprehensive leak detection programme can also be used to obtain plant-specific activity data for developing Tier 3 estimates of $CH_4$ emissions. However the plant-specific leak detection programme should provide fugitive $CH_4$ emissions data for all of the relevant $CH_4$-emitting plant equipment. Similarly, the plant-specific measurement data for stacks and vents would need to cover the major portion of stack and vent $CH_4$ emissions sources at the plant in order to provide a basis for a Tier 3 emission calculation.

Emissions of $CH_4$ from process stacks and vents may be estimated by direct measurement of the $CH_4$ concentration of the exhaust gas or estimated as a component of the total VOC concentration measured in the exhaust gas. Fugitive emissions of $CH_4$ from plant equipment (e.g., valves, fittings) may be estimated through application of plant-specific leak detection data and plant equipment inventories, provided that the plant-specific leak detection program and equipment inventory are comprehensive, such that the program provides fugitive $CH_4$ emissions data for all of the relevant $CH_4$-emitting plant equipment. Similarly, the plant-specific measurement data for stacks and vents would need to cover the major portion of stack and vent $CH_4$ emissions sources at the plant in order to provide a basis for a Tier 3 emission calculation.

Measurement of fugitive emissions may also be based on the $CH_4$ concentration in the atmosphere immediately above the plant or in a plume downwind. Such atmospheric measurement data would generally measure emissions from the entire plant, and does not separate between the different sources. In addition to $CH_4$ concentration the area of the plume and the wind speed must be measured. The emissions are given by Equation 3.26.

### EQUATION 3.26
### TIER 3 $CH_4$ EMISSION CALCULATION BASED ON ATMOSPHERIC MEASUREMENT DATA

$$CH4_{Emissions} = \int_t \left[ \left( C_{total\ VOCs} \bullet CH_4\ fraction - CH_4 background\ level \right) \bullet WS \bullet PA \right]$$

Where:

$CH4_{Emissions}$ = total plant $CH_4$ emissions, µg/s

$C_{total\ VOCs}$ = VOC concentration at the plant, µg/m$^3$

$CH_4$ fraction = fraction of total VOC concentration that is $CH_4$, fraction

$CH_4$ background level = ambient $CH_4$ concentration at background location, µg/m$^3$

WS = wind speed at the plant, m/s

PA = plume area, m$^2$

Note: $\int_t$ means the quantity should be summed over time.

Note that the Tier 3 methodology does not direct inventory compilers to conduct atmospheric measurements or other specific types of direct measurements to estimate site-specific $CH_4$ emissions. It is anticipated that plant-specific leak detection data and plant-specific stack and vent emission data will be more readily available than atmospheric measurement data. However, if atmospheric measurement data are available the data may be used to develop Tier 3 estimates of $CH_4$ emissions, or to verify other estimates. Atmospheric measurement data may provide a more accurate estimate of process $CH_4$ emissions than leak detection data and stack and vent emission data. A plant would use either i) Equation 3.26 or ii) Equations 3.27, 3.28, and 3.29 to estimate $CH_4$ emissions. Process vent emissions are assumed to be monitored either discretely or continuously. The method of calculation will vary depending upon the type of data, and therefore no separate equation is provided for process vent emissions calculation.

Overall emissions of $CH_4$ from the petrochemical production process based on plant-specific leak detection data and plant-specific stack and vent emissions data are calculated using Equation 3.27

### EQUATION 3.27
### TIER 3 $CH_4$ EMISSIONS CALCULATION EQUATION

$$ECH4_i = E_{Combustion,i} + E_{Process\,Vent,i} + E_{Flare,i}$$

Where:

$ECH4_i$ = total emissions of $CH_4$ from production of petrochemical *i*, kg

$E_{Combustion,i}$ = emissions of $CH_4$ from fuel or process by-products combusted to provide heat or thermal energy to the production process for petrochemical *i*, kg

$E_{Process\ Vent,i}$ = emissions of $CH_4$ from process vents during production of petrochemical *i*, kg

$E_{Flare,i}$ = emissions of $CH_4$ from flared waste gases during production of petrochemical *i*, kg

$E_{combustion}$ and $E_{flare}$ are given by Equations 3.28 and 3.29 where plant specific or national net calorific value data should be used.

**EQUATION 3.28**
**FUEL COMBUSTION TIER 3 $CH_4$ EMISSIONS CALCULATION**

$$E_{Combustion,i} = \sum_k \left( FA_{i,k} \bullet NCV_k \bullet EF_k \right)$$

Where:

$FA_{i,k}$ = amount of fuel *k* consumed for production of petrochemical *i*, tonnes

$NCV_k$ = net calorific value of fuel *k*, TJ/tonne
(Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$ = $CH_4$ emission factor of fuel *k*, kg/TJ

**EQUATION 3.29**
**FLARE GAS TIER 3 $CH_4$ EMISSIONS CALCULATION**

$$E_{Flare,i} = \sum_k \left( FG_{i,k} \bullet NCV_k \bullet EF_k \right)$$

Where:

$FG_{i,k}$ = amount of gas *k* flared during production of petrochemical *i*, tonnes

$NCV_k$ = net calorific value of flared gas *k*, TJ/tonne
(Note: In Table 1.2 in Chapter 1 of Volume2, net calorific values are expressed in TJ/kg)

$EF_k$ = $CH_4$ emission factor of flared gas *k*, kg/TJ

### 3.9.2.2 CHOICE OF EMISSION FACTORS

This section includes a discussion of the choice of emission factors for the Tier 1 method. The Tier 2 method is based on mass balance principles and the Tier 3 method is based on plant-specific data; therefore there are no default emission factors applicable to the Tier 2 and Tier 3 methods.

**TABLE 3.11**
**PETROCHEMICAL PRODUCTION TIER 1 DEFAULT FEEDSTOCKS AND PROCESSES**

| Petrochemical Process | Default Feedstock | Default Process |
|---|---|---|
| Methanol | Natural Gas | Conventional steam reforming without primary reformer |
| Ethylene | North America, South America, Australia - Ethane<br>Other Continents - Naphtha | Steam cracking<br>Steam cracking |
| Ethylene Dichloride / Vinyl Chloride Monomer | Ethylene | Balanced Process for EDC production with integrated VCM production plant |
| Ethylene Oxide | Ethylene | Catalytic Oxidation, Air Process, with thermal treatment |
| Acrylonitrile | Propylene | Direct Ammoxidation with secondary products burned for energy recovery or flared |
| Carbon Black | Carbon black feedstock and natural gas | Furnace black process with thermal treatment |

#### TIER 1

Tier 1 emission factors for $CO_2$ emissions and $CH_4$ emissions for petrochemical products are provided below. Tier 1 emission factors for $CO_2$ emissions do not include carbon emitted as CO, $CH_4$, or NMVOC. Separate Tier 1 emission factors are provided for $CH_4$ emissions from petrochemical processes. Tier 1 emission factors are not provided for carbon monoxide and NMVOC emissions.

The Tier 1 method allows for the selection of a 'default' feedstock and 'default' process in instances where activity data are not available to identify the feedstock or the process utilised to produce the petrochemical. Table 3.11 provides the default feedstocks and default processes for each petrochemical production process. In the event that no activity data are available concerning the specific processes and feedstocks used within a country to produce the petrochemical, the default process and default feedstock identified in Table 3.11 and the associated Tier 1 emission factors identified in the subsequent tables in this section are used to estimate the $CO_2$ emissions from the petrochemical production process. Country-specific emission factors may be used instead of the default emission factors if country-specific factors are available.

## Methanol

### *Carbon dioxide emissions*

Emissions of $CO_2$ from methanol production from the steam reforming and partial oxidation processes may be estimated by applying the default process feedstock emission factors, or the feedstock-specific and process-specific emission factors in Table 3.12, to activity data for methanol production, process configuration and process feedstock. The default emission factors are based on the average of plant-specific $CO_2$ emissions data reported for four methanol plants using the conventional steam reforming process without primary reformer and using natural gas feedstock. Emissions data used in developing the default $CO_2$ emission factor were reported for conventional process methanol plants in New Zealand, Chile, and Canada and in the Netherlands. Emission factors in the table include both the $CO_2$ emissions arising from the process feedstock and the $CO_2$ emissions arising from feedstock combusted within the steam reforming process. Table 3.13 summarises the total feedstock consumption, in units of GJ/tonne methanol produced, for the various methanol production process configurations and feedstocks shown in Table 3.12.

The conventional reforming process can include a single reformer unit or both a primary reformer unit and a secondary reformer. The emission factors differ depending upon the number of reformer units. Lurgi is a provider of methanol process technology and has published emission factors for several conventional reforming process technologies, see Table 3.12. The production capacity of Mega Methanol plants is generally greater than 5 000 tonnes per day of methanol. The emission factors for the Lurgi Conventional process technologies should be applied only if the specific process technology is known. Otherwise the emission factor for conventional steam reforming without primary reformer, or the emission factor for conventional steam reforming with primary reformer, should be applied.

The conventional steam reforming process for methanol production can be integrated with an ammonia production process. The emission factor for integrated methanol and ammonia production should be used only if the specific process technology is known.

**TABLE 3.12**
**METHANOL PRODUCTION $CO_2$ EMISSION FACTORS**

| | tonne $CO_2$/tonne methanol produced | | | | |
|---|---|---|---|---|---|
| **Process Configuration** **Feedstock** | **Nat. gas** | **Nat. gas + $CO_2$** | **Oil** | **Coal** | **Lignite** |
| Conventional Steam Reforming, without primary reformer (a)<br>(Default Process and Natural Gas Default Feedstock) | 0.67 | | | | |
| Conventional Steam Reforming, with primary reformer (b) | 0.497 | | | | |
| Conventional Steam Reforming, Lurgi Conventional process (c1) | 0.385 | 0.267 | | | |
| Conventional Steam Reforming, Lurgi Low Pressure Process (c2) | 0.267 | | | | |
| Combined Steam Reforming, Lurgi Combined Process (c3) | 0.396 | | | | |
| Conventional Steam Reforming, Lurgi Mega Methanol Process (c4) | 0.310 | | | | |
| Partial oxidation process (d) | | | 1.376 | 5.285 | 5.020 |
| Conventional Steam Reforming with integrated ammonia production | 1.02 | | | | |

Nat. gas + $CO_2$ feedstock process based on 0.2-0.3 tonne $CO_2$ feedstock per tonne methanol

Emission factors in this table are calculated from the feedstock consumption values in Table 3.13 based on the following feedstock carbon contents and heating values:

| | | |
|---|---|---|
| Natural Gas: | 56 kg $CO_2$/GJ | 48.0 GJ/tonne |
| Oil: | 74 kg $CO_2$/GJ | 42.7 GJ/tonne |
| Coal: | 93 kg $CO_2$/GJ | 27.3 GJ/tonne |
| Lignite: | 111 kg $CO_2$/GJ | |

Uncertainty values for this table are included in Table 3.27

Sources: (a) Struker, A, and Blok, K, 1995; Methanex, 2003: (b) Hinderink, 1996: (c1 – c4) Lurgi, 2004a; Lurgi, 2004b; Lurgi, 2004c: (d) FgH-ISI, 1999

**TABLE 3.13**
**METHANOL PRODUCTION FEEDSTOCK CONSUMPTION FACTORS**

| | GJ feedstock input /tonne methanol produced | | | | |
|---|---|---|---|---|---|
| **Process Configuration** **Feedstock** | **Nat. gas** | **Nat. gas + $CO_2$** | **Oil** | **Coal** | **Lignite** |
| Conventional Steam Reforming, without primary reforme (a)<br>(Default Process and Natural Gas Default Feedstock) | 36.5 | | | | |
| Conventional Steam Reforming, with primary reformer (b) | 33.4 | 29.3 | | | |
| Conventional Steam Reforming, Lurgi Conventional process (c1) | 31.4 | | | | |
| Conventional Steam Reforming, Lurgi Low Pressure Process (c2) | 29.3 | | | | |
| Combined Steam Reforming, Lurgi Combined Process (c3) | 31.6 | | | | |
| Conventional Steam Reforming, Lurgi Mega Methanol Process (c4) | 30.1 | | | | |
| Partial oxidation process (d) | | | 37.15 | 71.6 | 57.6 |

Nat. gas + $CO_2$ feedstock process based on 0.2-0.3 tonne $CO_2$ feedstock per tonne methanol

Sources: (a) Struker, A, and Blok, K, 1995; Methanex, 2003: (b) Hinderink, 1996: (c1 – c4) Lurgi, 2004a; Lurgi, 2004b; Lurgi, 2004c : (d) FgH-ISI, 1999

Uncertainty values for this table are included in Table 3.27

### *Methane emissions*

Methanex reported $CH_4$ emissions from two Canadian methanol production plants in their 1996 Climate Change Action Plan (Methanex, 1996). Methanex reported that $CH_4$ emissions from methanol production may arise from reformers, package boilers, methanol distillation units, and crude methanol storage tanks. $CH_4$ emissions from the plants accounted for approximately 0.5 percent to 1.0 percent of the total greenhouse gas emissions from the plants, but were reported to vary depending upon the level of maintenance and operational control of the plant equipment. The average emission factor reported for two reporting years is 2.3 kg $CH_4$ emissions per tonne of methanol produced. $CH_4$ emissions from a second Methanex methanol production plant were reported to be 0.15 kg $CH_4$ per tonne of methanol produced. The higher of the two reported values, 2.3 kg $CH_4$ per tonne of methanol produced, should be applied as the default $CH_4$ emission factor for methanol production. $CH_4$ emissions as low as 0.1 kg/tonne have been estimated for the methanol plant Tjeldbergodden, Norway (SFT, 2003a).

## Ethylene

### *Carbon dioxide emissions*

Emissions of $CO_2$ from steam cracking for ethylene production may be estimated using the feedstock-specific emission factors in Table 3.14 and activity data for the amount of ethylene produced from the steam cracking processes. Separate emission factors are provided in Table 3.14 for the $CO_2$ emissions from feedstock consumption and from supplemental energy consumption in the steam cracking process. However, the $CO_2$ emissions from both feedstock consumption and supplemental energy consumption are to be reported as Industrial Process emissions under the reporting convention discussed above. The default emission factors are derived from plant-specific data for steam crackers operating in Western Europe. The emission factors may be adjusted by applying the default geographic adjustment factors in Table 3.15 to account for differences in the energy efficiency of steam cracking units among various countries and regions. Note that as indicated in Table 3.11, the default feedstock for steam crackers operating in North and South America and Australia is ethane, and the default feedstock for steam crackers operating on other continents is naphtha.

These default emission factors do not include $CO_2$ emissions from flaring. Emissions from flaring amount to about 7 percent of total emissions in a well-maintained plant in Norway. Steam cracking processes that utilise naphtha, propane, and butane feedstocks are assumed to be energy neutral, requiring no use of supplemental fuel, therefore there are assumed to be no $CO_2$ emissions associated with supplemental fuel consumption for these feedstocks.

**TABLE 3.14**
**STEAM CRACKING ETHYLENE PRODUCTION TIER 1 $CO_2$ EMISSION FACTORS**

| | tonnes $CO_2$/tonne ethylene produced | | | | | |
|---|---|---|---|---|---|---|
| **Feedstock** | **Naphtha** | **Gas Oil** | **Ethane** | **Propane** | **Butane** | **Other** |
| Ethylene (Total Process and Energy Feedstock Use) | 1.73 | 2.29 | 0.95 | 1.04 | 1.07 | 1.73 |
| - Process Feedstock Use | 1.73 | 2.17 | 0.76 | 1.04 | 1.07 | 1.73 |
| - Supplemental Fuel (Energy Feedstock) Use | 0 | 0.12 | 0.19 | 0 | 0 | 0 |

Source: Neelis, M., Patel, M., and de Feber, M., 2003, Table 2.3, Page 26.

Default feedstocks for ethylene production are identified in Table 3.11. The emission factors do not include supplemental fuel use in flares.

Other feedstocks are assumed to have the same product yields as naphtha feedstock.

Uncertainty values for this table are included in Table 3.27.

The emission factors in Table 3.14 may be used in the event that activity data are available only for the amount of ethylene produced by the steam cracking process. Steam cracking is a multi-product process that leads to ethylene, propylene, butadiene, aromatics, and several other high-value chemicals. There is an inherent assumption of a specific product mix in the default emission factors in Table 3.14. The default product mix for each emission factor in Table 3.14 is identified in the ethylene steam cracking feedstock-product matrix in Section 3.9.2.3. The feedstock/product matrix identifies the default values for production of ethylene, propylene, and other hydrocarbon products from the steam cracking process in units of kilograms of each product produced per tonne of feedstock. In order to develop the emission factors for steam cracking shown in Table 3.14 the total $CO_2$ process emissions of a steam cracker have been divided by the output of ethylene only. In other words ethylene has been chosen as the reference for estimating the total $CO_2$ emissions from the steam cracking process as a whole. Multiplication of the emission factors in Table 3.14 by the ethylene production therefore leads to the total $CO_2$ emissions resulting not only from the production of ethylene but also from the production of propylene, butadiene, aromatics, and all other chemicals produced by the steam cracking process. The default emission factors in Table 3.14 provide the total $CO_2$ emissions from the steam cracking process, not only the $CO_2$ emissions associated with the production of the ethylene from the steam cracking process.

**TABLE 3.15**
**DEFAULT GEOGRAPHIC ADJUSTMENT FACTORS FOR TIER 1 $CO_2$ EMISSION FACTORS FOR STEAM CRACKING ETHYLENE PRODUCTION**

| Geographic Region | Adjustment Factor | Notes |
|---|---|---|
| Western Europe | 100% | Values in Table 3.14 are based on data from Western European steam crackers |
| Eastern Europe | 110% | Not including Russia |
| Japan and Korea | 90% | |
| Asia, Africa, Russia | 130% | Including Asia other than Japan and Korea |
| North America and South America and Australia | 110% | |

Source: Adjustment factors are based on data provided by Mr. Roger Matthews in personal communication to Mr. Martin Patel, May 2002.

Uncertainty values for this table are included in Table 3.27.

### *Methane emissions*

Default fugitive $CH_4$ emission factors for steam cracking of ethane and naphtha for ethylene production are estimated from total VOC emissions factors and VOC species profile data from EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005). Overall volatile organic compound emissions from steam cracking are estimated to be 5 kg/tonne ethylene produced based on a European publication, for which the feedstock is assumed to be naphtha, and estimated to be 10 kg VOC/tonne ethylene produced based on a U.S. publication, for which the feedstock is assumed to be ethane. From the total VOC emission factors the overall $CH_4$ emissions from steam cracking of naphtha are estimated from the VOC species profile to be 3 kg/tonne ethylene produced, primarily from leakage losses, and the overall $CH_4$ emissions from cracking of ethane are estimated from the species profile to be twice those from cracking of naphtha (6 kg/tonne ethylene produced); however these factors are subject to uncertainty as the overall VOC emission factors of 5 kg VOC/tonne ethylene for naphtha feedstock and 10 kg VOC/tonne ethylene for ethane feedstock are each based on a single publication. Emissions of $CH_4$

from steam cracking of feedstocks other than ethane and naphtha have been assumed to be the same as that estimated from the EMEP/CORINAIR data for steam cracking of naphtha.

Published data show a large variability in reported $CH_4$ emission factors for ethylene production. The European Association of Plastics Manufacturers (APME) Eco-Profiles of the European Plastics Industry reports a $CH_4$ emission factor for ethylene production of 2.9 kg $CH_4$/tonne ethylene produced, as referenced in the APME Eco-Profiles for Olefins Production (Boustead, 2003a). The $CH_4$ emission factor for ethylene steam cracker process operations is based on life-cycle analysis data for 15 European steam crackers. Emissions as low as 0.14 kg $CH_4$/tonne ethylene are estimated on the basis of direct measurement at a Norwegian ethylene plant (SFT 2003b) and as low as 0.03 kg $CH_4$/tonne ethylene based on company data reported in the Australian Methodology for the Estimation of Greenhouse Gas Emissions and Sinks, 2003 (AGO, 2005). Other European and Australian steam cracker operators reported plant-specific $CH_4$ emissions on the order of 10 percent of the values reported in Table 3.16 (DSM, 2002; Qenos, 2003; Qenos, 2005). Therefore, the emission factors in Table 3.16 should not be used to estimate $CH_4$ emissions from steam cracker ethylene plants for which plant-specific data are available. In this case the plant-specific data and the Tier 3 method should be used. Default $CH_4$ emission factors for various process feedstocks are shown in Table 3.16. Note that the default feedstocks for ethylene production are identified in Table 3.11.

**TABLE 3.16**
**DEFAULT METHANE EMISSION FACTORS FOR ETHYLENE PRODUCTION**

| Feedstock | kg $CH_4$/ tonne ethylene produced |
|---|---|
| Ethane | 6 |
| Naphtha | 3 |
| All Other Feedstocks | 3 |

Source: EEA, 2005 (EMEP/CORINAIR Emission Inventory Guidebook)
Uncertainty values for this table are included in Table 3.27.

### Ethylene dichloride and vinyl chloride monomer

#### *Carbon dioxide emissions*

Emission factors are provided in Table 3.17 for the ethylene dichloride and vinyl chloride monomer production processes, including the direct chlorination process, oxychlorination process, and balanced process. The $CO_2$ emission factors are derived by averaging plant-specific $CO_2$ emissions data for European plants reported in the Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry (European IPPC Bureau, February 2003; referred to in this section as the IPPC LVOC BAT Document). Note that as indicated in Table 3.11, the default process is the balanced process for EDC production with an integrated VCM production plant. The total $CO_2$ emission factor for each process includes noncombustion $CO_2$ emissions from the ethylene dichloride process vent and combustion $CO_2$ emissions from ethylene dichloride plant combustion sources. Plant combustion source emission factors include combustion of both process waste gas and auxiliary fuel in the process waste gas thermal incinerator. The combustion-related emission factor does not include emissions from flares. Combustion-related emission factors in Table 3.17 are based on data from oxychlorination process plants but the emission factors are assumed also to apply to direct chlorination and balanced process plants. Feedstock consumption factors for ethylene dichloride and vinyl chloride monomer production processes are provided in Table 3.18. The PlasticsEurope EcoProfiles (Boustead, 2005) for EDC production indicates ethylene utilisation of 0.306 tonnes ethylene per tonne EDC produced, based on eight European plants.

It should be noted that the $CO_2$ emission factors in Table 3.17 in units of tonnes $CO_2$ per tonne EDC produced and in units of tonnes $CO_2$ per tonne VCM produced are not additive. The two $CO_2$ emission factors both apply to the integrated EDC/VCM production process, however the tonnes $CO_2$ per tonne EDC factor is based on EDC production activity data while the tonnes $CO_2$ per tonne VCM factor is based on VCM production activity data. The $CO_2$ emission factor that will be applied will depend upon whether activity data for EDC production or activity data for VCM production are available. Similarly, the feedstock consumption factors in Table 3.18 in units of tonnes ethylene consumed per tonne EDC produced and in units of tonnes ethylene consumed per tonne VCM produced are not additive. The feedstock consumption factor that will be applied will depend upon whether activity data are available for EDC production or for VCM production.

**TABLE 3.17**
**ETHYLENE DICHLORIDE/VINYL CHLORIDE PRODUCTION PROCESS TIER 1 $CO_2$ EMISSION FACTORS**

| Process Configuration | tonne $CO_2$/tonne EDC produced | tonne $CO_2$/tonne VCM produced |
|---|---|---|
| **Direct Chlorination Process** | | |
| Noncombustion Process Vent | negligible emissions | negligible emissions |
| Combustion Emissions | 0.191 | 0.286 |
| Total $CO_2$ Emission Factor | **0.191** | **0286** |
| **Oxychlorination Process** | | |
| Noncombustion Process Vent | 0.0113 | 0.0166 |
| Combustion Emissions | 0.191 | 0.286 |
| Total $CO_2$ Emission Factor | **0.202** | **0.302** |
| **Balanced Process [default process]** | | |
| Noncombustion Process Vent | 0.0057 | 0.0083 |
| Combustion Emissions | 0.191 | 0.286 |
| Total $CO_2$ Emission Factor | **0.196** | **0.294** |

Values for $CO_2$ emissions from EDC and VCM production for several European production plants were provided in Tables 12.6 and 12.7 of the IPPC LVOC BAT Document (European IPPC Bureau, 2003). These values were averaged to calculate $CO_2$ emission factors for EDC and VCM production. One EDC plant that is equipped with a $CO_2$ control device and that reported zero $CO_2$ emissions from the process is not included in the average emission factor.

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Tables 12.6 and 12.7 data).
Uncertainty values for this table are included in Table 3.27.

**TABLE 3.18**
**ETHYLENE DICHLORIDE/VINYL CHLORIDE MONOMER PROCESS TIER 1 FEEDSTOCK CONSUMPTION FACTORS**

| Process Configuration | tonne ethylene/tonne EDC produced | tonne ethylene/tonne VCM produced |
|---|---|---|
| Direct Chlorination Process | 0.290 | -- |
| Oxychlorination Process | 0.302 | -- |
| Balanced Process | 0.296 | 0.47 |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 12.3.1, Page 299-300, Section 12.1 Table 12.3, Page 293).
Uncertainty values for this table are included in Table 3.27.

### *Methane emissions*

The EMEP/CORINAIR ‘species profile’ for the ethylene dichloride/vinyl chloride monomer balanced process indicates that there are no $CH_4$ emissions from the process other than $CH_4$ emissions from combustion sources. The EMEP/CORINAIR species profile reports that VOC emissions from leakage losses and storage and handling do not contain $CH_4$. The EMEP/CORINAIR also reports that 2 percent of the total VOC emissions from the balanced process are from combustion sources and that $CH_4$ constitutes 1.2 percent of overall VOC emissions. Therefore it may be assumed that non-combustion $CH_4$ emissions from ethylene dichloride/vinyl chloride monomer production are negligible.

$CH_4$ emissions from combustion of natural gas supplemental fuel in the ethylene dichloride/vinyl chloride monomer production process may be estimated from activity data for natural gas supplemental fuel consumption and $CH_4$ emission factor for natural gas combustion. Natural gas consumption for integrated ethylene dichloride/vinyl chloride monomer production is estimated to be 110.1 $Nm^3$ natural gas/tonne VCM produced for an integrated ethylene dichloride/vinyl chloride monomer production plant in the Netherlands and 126.4 $Nm^3$ natural gas/tonne VCM produced for an integrated ethylene dichloride/vinyl chloride monomer production plant in Germany. The average of these two values is 118.3 $Nm^3$ natural gas/tonne VCM. The $CH_4$ emission factor for the integrated EDC/VCM production process is based on a $CH_4$ emission factor of 5 g $CH_4$/GJ natural gas combusted and the average natural gas consumption of the two European plants. The default $CH_4$ emission factor for the integrated ethylene dichloride/vinyl chloride monomer production process is provided in Table 3.19. The default emission factor is not applicable to stand-alone EDC production plants. If natural gas consumption activity data are available, the $CH_4$ emission factor of 5 g $CH_4$/GJ may be applied directly to the activity data, rather than using the default emission factor.

**TABLE 3.19**
**ETHYLENE DICHLORIDE/VINYL CHLORIDE PROCESS TIER 1 DEFAULT $CH_4$ EMISSION FACTOR**

| **Process Configuration** | **kg $CH_4$/tonne VCM product produced** |
|---|---|
| Integrated EDC/VCM Production Plant | 0.0226 |

Sources: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 12.3.1, Table 12.4, Page 300); EEA, 2005 (EMEP/CORINAIR Emission Inventory Guidebook, Processes in Organic Chemical Industries (Bulk Production) 1, 2-Dichloroethane and Vinyl Chloride (Balanced Process), Activity 040505, February 15, 1996, Section 3.4, Page B455-3, and Table 9.2, B455-5).

## Ethylene oxide

### *Carbon dioxide emissions*

Emissions of $CO_2$ from ethylene oxide production may be estimated using emission factors based on activity data for ethylene oxide production, and activity data for process configuration and catalyst selectivity. Separate $CO_2$ emission factors are provided in Table 3.20 for the $CO_2$ emissions from the air process and for the $CO_2$ emissions from the oxygen process for a range of catalyst selectivity. The default emission factors for the air process and for the oxygen process are estimated from process-specific catalyst selectivity data provided in the IPPC LVOC BAT document. Specific data concerning the type of process and the selectivity of the process catalyst are needed in order to select emission factors from Table 3.20. The emission factors are derived from the catalyst selectivity using stoichiometric principles and are based on the assumption that emissions of $CH_4$ and NMVOC from the process are negligible and that all of the carbon contained in the ethylene feedstock is converted either into ethylene oxide product or to $CO_2$ emissions. The emission factors in Table 3.20 do not include emissions from flares.

As shown in Table 3.20, the default emission factor for the air process is based on a default process catalyst selectivity of 70 percent and the default emission factor for the oxygen process is based on a default catalyst selectivity of 75 percent. If activity data are not available for the process configuration or the catalyst selectivity, the default process configuration is the air process and the default catalyst selectivity is 70 percent. If activity data are available that identify the process used as the oxygen process, but activity data are not for the catalyst selectivity for the oxygen process, the emission factor for the default catalyst selectivity of 75 percent for the oxygen process in Table 3.20 should be used.

**TABLE 3.20**
**ETHYLENE OXIDE PRODUCTION FEEDSTOCK CONSUMPTION AND $CO_2$ EMISSION FACTORS**

| **Process Configuration** | **Catalyst Selectivity** | **Feedstock Consumption (tonne ethylene/ tonne ethylene oxide)** | **Emission Factor (tonne $CO_2$/ tonne ethylene oxide)** |
|---|---|---|---|
| Air Process [default process] | Default (70) | 0.90 | 0.863 |
| | 75 | 0.85 | 0.663 |
| | 80 | 0.80 | 0.5 |
| Oxygen Process | Default (75) | 0.85 | 0.663 |
| | 80 | 0.80 | 0.5 |
| | 85 | 0.75 | 0.35 |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 9.2.1, Page 224, Section 9.3.1.1, Page 231, Figure 9.6)

### *Methane emissions*

The IPPC LVOC BAT document for ethylene oxide production reported $CH_4$ emissions factors (in units of kilograms methane per tonne ethylene oxide produced) for the ethylene oxide process vent, ethylene oxide purification process exhaust gas steam, and fugitive emissions sources. $CH_4$ emission factors were reported in the IPPC LVOC BAT document for European ethylene oxide plant carbon dioxide removal vents before and after treatment. $CH_4$ emissions were also reported for two ethylene oxide plants in the Netherlands. $CH_4$ emission factors for ethylene oxide production were developed by averaging these data. Emissions of $CH_4$ may be estimated by applying the emissions factors included in Table 3.21 to activity data for ethylene oxide production. The default $CH_4$ emission factor for ethylene oxide production assumes no thermal treatment process.

**TABLE 3.21**
**ETHYLENE OXIDE PRODUCTION TIER 1 $CH_4$ EMISSION FACTORS**

| Process Configuration | kg $CH_4$/tonne ethylene oxide produced |
|---|---|
| No Thermal Treatment [default factor] | 1.79 |
| Thermal Treatment | 0.79 |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Table 9.6, Page 233; Table 9.8, Page 236; Table 9.9, Page 236).

## Acrylonitrile

### *Carbon dioxide emissions*

Process vent $CO_2$ emissions from the acrylonitrile production process by the direct ammoxidation of propylene may be calculated from acrylonitrile production activity data using the emission factors provided in Table 3.22:

**TABLE 3.22**
**ACRYLONITRILE PRODUCTION $CO_2$ EMISSION FACTORS**

| Process Configuration Direct Ammoxidation of Propylene | tonnes $CO_2$/tonne acrylonitrile produced |
|---|---|
| Secondary Products Burned for Energy Recovery/Flared (default) | 1.00 |
| Acetonitrile Burned for Energy Recovery/Flared | 0.83 |
| Acetonitrile and Hydrogen Cyanide Recovered as Product | 0.79 |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 11.3.1.1, Table 11.2, Page 274 and Section 11.3.1.2, Page 275)

The emission factors in Table 3.22 are based on an average (default) propylene feedstock consumption factor of 1.09 tonnes propylene feedstock per tonne acrylonitrile produced, corresponding to a primary product yield factor of approximately 70 percent. The default $CO_2$ emission factor is based on conversion of propylene feedstock to secondary product acetonitrile at 18.5 kilograms per tonne acrylonitrile produced, and conversion of propylene to secondary product hydrogen cyanide at 105 kilograms per tonne acrylonitrile produced, and is based on process-specific acrylonitrile yield data and process-specific feedstock consumption data reported in the IPPC LVOC BAT document (European IPPC Bureau, 2003). Note however that the acrylonitrile production process may be configured and operated to produce a greater or lesser amount of secondary products. The default $CO_2$ emission factor is based on the assumption that the secondary products (acetonitrile and hydrogen cyanide) of the acrylonitrile production process and hydrocarbon by products in the main absorber vent gas are either burned for energy recovery or flared to $CO_2$ and are not recovered as products or emitted to the atmosphere without combustion treatment. The $CO_2$ emission factors do not include $CO_2$ emissions from any combustion of auxiliary fuel (e.g., natural gas) for the process waste gas energy recovery or flare systems.

If activity data are not available concerning whether secondary products are recovered for sale, the default assumption is that the secondary products are either burned for energy recovery or flared to $CO_2$ and the default primary product process yield factor is 70 percent.

For the process configuration where secondary products (acetonitrile and hydrogen cyanide) are recovered for sale and are not either flared to $CO_2$ or burned for energy recovery, the overall process yield factor of primary and secondary products is 85 percent.

If activity data for propylene feedstock consumption are not available, the propylene feedstock consumption may be estimated from the acrylonitrile production activity data by applying a default feedstock consumption factor of 1.09 tonnes propylene feedstock consumed per tonne acrylonitrile produced.

### *Methane emissions*

The Life-Cycle Analysis Data Summary for Acrylonitrile reports a $CH_4$ emission factor for acrylonitrile production of 0.18 kg $CH_4$/tonne acrylonitrile produced, as referenced in the European Association of Plastics Manufacturers (APME) Life-Cycle Analysis Report (Boustead, 1999). The $CH_4$ emission factor for acrylonitrile process operations is based on life-cycle analysis data for European acrylonitrile plants in Germany, Italy, and the United Kingdom collected between 1990 and 1996. $CH_4$ emissions from acrylonitrile production may be estimated by applying this default emission factor to the acrylonitrile production data.

## Carbon black

### *Carbon dioxide emissions*

Emissions of $CO_2$ from carbon black production may be estimated by applying the process and feedstock-specific emission factors to the carbon black production activity data. Separate emission factors are provided in Table 3.23 for the furnace black process, thermal black process, and acetylene black process and their associated feedstocks, and separate emission factors are provided for primary feedstock and secondary feedstock. The emission factors are based on the assumption that process emissions are subjected to a thermal treatment process.

A range of values for primary and secondary carbon black feedstock is included in Table 4.11 of the draft Integrated Pollution Prevention and Control (IPPC) Reference Document for Best Available Techniques in the Large Volume Inorganic Chemicals (LVIC) Solid and Others Industry (European IPPC Bureau, June 2005; referred to in this chapter as the Draft IPPC LVIC BAT Document.) The $CO_2$ emission factors in Table 3.23 are based on the average of the range of values. Primary and secondary feedstock consumption is converted to carbon consumption using average values for carbon black feedstock carbon content. The $CO_2$ emission factors are calculated from the carbon input to the process (primary and secondary feedstocks) and carbon output (carbon black) from the process, using an average value for carbon black carbon content.

**TABLE 3.23**
**CARBON BLACK PRODUCTION TIER 1 $CO_2$ EMISSION FACTORS**

| **Process Configuration** | **tonnes $CO_2$/tonne carbon black produced** | | |
|---|---|---|---|
| | **Primary Feedstock** | **Secondary Feedstock** | **Total Feedstock** |
| Furnace Black Process (default process) | 1.96 | 0.66 | 2.62 |
| Thermal Black Process | 4.59 | 0.66 | 5.25 |
| Acetylene Black Process | 0.12 | 0.66 | 0.78 |

Source: European IPPC Bureau, 2005 (Draft IPPC LVIC BAT Document, Table 4.11 data)

### *Methane emissions*

$CH_4$ emissions for the carbon black production process are provided in Table 3.24. The draft IPPC LVIC BAT document for carbon black reported the $CH_4$ content of uncombusted tail gas from the carbon black production process and the estimated rate of generation of tail gas from the carbon black production process. Based on 10,000 $Nm^3$ tail gas per tonne carbon black produced and an average reported $CH_4$ concentration of 0.425 percent by volume, the uncontrolled $CH_4$ emission factors is 28.7 kg $CH_4$/tonne carbon black produced. Combustion flare efficiency for carbon black process flare systems was reported in the Draft IPPC LVIC BAT Document as 99.8 percent for carbon monoxide, and the same efficiency is assumed to apply to $CH_4$. The $CH_4$ emission factor for carbon black production after application of combustion control is 0.06 kg $CH_4$/tonne carbon black produced. An overall $CH_4$ emission factor of 0.11 kg $CH_4$/tonne carbon black, based on company data, was reported in the Australian Methodology for the Estimation of Greenhouse Gas Emissions and Sinks, 2003 (AGO, 2005.) Three carbon black production plants in Germany reported a common $CH_4$ emission factor of 0.03 kg $CH_4$/tonne carbon black produced, based on measurement data after waste gas combustion using BAT (Thermische Nachverbrennung als Stand der Technik.)

**TABLE 3.24**
**CARBON BLACK PRODUCTION TIER 1 $CH_4$ EMISSION FACTORS**

| **Process Configuration** | **kilogram $CH_4$/tonne carbon black produced** (Carbon Black Process Tail Gas ) |
|---|---|
| No Thermal Treatment | 28.7 |
| Thermal Treatment (default process) | 0.06 |

Source: European IPPC Bureau, 2005 (Draft IPPC LVIC BAT Document, Table 4.8, Page 209; Table 4.10, Page 213, Section 4.3.2.3, Page 210).

## TIER 2

The Tier 2 methodology is based on mass balance calculations and therefore there are no emission factors associated with the methodology.

### TIER 3

For the Tier 3 method plant specific emissions may be estimated using Equations 3.20 through 3.22 for $CO_2$, and using either Equation 3.26 or Equations 3.27 through 3.29 for $CH_4$. The emission factors may be related to annual production for estimation of emissions between measurements when these are not continuous.

## 3.9.2.3 CHOICE OF ACTIVITY DATA

General aspects of data collection for obtaining activity data are discussed in Chapter 2 of Volume 1. When using the Tier 3 method plant-specific activity data should be obtained from the production plants. Direct measurements of the total flow to the steam cracker and flare system together with an analysis of the gas carbon content will provide the most accurate basis for an emissions estimate.

Plant specific energy balance and/or carbon balance may also be used to derive plant specific emission factors. The variety of energy and carbon flows across the plant boundary makes this a data intensive but still much less resource intensive approach. While feedstock consumption data may be hard to obtain sales data and national statistics may provide approximate production volumes of the chemicals.

### METHANOL

Emissions of $CO_2$ from methanol production may be calculated from specific feedstock (e.g., natural gas) consumption and product (methanol) production activity data and carbon mass balance calculations.

### ETHYLENE

Emissions of $CO_2$ from ethylene production may be calculated from specific feedstock consumption and product production activity data and carbon mass balance calculations. In order to create a complete mass balance for the ethylene production process and implement the Tier 2 methodology for ethylene production, all feedstocks and the production and disposition of all primary and secondary products of the process should be identified using activity data. In cases where activity data are available for ethylene production but not available for production of secondary products from the steam cracking process, the production of secondary products may be estimated using the default factors in Table 3.25 and Equation 3.18. However, use of these default factors is a less accurate method than use of specific activity data for all primary and secondary products, and will increase the uncertainty of the estimate, as performance of steam crackers may vary depending on site-specific conditions. For example, site-specific data reported for steam crackers operating in Germany indicate that hydrocarbon losses under normal operating conditions are on the order of 8.5 kg per tonne of hydrocarbon feedstock (BASF, 2006) whereas the default value for hydrocarbon losses shown in Table 3.25 is 5 kg per tonne of hydrocarbon feedstock. In the event that activity data are not available for all secondary products, the Tier 1 method can be applied instead of the Tier 2 method.

Secondary products produced by the steam cracking process may recovered and transferred to a petrochemical plant or petroleum refinery for material reuse, recycled within the steam cracking process as feedstock, or burned for energy recovery. Typically C4+ secondary products are recycled as feedstock or recovered for material reuse (BASF, 2006). Allocation of $CO_2$ emissions from combustion of secondary products for energy recovery is described in Box 1.1 in Chapter 1 of this volume. If activity data are not available for the disposition of C4+ secondary products the default assumption is that the C4+ secondary products are recovered and transferred to another process for material reuse. If data are not available for the disposition of $CH_4$ produced by the steam cracking process, the default assumption is that the $CH_4$ is burned for energy recovery within the steam cracking process and results in $CO_2$ emissions from the process.

Steam crackers operated within the petrochemical industry may obtain the petrochemical feedstock for the ethylene production process directly from an adjacent petroleum refinery. Depending upon the feedstock and process operating conditions, steam crackers may also generate ‘backflows’ of hydrocarbon by-products that are returned to the adjacent refinery for further processing. Any $CO_2$ emissions from processing backflows at petroleum refineries are not included in the process $CO_2$ emission factors for the steam cracker ethylene production process, but are considered in the feedstock and carbon flow analysis for the process.

**TABLE 3.25**
**ETHYLENE STEAM CRACKING FEEDSTOCK-PRODUCT MATRIX**

| | kg product/tonne feedstock | | | | | |
|---|---|---|---|---|---|---|
| **Product Feedstock** | **Naphtha** | **Gas oil** | **Ethane** | **Propane** | **Butane** | **Others** |
| High Value Chemicals | **645** | **569** | **842** | **638** | **635** | **645** |
| Ethylene | 324 | 250 | 803 | 465 | 441 | 324 |
| Propylene | 168 | 144 | 16 | 125 | 151 | 168 |
| Butadiene | 50 | 50 | 23 | 48 | 44 | 50 |
| Aromatics | 104 | 124 | 0 | 0 | 0 | 104 |
| Fuel grade products and backflows | **355** | **431** | **157** | **362** | **365** | **355** |
| Hydrogen | 11 | 8 | 60 | 15 | 14 | 11 |
| Methane | 139 | 114 | 61 | 267 | 204 | 139 |
| Ethane and propane after recycle | 0 | 0 | 0 | 0 | 0 | 0 |
| Other C4 | 62 | 40 | 6 | 12 | 33 | 62 |
| C5/C6 | 40 | 21 | 26 | 63 | 108 | 40 |
| C7+ non-aromatics | 12 | 21 | 0 | 0 | 0 | 12 |
| <430C | 52 | 26 | 0 | 0 | 0 | 52 |
| >430C | 34 | 196 | 0 | 0 | 0 | 34 |
| Losses | 5 | 5 | 5 | 5 | 5 | 5 |
| Total | **1 000** | **1 000** | **1 000** | **1 000** | **1 000** | **1 000** |

Source: Neelis, M; Patel, M; de Feber, M; Copernicus Institute, April 2003, Table 2.2, Page 24

### ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER

Emissions of $CO_2$ from ethylene dichloride and vinyl chloride monomer production may be calculated from specific feedstock (ethylene) consumption and product (ethylene dichloride) production activity data and carbon mass balance calculations.

### ETHYLENE OXIDE

Emissions of $CO_2$ from ethylene oxide production may be calculated from specific feedstock (ethylene) consumption and product (ethylene oxide) production activity data and carbon mass balance calculations.

### ACRYLONITRILE

In the event that activity data are not available for production of secondary products (acetonitrile and hydrogen cyanide), the default values in Table 3.26 and Equation 3.19 may be applied to the activity data for primary product production to estimate secondary product production.

**TABLE 3.26**
**SECONDARY PRODUCT PRODUCTION FACTORS FOR ACRYLONITRILE PRODUCTION PROCESS**

| **Secondary Product** | **kg secondary product/tonne acrylonitrile produced** |
|---|---|
| Acetonitrile | 18.5 |
| Hydrogen Cyanide | 105 |

Note: The secondary product production factors in this table are based on acrylonitrile production from propylene feedstock. In the event that feedstocks other than propylene are used, the factors in this table would not apply. Process-specific factors would need to be developed in order to apply the Tier 2 mass balance approach to acrylonitrile production from feedstocks other than propylene.

Source: European IPPC Bureau, 2005 (IPPC LVOC BAT Document, Section 11.3.4, Page 27)

If no activity data are available concerning acetonitrile product recovery it may be assumed that it is not recovered as product and is burned for energy recovery to $CO_2$. If no activity data are available concerning thermal treatment of the acetonitrile main absorber vent gas it may be assumed that the vent gas is thermally treated and combusted to $CO_2$ and is not vented to the atmosphere uncontrolled.

### CARBON BLACK

Emissions of $CO_2$ from carbon black production may be calculated from specific primary feedstock (e.g., carbon black feedstock) and secondary feedstock (e.g., natural gas) consumption and product (carbon black) production activity data and carbon mass balance calculations.

## 3.9.2.4 COMPLETENESS

In estimating $CO_2$ emissions from petrochemical and carbon black processes, there is a risk of double-counting or omission in either the IPPU or the Energy Sector. Petrochemical and carbon black plants produce methane and non-methane hydrocarbon by-products that may be burned for energy recovery and such energy recovery may be reported in national energy statistics under ‘other’ fuels or some similar categorisation. If $CO_2$ emissions from ‘other’ fuel combustion include industrial process off gases that are burned for energy recovery some adjustment to the energy statistics or to the $CO_2$ emissions calculation for petrochemical production would be needed to avoid double counting of the $CO_2$ emissions.

### METHANOL

There may be production of methanol from biogenic (renewable) sources. Such biogenic methanol may be incorporated into methanol national production statistics, which would result in overestimation of $CO_2$ emissions from fossil fuel (e.g., natural gas) derived methanol unless adjustments are made to the methanol production activity data.

### ETHYLENE

There may be production of ethylene from petroleum refining processes or from petrochemical processes other than steam crackers. Such ethylene may be incorporated into ethylene national production statistics, which would result in overestimation of $CO_2$ emissions from steam cracker derived ethylene unless adjustments are made to the ethylene production activity data.

### ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER

Ethylene dichloride is an intermediate petrochemical product used to manufacture vinyl chloride monomer and other products. Activity data for production of ethylene dichloride may not be complete because the ethylene dichloride may be converted directly to vinyl chloride monomer in an integrated EDC/VCM plant. Therefore it may be the case that the vinyl chloride monomer production activity data are more complete with respect to industry coverage than the ethylene dichloride production activity data. However, utilisation of vinyl chloride monomer activity data as a surrogate for ethylene dichloride data also has issues related to completeness because not all of the ethylene dichloride is used to manufacture vinyl chloride monomer. Therefore adjustments to the activity data for vinyl chloride monomer may be needed to account for utilisation of ethylene dichloride in the production of other products. Based on data for North America and Europe utilisation of ethylene dichloride for products other than vinyl chloride monomer would amount to the order of 5 percent of total ethylene dichloride production.

### ETHYLENE OXIDE

Ethylene oxide is an intermediate petrochemical product used to manufacture ethylene glycols and other products. Activity data for production of ethylene oxide may not be complete because the ethylene oxide may be converted directly to ethylene glycol in an integrated EO/EG plant. Ethylene oxide may also be converted into other products (e.g., amines, ethers, etc.) in integrated plants. Since only on the order of 70 percent of ethylene oxide production worldwide is used in the manufacture of ethylene glycols, production activity data for chemical products of ethylene oxide may not be more complete with respect to industry coverage than the ethylene oxide production activity data.

### CARBON BLACK

There may be small amounts of production of carbon black from biogenic (renewable) sources such as animal black and bone black. Such biogenic carbon black may be incorporated into carbon black national production statistics, which would result in overestimation of $CO_2$ emissions from fossil fuel derived carbon black. There also may be carbon black production within the physical boundaries of petroleum refineries rather than within the chemical industry. Carbon black produced within petroleum refineries is anticipated to be incorporated into national carbon black production statistics, therefore $CO_2$ emissions from carbon black production within petroleum refineries should be reported along with other emissions from carbon black production within the chemical industry as industrial process emissions.

There may be gaps in completeness with respect to carbon black feedstock consumption activity data. Activity data for carbon black feedstock derived from coal tar products, waste gases, or acetylene may not be available, which would result in underestimating of $CO_2$ emissions from carbon black production if a higher-tier carbon balance approach was used.

### 3.9.2.5 DEVELOPING CONSISTENT TIME SERIES

The emissions from petrochemical and carbon black production should be estimated using the same Tier and type of activity data for all years. Constructing a time series for emissions from petrochemical and carbon black production using plant specific measurement activity data will give the most accurate current emissions. However activity data on flaring and fugitive emissions will most likely not be available for previous years. If no technology upgrades have taken place calculating a plant specific emission factor based on recent measurement data related to production of petrochemicals may provide a reasonable result. Petrochemical production is often integrated in an industrial complex producing more than one chemical, or exchanges energy or chemical flows with adjacent industrial plants, and carbon black may be produced within petroleum refineries. When constructing a time series based on feedstock consumption great care should be taken to assure that the activity data includes the same flows every year in the time series. Again a Tier 1 type calculation using emission factors developed from recent plant specific emission estimates based on Tier 2 carbon balance calculation may be used. Investigations to uncover a change in choice of feedstock as well as variations in primary and secondary chemicals produced both within a single year and between years. Reconstruction of gaps in emission estimates and recalculations should follow the guidance in Volume 1, Chapter 5.

## 3.9.3 Uncertainty assessment

Uncertainty assessments for each emissions factor and activity data applicable to each process are discussed in this section. Uncertainty ranges for the emission factors and activity data included in the Tables in the previous sections are summarised in Table 3.27.

### METHANOL

Much of the uncertainty in emission estimates for methanol production is related to the difficulty in determining activity data including the quantity of methanol produced and, for higher tier methodologies, the amount of natural gas and other feedstocks consumed on an annual basis. Natural gas and other feedstock consumption may only be reported on an annual basis in national energy statistics, without any breakout of consumption for methanol production. If natural gas consumption activity data are not available then only an emission factor approach rather than a higher tier carbon balance approach is applicable. If activity data are not available for consumption of other feedstocks for methanol production, it may be assumed that all of the national methanol production is from natural gas feedstock. However, this assumption would introduce some uncertainty. Further, activity data may not be available for annual $CO_2$ feedstock consumption in methanol production plants that utilise $CO_2$ as a supplemental feedstock in the production process.

### ETHYLENE

Uncertainty in activity data for ethylene production is related to the difficulty in determining the types, quantities, and characteristics of feedstocks to the steam cracking process (e.g., ethane, naphtha) and the types, quantities, and characteristics of products from the process (e.g., ethylene, propylene). Feedstock consumption and product production may only be reported on an annual basis in national energy statistics and commodity statistics, without any breakout of feedstock consumption for ethylene production or product production from the steam cracking ethylene production process. The ability to conduct a carbon balance calculation for ethylene production depends upon the availability of both activity data for consumption of specific feedstocks and production of specific products of the steam cracking process. If only activity data for national annual ethylene production are available, the default feedstock for the country/region may be assumed and the default emission factor applied. In this case the feedstocks analysis would be conducted by utilising the default yield table for the default feedstock. However, considering the wide variability in emission factors and yield factors among the feedstocks, the unavailability of specific feedstock consumption data would introduce significant uncertainty into the emissions calculations and feedstocks analysis. If specific feedstock consumption activity data are available then a separate emissions estimate and feedstocks analysis may be conducted for each feedstock, which would reduce the uncertainty. Ideally, however, activity data would be available for both specific feedstock consumption and specific product production, allowing a higher tier carbon balance calculation to be conducted.

Another source of uncertainty is related to the difficulty in determining other details of the steam cracking ethylene process configuration, including backflows of products of the steam cracking process from the petrochemical plant to the [potentially adjacent] petroleum refinery and flows of by products to energy recovery or flaring. The unavailability of activity for refinery backflows would introduce uncertainty into the feedstocks analysis.

## ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER

Sources of uncertainty for ethylene dichloride include the difficulty in determining the specific process utilised for the ethylene dichloride production and in determining activity data for the consumption of ethylene feedstock in the production process. If only activity data for ethylene dichloride production are available, the emission calculation may be conducted using the default [balanced] process product yield factor and default emission factor for the process. However, considering the variability in emission factors and yield factors for the oxychlorination process, direct oxidation process, and balanced process, the unavailability of specific ethylene feedstock consumption data by process would introduce significant uncertainty into the emissions calculations

## ETHYLENE OXIDE

A main source of uncertainty for ethylene oxide production is the difficulty in determining activity data for the consumption of ethylene feedstock for ethylene oxide production. If ethylene consumption activity data are not available then only an emission factor approach rather than a higher tier carbon balance approach is applicable. If only activity data for national annual ethylene oxide production are available, the default product yield may be assumed and the default emission factor applied. In this case the feedstocks analysis would be conducted by utilising the default product yield factor. However, considering the range of reported product yield factors and emission factors for the ethylene oxide process, the unavailability of specific ethylene feedstock consumption data would introduce significant uncertainty into the emissions calculations.

## ACRYLONITRILE

Sources of uncertainty for acrylonitrile production include the difficulty in determining the specific process configuration for acrylonitrile production, in determining activity data for the consumption of propylene feedstock in the production process, and in determining activity data for the production of acrylonitrile and acetonitrile from the process. If only activity data for acrylonitrile production are available, the emission calculation may be conducted using the default process configuration (assuming no acetonitrile recovery) and default emission factor for the process. However, the assumption that acetonitrile is not recovered from the process introduces significant uncertainty in the emission and feedstocks calculations and may result in overestimation of emissions and underestimation of feedstocks flows from the acrylonitrile process. Activity data for national production of both acrylonitrile and acetonitrile from the acrylonitrile production process would allow application of the process-specific emission factor for the percentage of national acrylonitrile production from which acetonitrile is recovered. Ideally, however, activity data for propylene consumption and activity data for acrylonitrile, acetonitrile, and hydrogen cyanide production from the acrylonitrile production process would allow utilisation of a higher-tier method, which would reduce the uncertainty.

## CARBON BLACK

Uncertainty in activity data for carbon black production is related to the difficulty in determining the types, quantities, and characteristics of primary and secondary feedstocks to the carbon black process, and in determining the type of process used for the carbon black production and the characteristics of the carbon black product from the process. Primary and secondary feedstock consumption and carbon black production may only be reported on an annual basis in national energy statistics and commodity statistics, without any breakout of feedstock consumption for carbon black production for each carbon black production process. Most worldwide production of carbon black is by the furnace black process, therefore if feedstock consumption activity data are not available by process, all of the carbon black production may be assumed to be from the furnace black process without introducing a large amount of uncertainty.

Also, if activity data are available for primary carbon black feedstock consumption, the data may be reported in generic terms as ‘carbon black feedstock’ without any indication of whether the feedstock is a petroleum-based feedstock produced at petroleum refineries or a coal tar-based feedstock produced from metallurgical coke production. Activity data may also not be available for other primary carbon black feedstocks (e.g., acetylene). Also, specific activity data may be available for natural gas consumption as secondary carbon black feedstock, however, activity data may not be available for other secondary feedstocks that may be used in carbon black production (e.g., coke oven gas). Unavailability of specific primary and secondary feedstock consumption data would add uncertainty to the feedstocks analysis.

The ability to conduct a carbon balance calculation for carbon black production depends upon the availability of activity data for the consumption and the characteristics of primary and secondary feedstocks. If only activity data for national annual carbon black production are available, the default feedstock characteristics and product yield may be assumed and the default emission factor may be applied. However, considering the variability in feedstock characteristics and origin, the unavailability of specific feedstock consumption and composition activity data would introduce significant uncertainty into the emissions and feedstocks calculations. If specific feedstock consumption and characteristics activity data and associated carbon black production activity data are available then a separate carbon balance and feedstocks analysis may be conducted for each feedstock and process using a higher tier method, which would reduce the uncertainty.

### UNCERTAINTY RANGES

Uncertainty ranges for Tier 1 emission factors and Tier 2 activity data and Tier 3 activity data for each process are provided in Table 3.27. The source of the data or expert judgement used in preparing the uncertainty estimate is identified in the table for each factor or activity data. Expert judgement elicitation was conducted by evaluating the range of available data. In many cases process-specific data were available only for several plants; the relatively large uncertainty ranges are the result of the relatively few data available and the expected variability of process configurations and feedstock utilisation efficiency among petrochemical and carbon black plants.

**TABLE 3.27**
**UNCERTAINTY RANGES FOR EMISSION FACTORS AND ACTIVITY DATA**

| Method | Reference | Factor | Uncertainty Range | Source |
|---|---|---|---|---|
| Tier 3 | | Direct measurement of fuel consumption together with gas composition samples for all substances | - 5 to + 5 % | Expert judgement by Lead Authors of Section 3.9, on the basis of discussions with national industry January 2005. |
| Tier 1 | Table 3.12 | Methanol production $CO_2$ emission factors | -30% to +30% | Expert judgement by Lead Authors of Section 3.9. |
| Tier 1 | Table 3.13 | Methanol Production Feedstock Consumption Factors | -30% to +30% | Expert judgement by Lead Authors of Section 3.9. |
| Tier 1 | | Methane Emission Factor for Methanol Production | -80% to +30% | Expert judgement by Lead Authors of Section 3.9 on the basis of Methanex plant data. |
| Tier 1 | Table 3.14 | Ethylene Production $CO_2$ Emission Factors | -30% to +30% | IPPC LVOC BAT Document, Figure 7.10, |
| Tier 1 | Table 3.15 | Geographic Adjustment Factors For $CO_2$ Emissions Factors For Ethylene Production | -10% to +10% | Expert judgement by Lead Authors of Section 3.9. |
| Tier 1 | Table 3.16 | Methane Emission Factors for Ethylene Production | -10% to +10% | Expert judgement by Lead Authors of Section 3.9. |
| Tier 1 | Table 3.17 | Ethylene Dichloride/Vinyl Chloride Production Process Vent $CO_2$ Emission Factors | -20% to +10% | IPPC LVOC BAT Document, Tables 12.6 and 12.7 |
| Tier 1 | Table 3.17 | Ethylene Dichloride/Vinyl Chloride Production $CO_2$ Emission Factors | -50% to +20% | IPPC LVOC BAT Document, Tables 12.6 and 12.7 |
| Tier 1 | Table 3.18 | Ethylene Dichloride/Vinyl Chloride Monomer Process Feedstock Consumption Factors | -2% to +2% | IPPC LVOC BAT Document, Section 12.3.1, Page 300 |
| Tier 1 | Table 3.19 | Ethylene Dichloride/Vinyl Chloride Monomer Process $CH_4$ Emission Factors | -10% to +10% | IPPC LVOC BAT Document, Section 12.3.1, Table 12.4, Page 300 |
| Tier 1 | Table 3.20 | Ethylene Oxide Production Feedstock Consumption and $CO_2$ Emission Factors | -10% to +10% | Expert judgement by<br>Lead Authors of Section 3.9. |
| Tier 1 | Table 3.21 | Ethylene Oxide Production $CH_4$ Emission Factors | -60% to +60% | IPPC LVOC BAT Document, Table 9.6, Page 233; Table 9.8, Page 236; Table 9.9, Page 236 |
| Tier 1 | Table 3.22 | Acrylonitrile Production $CO_2$ Emission Factors | -60% to +60% | IPPC LVOC BAT Document, Section 11.3.1.1, Table 11.2, Page 274. |

**TABLE 3.27 (CONTINUATION)**
**UNCERTAINTY RANGES FOR EMISSION FACTORS AND ACTIVITY DATA**

| Method | Reference | Factor | Uncertainty Range | Source |
|---|---|---|---|---|
| Tier 1 | | Acrylonitrile Production $CH_4$ Emission Factors | -10% to +10% | Boustead, 2003b (Eco-Profiles of the European Plastics Industry Methodology I. Boustead, Report prepared for APME, July 2003, Page 40) |
| Tier 1 | Table 3.23 | Carbon Black Production $CO_2$ Emission Factors | -15% to +15% | Draft IPPC LVIC BAT Document, Table 4.11, Page 214 |
| Tier 1 | Table 3.24 | Carbon Black Production $CH_4$ Emission Factors | -85% to +85% | Draft IPPC LVIC BAT Document, Table 4.8, Page 209 |
| Tier 2 | Table 3.25 | Ethylene Steam Cracking Feedstock-Product Matrix | -10% to + 10% | Expert judgement by Contributing Authors of Section 3.9 |
| Tier 2 | Table 3.26 | Secondary Product Production Factors for Acrylonitrile Production Process | -20% to +20% | Expert judgement by Lead Authors of Section 3.9. |

## 3.9.4 Quality Assessment/Quality Control (QA/QC), Reporting and Documentation

### 3.9.4.1 QUALITY ASSESSMENT/QUALITY CONTROL

Quality Assurance/Quality Control for emissions factors and activity data involves methods to improve the quality or better understand the uncertainty of the emissions estimates. It is *good practice* to conduct quality control checks for the Tier 1 method as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable, if Tier 2 or Tier 3 methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for key categories as identified in Volume 1, Chapter 4.

#### Evaluation of Tier 1 and Tier 2 method activity data

The Tier 1 and Tier 2 methods both depend upon the application of activity data for petrochemical and carbon black production and/or activity data for feedstock consumption. These activity data should not be expected to vary by more than about +/- 10 percent year to year, barring significant changes in the overall economic output of the country, the construction of new petrochemical production capacity, or other similar factors. If the activity data vary by more than about +/-10 percent year to year, it is *good practice* to assess and document the country-specific conditions that account for the differences.

#### Evaluation of Tier 1 method emission factors

Inventory compilers that develop country-specific emission factors for petrochemical and carbon black production and apply the Tier 1 method should assess whether the estimated emission factors are within the range of the default emission factors and process-specific emission factors provided for the Tier 1 method in this guidance. If the emission factors are outside of the range of factors reported in this Guidance, then the reasons why this is the case should be investigated (e.g., the process configuration differs from that for the emission factors reported in this guidance; the feedstock is a unique material not considered in this Guidance.) Inventory compilers should also ensure that the country-specific emission factors are consistent with the values derived from analysis of the process chemistry. For example, for methanol production from natural gas the carbon content of the $CO_2$ generated, as estimated using the emission factor, should equal approximately the difference between the carbon content of the natural gas feedstock and the carbon content of the methanol product. If the emission factors are outside of the estimated ranges, it is *good practice* to assess and document the plant-specific conditions that account for the differences. It is also *good practice* or inventory compilers using Tier 1 method emission factors included in this Guidance to conduct quality control checks to assess whether the data characteristics of the emission factor conform to the characteristics of the petrochemical and carbon black production processes in the country in which the emission factor is applied.

### Evaluation of Tier 2 method mass balance calculations

Application of the Tier 2 mass balance method depends upon the identification and characterisation of process flows. For the Tier 2 method, failure to identify all carbon-containing process flows or mischaracterisation of the flow rates or carbon contents of such process flows could result in significant deviation of the estimated $CO_2$ emissions from the actual $CO_2$ emissions. The quality of Tier 2 mass balance calculation results are generally more dependent upon the quality of the activity data than are Tier 1 calculation results because in general a greater number of activity data need to be applied to the Tier 2 method than to the Tier 1 method. Therefore, it is *good practice* to assess and document the quality of each activity data applied to the Tier 2 method and the completeness of the activity data prior to applying the Tier 2 method. If the data quality or completeness are deemed not adequate for application of the Tier 2 method then the Tier 1 method should be applied.

### Evaluation of Tier 3 method plant-specific data

The Tier 3 method is based on the application of plant-specific emissions data. It is *good practice* for inventory compilers that conduct audits of plant-specific emissions estimates used in the inventory. This involves evaluating whether the plant-specific data are representative of plant emissions and, if plant-specific data for a specific plant are applied to the national inventory, evaluating whether the plant-specific data representative of petrochemical and carbon black production processes in the country as a whole. Audits of plant-specific data would involve the evaluation of:

- Documentation of plant-specific measurement methodology;
- Documentation of plant-specific measurement results;
- Emissions estimation method and calculations;
- Process feedstock(s) and product(s)
- Activity data employed in emissions calculations;
- Documentation of process technology and configuration;
- List of assumptions;

If the specific process for which plant-specific data are obtained is deemed not to be representative of other plants in the country producing the same petrochemical (e.g., if the feedstock differs or the process configuration differs) then the plant-specific data should not be applied to the overall inventory but only to the activity data for the specific plant. If emission measurements from individual plants are collected, inventory compilers should ensure that the measurements were made according to recognised national or international standards and the quality control methods were applied to the emissions measurement. Quality control procedures in use at the plant should be directly referenced and included in the quality control plan. If the measurement practices were not consistent with quality control standards or if the measurement procedures and results cannot be adequately documented, the inventory compiler should reconsider the use of the plant-specific data.

## 3.9.4.2 REPORTING AND DOCUMENTATION

Combustion emissions from combustion of off gases generated by petrochemical production processes are attributed to the IPPU Sector source category which produces them, and are reported as industrial process emissions. However, if any portion of the off gases generated by an IPPU Sector source category is combusted within a different IPPU Sector source category, or combusted within an Energy Sector source category, the corresponding emissions are reported as fuel combustion emissions rather than as industrial process emissions. This means that if the combustion emissions occur within the IPPU Sector source category which produced the off gases, then the emissions are reported as industrial process emissions attributed to that IPPU Sector source category. However, if the off gases are transferred out of the process to another source category in the IPPU Sector or a source category in the Energy Sector, then the emissions from the combustion of the off gases are reported as fuel combustion emissions within that source category. When the total emissions from the combustion of the off gases are calculated, the quantity transferred to and reported in the Energy Sector and the quantity transferred to and reported in a different IPPU Sector source category should be clearly quantified in the IPPU Sector source category calculations and in the Energy Sector source category calculations. If a country-specific emission factor was developed, the corresponding data should be provided as how the emission factor was developed and applied in the emission factor calculation, including reporting of the production process configuration upon which the emission factor and calculation are based.

### METHANOL

The amount of methanol produced, the amount of natural gas feedstock consumed in methanol production, and the amount of supplemental $CO_2$ feedstock consumed in methanol production are to be reported when available.

If a default emission factor is used, this should be noted in the reporting documentation, and the methanol production process configuration should be reported in the event that the default process configuration is not used.

### ETHYLENE

The amount of each feedstock consumed in ethylene production and the amounts of ethylene and each other primary product produced and recovered as product are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the ethylene production process configuration and feedstock(s) should be reported in the event that the default process configuration and default feedstock for the country/region are not used.

### ETHYLENE DICHLORIDE

The amount of ethylene dichloride produced and ethylene feedstock consumed in ethylene dichloride production are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the ethylene dichloride production process configuration should be reported in the event that the default process configuration is not used.

### ETHYLENE OXIDE

The amount of ethylene oxide produced and ethylene feedstock consumed in ethylene oxide production are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the ethylene oxide production process configuration should be reported in the event that the default process configuration is not used.

### ACRYLONITRILE

The amount of propylene feedstock consumed in acrylonitrile production and the amounts of acrylonitrile, acetonitrile, and hydrogen cyanide produced and recovered as product are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the acrylonitrile production process configuration should be reported in the event that the default process configuration is not used.

### CARBON BLACK

The amount of carbon black produced and the amounts and characteristics (carbon content) of each primary and secondary feedstock consumed in carbon black production are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the carbon black production process configuration should be reported in the event that the default process configuration is not used.

# Annex 3.9A Feedstock-product flow diagrams

**Figure 3.11 Methanol production feedstock-product flow diagram**

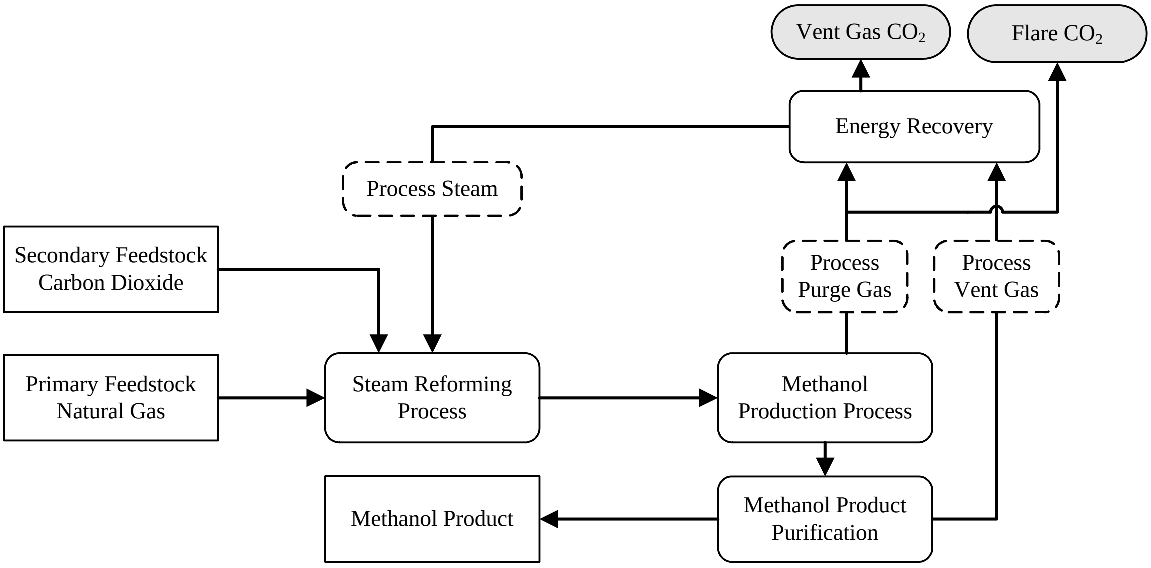


**Figure 3.12 Ethylene dichloride production feedstock-product flow diagram**

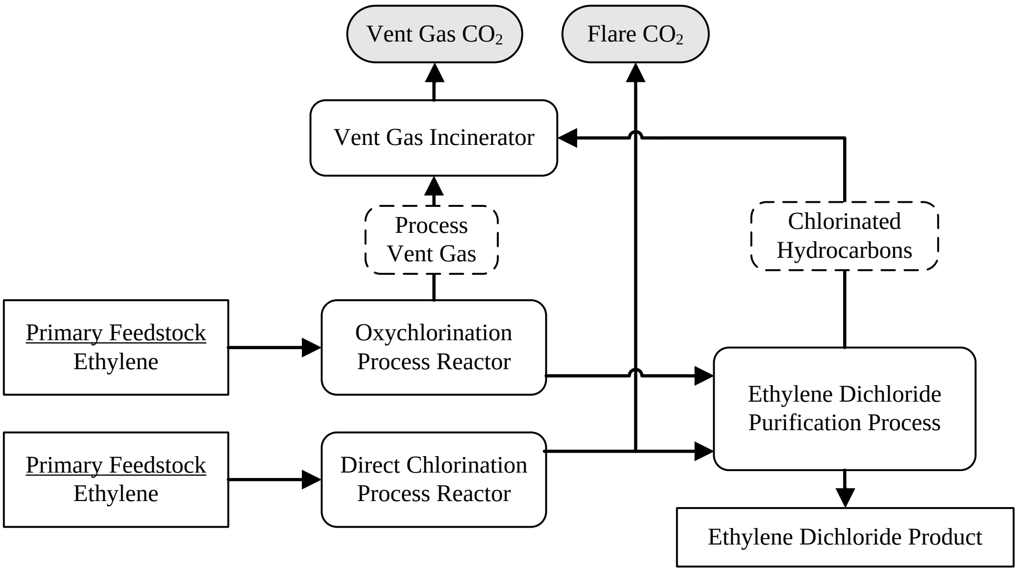


**Figure 3.13 Ethylene oxide production feedstock-product flow diagram**

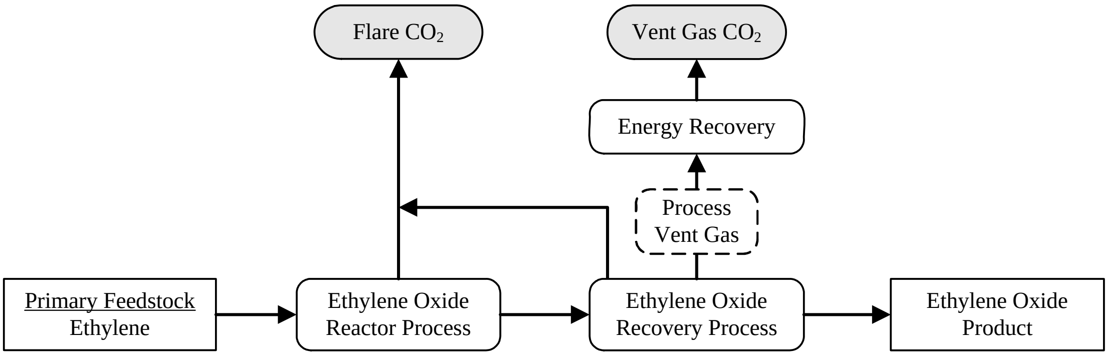


**Figure 3.14 Acrylonitrile production feedstock-product flow diagram**

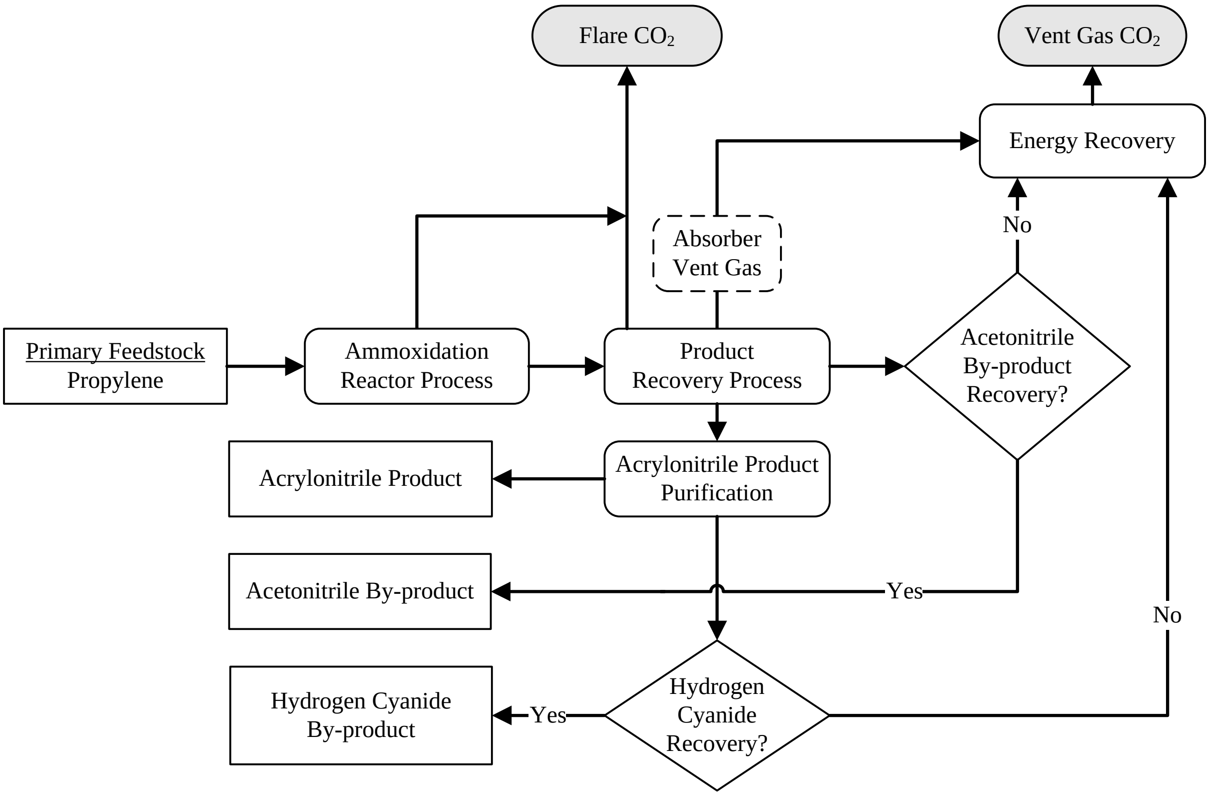
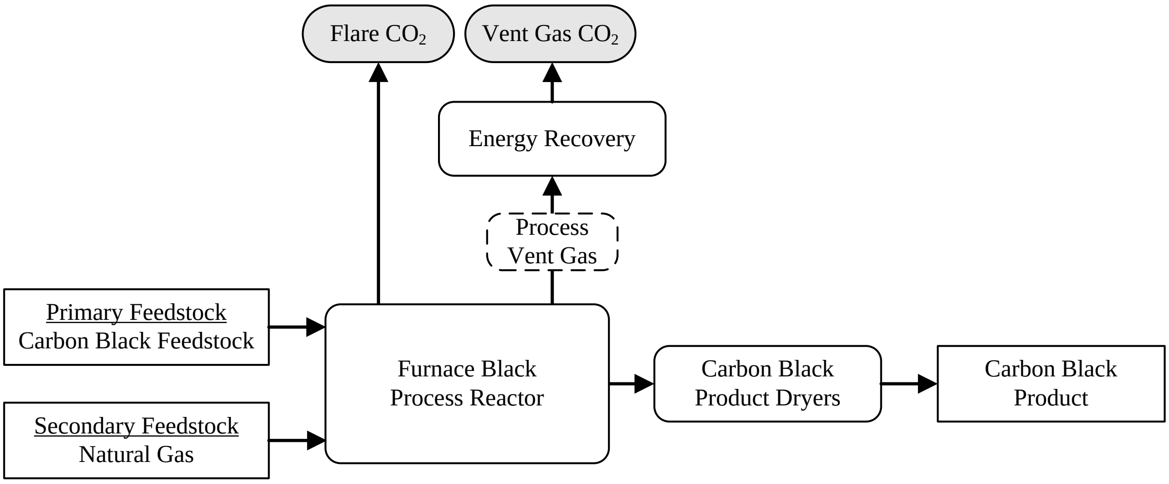


**Figure 3.15 Carbon black production feedstock-product flow diagram**



# 3.10 FLUOROCHEMICAL PRODUCTION

## 3.10.1 HFC-23 emission from HCFC-22 production

### 3.10.1.1 INTRODUCTION

Trifluoromethane (HFC-23 or $CHF_3$), is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22 or $CHClF_2$).[3] Materials such as HFC-23 (and other HFCs, PFCs and $SF_6$) are not significantly removed by aqueous (acidic, neutral or alkaline) scrubbing processes and will be released into the atmosphere. It is estimated that in 1990 the HFC-23 released from HCFC-22 plants was at most 4 percent of the production of HCFC-22 (U.S. EPA, 2001), in the absence of abatement measures. There are a small number of HCFC-22 production plants globally and thus a discrete number of point sources of HFC-23 emissions. While the methodology described here is applicable to by-product emissions of any fluorinated greenhouse gas, it has been written specifically for HFC-23. The methodology for emissions of fluorinated by-products in general and ‘fugitive emissions’ is covered by Section 3.10.2.

### 3.10.1.2 METHODOLOGICAL ISSUES

#### CHOICE OF METHOD

There are two broad measurement approaches to estimating HFC-23 emissions from HCFC-22 plants. These are described in IPCC (2000), DEFRA (2002a and 2002b), EFCTC (2003) and UN (2004) and have been translated into Tier 2 and 3 methodologies described below. National emissions using either of these methodologies are the sum of those from the individual facilities. Tier 1 (default) methodology can be applied to individual plants or, if there is no abatement by destruction, to the total national output of HCFC-22. Accounting for HFC-23 emissions is not simply mechanistic but requires information on the process operations responsible for producing and emitting HFC-23, so that the most appropriate methodology and factors can be adopted. Therefore, it is *good practice*, to the extent possible, to establish contacts with plant managers in order to obtain the necessary data.

The Tier 1 method is relatively simple, involving the application of a default emission factor to the quantity of HCFC-22 produced. This method can be applied at the plant level or the national level. Tier 2 and Tier 3 methodologies are suitable only for plant level calculations because they rely on data that are only available from plants. In cases where there are Tier 3 data available for some plants, the Tier 1 or Tier 2 methods can be applied to the remainder to ensure complete coverage.

It is *good practice* to estimate national emissions by summing measured parameters from all HCFC-22 plants in a country. Tier 3 plant emission measurements are the most accurate, followed by Tier 2 measurements based on plant efficiencies. Direct measurement is significantly more accurate than Tier 1 because it reflects the conditions specific to each manufacturing facility. In most cases, the data necessary to prepare Tier 3 estimates should be available because facilities operating to good business practice perform regular or periodic sampling of the final process vent or within the process itself as part of routine operations. The Tier 1 (default) method should be used only in cases where plant-specific data are unavailable and this subcategory is not identified as significant subcategory under *key category*. (See Section 4.2 of Volume 1.) Modern plant using process optimization will need to keep accurate HFC-23 generation data as part of this optimization, so plant-specific data should be available to most countries in most cases.

The choice of *good practice* method will depend on national circumstances. The decision tree in Figure 3.16 describes *good practice* in adapting the methods in these *Guidelines* to country-specific circumstances.

Procedures to abate emissions include destruction of HFC-23 in a discrete facility and, in this case, emissions occur only when the destruction facility is not in operation. The tiers of methodology provide estimates for the quantity of HFC-23 that is produced and the share of production that is ultimately emitted depends on the length of time that the destruction facility is not operated. For facilities using abatement techniques such as HFC-23 destruction, verification of the abatement efficiency is also done routinely. It is *good practice* to subtract abated HFC-23 emissions from national estimates where the abatement has been verified by process records on every plant.

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[3] HCFC-22 is used as a refrigerant in several different applications, as a blend component in foam blowing, and as a chemical feedstock for manufacturing synthetic polymers.

### Tier 1

In the Tier 1 methodology, a default factor is used to estimate production (and potential emissions) of HFC-23 from the total HCFC-22 production from each facility (for both potentially dispersive uses, as reported under the Montreal Protocol, and feedstock uses, which are reported separately to the Ozone Secretariat). See Equation 3.30.

**EQUATION 3.30**
**TIER 1 CALCULATION OF HFC-23 FROM HCFC-22 (PRODUCED) USING DEFAULT FACTOR**

$$E_{HFC-23} = EF_{default} \bullet P_{HCFC-22}$$

Where:

$E_{HFC-23}$ = by-product HFC-23 emissions from HCFC-22 production, kg

$EF_{default}$ = HFC-23 default emission factor, kg HFC-23/kg HCFC-22

$P_{HCFC-22}$ = total HCFC-22 production, kg

This methodology is suitable where plant-specific measurements are not available and, in that case, the default condition is that all of the estimated HFC-23 production is released into the atmosphere.

### Tier 2

In the Tier 2 methodology, the HFC-23 emission factor is derived from records of process efficiencies and used in the calculation shown as Equation 3.31. This is a material balance approach and relies on calculating the difference between the expected production of HCFC-22 and the actual production and then assigning that difference to loss of raw materials, loss of product (HCFC-22) and conversion to by-products, including HFC-23. These parameters will be different for each plant and so should be assessed separately for each facility reporting into the national data.

**EQUATION 3.31**
**TIER 2 CALCULATION OF HFC-23 FROM HCFC-22 (PRODUCED) USING FACTOR(S) CALCULATED FROM PROCESS EFFICIENCIES**

$$E_{HFC-23} = EF_{calculated} \bullet P_{HCFC-22} \bullet F_{released}$$

Where:

$E_{HFC-23}$ = by-product HFC-23 emissions from HCFC-22 production, kg

$EF_{calculated}$ = HFC-23 calculated emission factor, kg HFC-23/kg HCFC-22

$P_{HCFC-22}$ = total HCFC-22 production, kg

$F_{released}$ = Fraction of the year that this stream was released to atmosphere untreated, fraction

The emission factor can be calculated from both the carbon efficiency (Equation 3.32) and the fluorine efficiency (Equation 3.33) and the value used in Equation 3.31 should normally be the average of these two values unless there are overriding considerations (such as a much lower uncertainty of one of the efficiency measures) that can be adequately documented. Annual average carbon and fluorine balance efficiencies are features of a well-managed HCFC-22 plant and are either normally available to the plant operator or may be obtained by examination of process accounting records. Similarly, if there is a vent treatment system, the length of time that this was in operation, and treating the vent stream from the HCFC-22 plant, should be available from records.

Total HCFC-22 production includes material that is used as a chemical feedstock as well as that which is sold for potentially dispersive uses.

**EQUATION 3.32**
**CALCULATION OF HFC-23 EMISSION FACTOR FROM CARBON BALANCE EFFICIENCY**

$$EF_{carbon\_balance} = \frac{(100 - CBE)}{100} \bullet F_{efficiency\ loss} \bullet FCC$$

Where:

$EF_{carbon\_balance}$ = HFC-23 emission factor calculated from carbon balance efficiency, kg HFC-23/kg HCFC-22

CBE = carbon balance efficiency, percent

$F_{efficiency\ loss}$ = factor to assign efficiency loss to HFC-23, fraction

FCC = factor for the carbon content of this component (= 0.81), kg HFC-23/kg HCFC-22

and

**EQUATION 3.33**
**CALCULATION OF HFC-23 EMISSION FACTOR FROM FLUORINE BALANCE EFFICIENCY**

$$EF_{fluorine\_balance} = \frac{(100 - FBE)}{100} \bullet F_{efficiency\ loss} \bullet FFC$$

Where:

$EF_{fluorine\_balance}$ = HFC-23 emission factor calculated from fluorine balance efficiency, kg HFC-23/kg HCFC-22

FBE = fluorine balance efficiency, percent

$F_{efficiency\ loss}$ = factor to assign efficiency loss to HFC-23, fraction

FFC = factor for the fluorine content of this component (= 0.54), kg HFC-23/kg HCFC-22

The factor to assign the efficiency loss to HFC-23 is specific to each plant and, if this method of calculation is used, the factor should have been established by the process operator. By default, the value is 1; that is all of the loss in efficiency is due to co-production of HFC-23. In practice, this is commonly the most significant efficiency loss, being much larger than losses of raw materials or products.

The factors for carbon and fluorine contents are calculated from the molecular compositions of HFC-23 and HCFC-22 and are common to all HCFC-22 plants at 0.81 for carbon and 0.54 for fluorine.

### Tier 3

Tier 3 methodologies are potentially the most accurate. The Tier 3 methodologies provided here give equivalent results and the choice between them will be dictated by the information available in individual facilities. In each case, the national emission is the sum of factory specific emissions, each of which may be determined using a Tier 3 method to estimate the composition and flowrate of gas streams vented to atmosphere (either directly and continuously – as in Tier 3a - or by continuous monitoring of a process parameter related to the emission - Tier 3b - or by monitoring the HFC-23 concentration continuously within the reactor product stream - Tier 3c):

**EQUATION 3.34**
**TIER 3a CALCULATION OF HFC-23 EMISSIONS FROM INDIVIDUAL PROCESS STREAMS (DIRECT METHOD)**

$$E_{HFC-23} = \sum_i \sum_j \int_t C_{ij} \bullet f_{ij} \qquad [\textstyle\int_t \text{ means the quantity should be summed over time.}]$$

Where:

$E_{HFC-23}$ = total HFC-23 emissions: the sum over all *i* plants, over all *j* streams in each plant of the emitted mass flows **f** and concentrations **C** is integrated over time *t*. (See Equation 3.37 for calculation of ‘instantaneous’ HFC-23 emissions in an individual process stream.)

or, where proxy methodology is used:

**EQUATION 3.35**
**TIER 3b CALCULATION OF HFC-23 EMISSIONS FROM INDIVIDUAL PROCESS STREAMS (PROXY METHOD)**

$$E_{HFC-23} = \sum_i \sum_j \int_t E_{ij} \qquad [\textstyle\int_t \text{ means the quantity should be summed over time.}]$$

Where:

$E_{HFC-23}$ = total HFC-23 emissions: $\mathbf{E_{i,j}}$ are the emissions from each plant and stream determined by the proxy methods. (See Equation 3.38 for calculation of HFC-23 emissions in an individual process stream.)

or, where the HFC-23 concentration within the reactor product stream is used:

**EQUATION 3.36**
**TIER 3C CALCULATION OF HFC-23 EMISSIONS FROM INDIVIDUAL PROCESS STREAMS (BY MONITORING REACTOR PRODUCT)**

$$E_{HFC-23} = \sum_i \int_t C_i \bullet P_i \qquad [\int_t \text{ means the quantity should be summed over time.}]$$

Where:

$E_{HFC-23}$ = total HFC-23 emissions: $\mathbf{P_i}$ is the mass flow of HCFC-22 product from the plant reactor at the plant *i*, and $\mathbf{C_i}$ is the concentration of HFC-23 relative to the HCFC-22 product at the plant *i*. (See Equation 3.40 for calculation of HFC-23 emissions at an individual facility by in-process measurement.)

### *Tier 3a*

The Tier 3a method is based on frequent or continuous measurement of the concentration and flow-rate from the vent at an individual plant. So that the quantity emitted to atmosphere is the mathematical product of the mass concentration of the component in the stream, the flowrate of the total stream (in units compatible with the mass concentration) and the length of time that this flow occurred:

**EQUATION 3.37**
**TIER 3a CALCULATION OF 'INSTANTANEOUS' HFC-23 EMISSIONS IN AN INDIVIDUAL PROCESS STREAM (DIRECT METHOD)**

$$E_{ij} = C_{ij} \bullet f_{ij} \bullet t$$

Where:

$E_{ij}$ = 'instantaneous' HFC-23 emissions from process stream *j* at plant *i*, kg

$C_{ij}$ = the concentration of HFC-23 in the gas stream actually vented from process stream *j* at plant *i*, kg HFC-23/kg gas

$f_{ij}$ = the mass flow of the gas stream from process stream *j* at plant *i* (generally measured volumetrically and converted into mass flow using standard process engineering methods), kg gas/hour

t = the length of time over which these parameters are measured and remain constant, hours

If any HFC-23 is recovered from the vent stream for use as chemical feedstock, and hence destroyed, it should be discounted from this emission; material recovered for uses where it may be emitted may be discounted here, if the emissions are included in the quantity calculated by the methods in Chapter 7. Because emissions are measured directly in this tier, it is not necessary to have a separate term for material recovered, unlike Tiers 3b and 3c.

The total quantity of HFC-23 released is then the annual sum of these measured instantaneous releases. Periods when the vent stream is processed in a destruction unit to remove HFC-23 should not be counted in this calculation. If it is necessary to estimate the quantity destroyed at each facility, the operator should calculate this based on the difference between the operating time of the plant and the duration of release (*t* above).

### *Tier 3b*

In many cases, measurements are not continuous but were gained during an intensive process survey or plant trial, and the results of the trial may be used to provide a proxy for calculating emissions during normal plant operation. In this case, the emission rate of the by-product is related to a more easily (or accurately) measurable parameter, such as feedstock flow rate. The trial(s) must meet the following conditions:

- There should have been no major process design, construction or operating changes that affect the plant upstream of the measurement point and so could render relationships between emissions and production invalid. (See also Box 3.14)
- The relationship between emissions and plant operating rate must be established during the trial(s), together with its uncertainty.

For almost all cases the rate of plant operation is a suitable proxy and the quantity of HFC-23 emitted depends on the current plant operating rate and the length of time that the vent flow was released.

**EQUATION 3.38**
**TIER 3b CALCULATION OF HFC-23 EMISSIONS IN AN INDIVIDUAL PROCESS STREAM (PROXY METHOD)**

$$E_{ij} = S_{ij} \bullet F_{ij} \bullet POR_{ij} \bullet t - R_{ij}$$

Where:

$E_{ij}$ = the mass emission of HFC-23 in vent stream *j* at plant *i*, kg

$S_{ij}$ = the standard mass emission of HFC-23 in vent stream *j* at plant *i* per 'unit' of proxy quantity, such as process operating rate (described in Equation 3.39, below), kg/'unit'

$F_{ij}$ = a dimensionless factor relating the measured standard mass emission rate to the emission rate at the actual plant operating rate. In many cases, the fraction produced is not sensitive to operating rate and $F_i$ is unity (i.e., the emission rate is proportional to operating rate). In other cases the emission rate is a more complex function of the operating rate. In all cases $F_i$ should be derived during the plant trial by measuring HFC-23 production at different operating rates. For situations where a simple function relating the emissions to the operating rate cannot be determined from testing, the proxy method is not considered appropriate and continuous measurement is desirable.

$POR_{ij}$ = the current process operating rate applicable to vent stream *j* at plant *i* averaged over *t* in 'unit/hour'. The units of this parameter must be consistent between the plant trial establishing the standard emission rate and the estimate of ongoing, operational emissions (described in Equation 3.39, below).

t = the actual total duration *of venting* for the year, or the period if the process is not operated continuously in hours. Annual emissions become the sum of all the periods during the year. The periods during which the vent stream is processed in a destruction system should not be counted here.

$R_{ij}$ = the quantity of HFC-23 recovered for vent stream *j* at plant *i* for use as chemical feedstock, and hence destroyed, kg. Material recovered for uses where it may be emitted potentially may be counted here if the emissions are included in the quantity calculated by the methods for ODS substitutes in Chapter 7 of this volume.

**EQUATION 3.39**
**TIER 3b CALCULATION OF STANDARD EMISSION FOR PROXY METHOD**

$$S_{T,ij} = C_{T,ij} \bullet f_{T,ij} / POR_{T,ij}$$

Where (for each test T):

$S_{ij}$ = the standard mass emission of HFC-23 in vent stream *j* at plant *i*, kg/'unit' (in units compatible with the factors in Equation 3.38, see $POR_{T,ij}$ below)

$C_{T,ij}$ = the average mass fractional concentration of HFC-23 in vent stream *j* at plant *i* during the trial, kg/kg

$f_{T,ij}$= the average mass flowrate of vent stream *j* at plant *i* during the trial, kg/hour

$POR_{T,ij}$ = the proxy quantity (such as process operating rate) at plant *i* during the trial, 'unit'/hour. The 'unit' depends on the proxy quantity adopted for plant *i* vent stream *j* (for example, kg/hour or $m^3$/hour of feedstock)

### *Tier 3c*

It is a relatively simple procedure to monitor the concentration of HFC-23 in the product of a reaction system relative to the amount of HCFC-22. This provides a basis for estimation of the quantity of HFC-23 released as the mathematical product of the monitored concentration and the mass flow of HCFC-22 made. If there is no vent treatment to abate emissions, this is a simple procedure. However, where there is abatement then it must be shown that this actually treats all streams that may be released into the atmosphere, including direct gas vents and the outgassing of aqueous streams. The latter, especially, may not be passed to the destruction facility. If all potential vent streams are not treated, the method cannot be used.

**EQUATION 3.40**

**TIER 3C CALCULATION OF HFC-23 EMISSIONS FROM AN INDIVIDUAL FACILITY BY IN-PROCESS MEASUREMENT**

$$E_i = C_i \bullet P_j \bullet t_F - R_i$$

Where:

$E_i$ = HFC-23 emissions from an individual facility *i*, kg

$C_i$ = the concentration of HFC-23 in the reactor product at facility *i*, kg HFC-23/kg HCFC-22

$P_i$ = the mass of HCFC-22 produced at facility *i* while this concentration applied, kg

$t_F$ = the fractional duration during which this HFC-23 is actually vented to the atmosphere, rather than destroyed, fraction

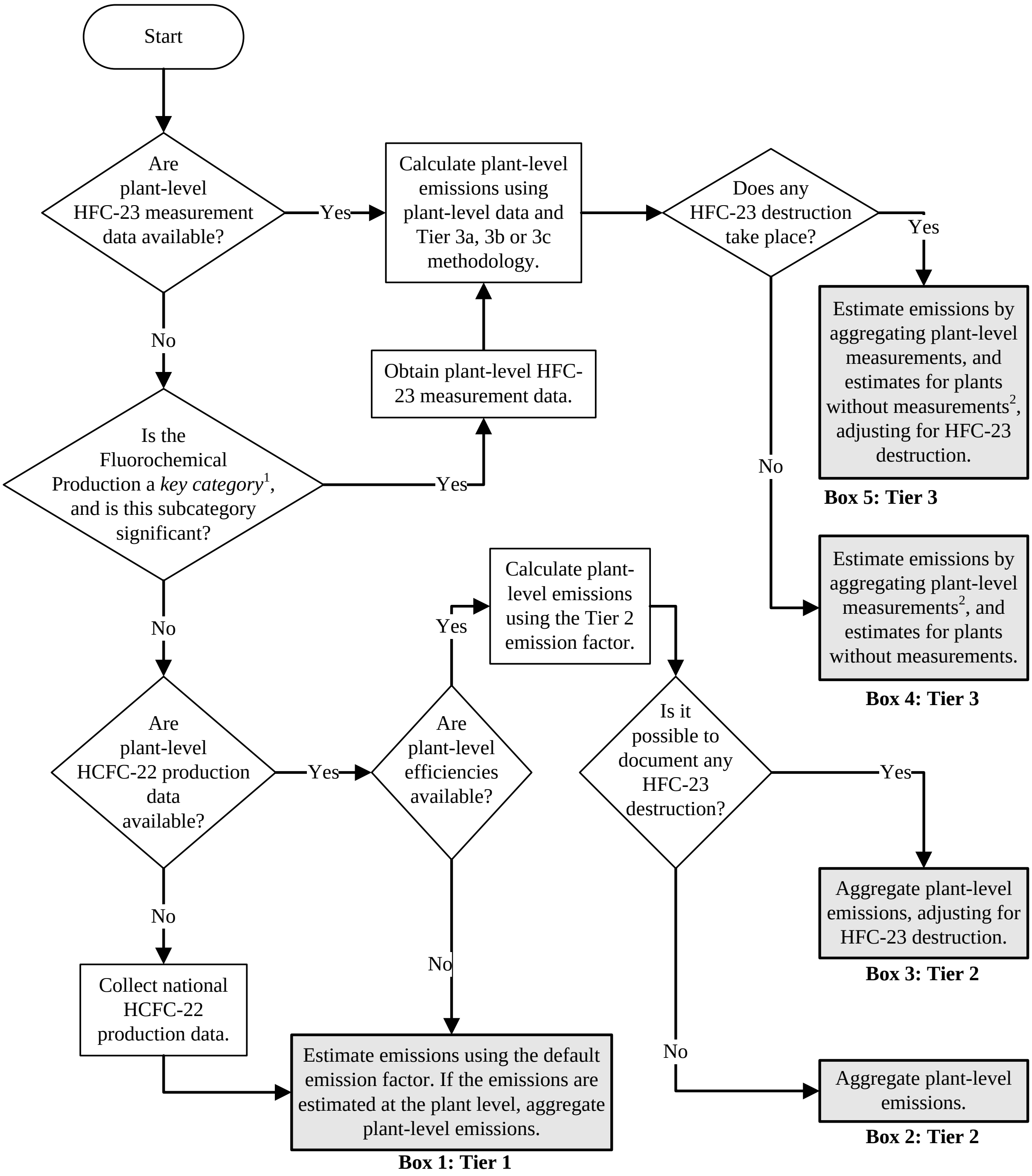
$R_i$ = the quantity of HFC-23 recovered from facility *i* for use as chemical feedstock, and hence destroyed, kg
Material recovered for uses where it may be emitted potentially may be counted here if the emissions are included in the quantity calculated by the methods in Chapter 7 of this volume.

The total quantity of HFC-23 released into the atmosphere is the sum of the quantities from the individual release periods and individual reaction systems.

HFC-23 that is recovered for use as chemical feedstock should be subtracted from the total quantity estimated here.

In summary, the Tier 1 method is relatively simple, involving the application of a default emission factor to the quantity of HCFC-22 produced. This method can be applied at the plant level or the national level. Tier 2 and Tier 3 methodologies are suitable only for plant level calculations. In cases where there are Tier 3 data available for some plants, the Tier 1 or Tier 2 methods can be applied to the remainder to ensure complete coverage. Uncertainty in the national emission is then calculated using production weighted uncertainties of the individual sources and standard statistical techniques. Regardless of the method, emissions abated should be subtracted from the gross estimate from each plant to determine net emissions before these are added together in the national estimate.

**Figure 3.16** **Decision tree for HFC-23 emissions from HCFC-22 production (or other similar by-product emissions from fluorochemical 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.
2. If there are Tier 3 data available for some plants, the Tier 1 or Tier 2 methods can be applied to the remainder to ensure complete coverage.

It is *good practice* to use the Tier 3 method if possible. Direct measurement is significantly more accurate than Tier 1 because it reflects the conditions specific to each manufacturing facility. In most cases, the data necessary to prepare Tier 3 estimates should be available because facilities operating to good business practice perform regular or periodic sampling of the final process vent or within the process itself as part of routine operations. For facilities using abatement techniques such as HFC-23 destruction, verification of the abatement efficiency is also done routinely. The Tier 1 (default) method should be used only in rare cases where plant-specific data are unavailable and this subcategory is not identified as significant subcategory under *key category*. (See Section 4.2 of Volume 1.)

## CHOICE OF EMISSION FACTORS

There are several measurement options within the Tier 3 method relating to the location and frequency of the sampling. In general, direct measurement of the emissions of HFC-23 may provide the highest accuracy but continuous or frequent measurement of parameters within the production process area itself may be more pragmatic and can be equally accurate. In both cases, the frequency of measurement must be high enough to represent the variability in the process (e.g., across the life of the catalyst). Issues related to measurement frequency are summarised in Box 3.14, Plant Measurement Frequency. General advice on sampling and representativeness is provided in Volume 1, Chapter 2.

In cases where plant-specific measurements or sampling are not available and Tier 1 methods are used, the default emission factor should be used, assuming no abatement methods. For plants in operation prior to 1995 the default emission factor is 0.04 kg HFC-23/kg HCFC-22 (4 percent) (IPCC, 1996; USEPA, 2001). This is a default to be used when there are no measurements and describes the output of HFC-23 from a typical HCFC-22 plant in the absence of recovery or destruction of HFC-23. The value is consistent with atmospheric observations of HFC-23 concentrations in the 1978-1995 time period (Oram *et al.,*1998). These showed globally averaged emissions to be equivalent to 2 percent of the total quantity of HCFC-22 produced at a time when significant HFC-23 was being recovered and converted into Halon 1301 (McCulloch, 1992) and abatement was required practice in several countries where there was significant production.

It is possible, by process optimisation, to reduce the production to between 0.014 and 0.03 kg HFC-23/kg HCFC-22 (1.4 to 3 percent) but it is not possible to completely eliminate HFC-23 formation this way (IPCC, 2000). Furthermore, the extent of the reduction is highly dependent on the process design and the economic environment (measures to reduce HFC-23 can often reduce the process output). In an optimised process HFC-23 production and emissions will, invariably, have been measured; it is not possible to optimise process operation without such measurements and so default values have no meaning in this context for an individual plant. However, the state of the technological art has been advanced by optimisation of individual plants and that art should have been built into the design of recent plants, suggesting a default emission factor of 0.03 kg HFC-23/kg HCFC-22 (3 percent). These default values have a large uncertainty (in the region of 50 percent). For more accurate assessments, the actual emissions should be determined by Tier 2 or Tier 3 methodology and, if necessary, assigned to previous years using the guidance provided in Chapter 7 of this volume.

**TABLE 3.28**
**HFC-23 DEFAULT EMISSION FACTORS**

| **Technology** | **Emission Factor (kg HFC-23/kg HCFC-22 produced)** |
|---|---|
| Old, unoptimised plants (e.g., 1940s to 1990/1995) | 0.04 |
| Plants of recent design, not specifically optimised | 0.03 |
| Global average emissions (1978 - 1995)[4] | 0.02 |
| *For comparison:* | |
| *Optimised large plant- requiring measurement of HFC-23 (Tier 3)* | *Down to 0.014* |
| *Plant with effective capture and destruction of HFC-23 (Tier 3)* | *Down to zero* |

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[4] The global average is calculated from the change in atmospheric concentration of HFC-23. It does not discriminate between plant emissions, which range from nothing to greater than 4 percent of the HCFC-22 production.

**BOX 3.14**
**PLANT MEASUREMENT FREQUENCY**

The accuracy and precision of the estimates of annual HFC-23 emissions depend on the number of samples (the frequency of sample collection) together with the accuracy of measurement of flowrates and the extent to which discrete flow measurements can represent the total quantity vented. Since production processes are not completely static, the greater the process variability, the more frequently plants need to measure. As a general rule, sampling and analysis should be repeated whenever a plant makes any significant process changes. Before choosing a sampling frequency, the plant should set a goal for accuracy and use statistical tools to determine the sample size necessary to achieve the goal. For example, a study of HCFC-22 producers indicates that sampling once per day is sufficient to achieve an extremely accurate annual estimate. This accuracy goal should then be revised, if necessary, to take into account the available resources. (RTI, Cadmus, 1998)

### CHOICE OF ACTIVITY DATA

When using the Tier 1 method, production data should be obtained directly from producers. There are several ways producers may determine their production levels, including shipment weights and measuring volume-times-density, using flow meters. These data should account for all HCFC-22 production for the year, whether for sale or for use internally as feedstock, and the plant should describe how the HCFC-22 production rate is determined. In some circumstances, producers may consider plant production data to be confidential. For national-level activity data, submission of HCFC-22 production data is already required under the Montreal Protocol.

### COMPLETENESS

It should be possible to obtain complete sampling data because there are only a small number of HCFC-22 plants in each country, and it is standard practice for each plant operator to monitor process efficiencies and hence HFC-23 losses, leading to the adoption of Tier 2 methodology. The destruction efficiencies of thermal oxidisers used to abate HFC-23 are generally high (>99 percent) but it is important to establish the composition of the exit gas in order to ensure that account is taken of emissions of fluorinated greenhouse gases from this point.

### DEVELOPING A CONSISTENT TIME SERIES

Emission of HFC-23 from HCFC-22 production should be estimated using the same method for the entire time series and appropriate emission factors. If data for any years in the time series are unavailable for the Tier 3 method, these gaps should be filled according to the guidance provided in Volume 1, Chapter 5.

## 3.10.1.3 UNCERTAINTY ASSESSMENT

### TIER 1

Unlike the other Tiers, where uncertainties are based on measurements and statistics, Tier 1 uncertainties are assessed through expert judgement and an error of approximately 50 percent could be considered for Tier 1 based upon knowledge of the variability in emissions from different manufacturing facilities. An error of this magnitude will completely outweigh the uncertainty in the activity.

### TIER 2

Uncertainty of the Tier 2 result is calculated by the root-squared sum of the individual uncertainties in production mass quantity and efficiencies, assuming the carbon and fluorine uncertainties are the same. Where the uncertainties in carbon and fluorine efficiency differ significantly (enough to cause a material difference to the calculated emission), the value with the lower uncertainty should be used throughout the calculation.

Uncertainty in the value derived by Tier 2 methods is much larger than that expected from Tier 3 but is, nevertheless, quantifiable. Typically, for a plant producing about 4 percent HFC-23, the carbon efficiency is in the region of 95 percent and the fluorine efficiency 92 percent. If these efficiencies can be measured to within 1 percent, then the error in the Tier 2 HFC-23 estimate would be less than 20 percent. Estimating efficiencies to this degree of accuracy will require rigorous accounting procedures and that all raw materials and product for sale should be weighed in or out of the facility. Such a regime sets the expected accuracy of the overall activity (for both Tiers 1 and 2); with good accounting and measurement of production by weight, it should be possible to reduce the error in the activity to below 1 percent.

#### TIER 3

For HFC-23, the Tier 3 method is significantly more accurate than either the Tier 2 measured or Tier 1 default methods. Regular Tier 3 sampling of the vent stream can achieve an accuracy of 1-2 percent at a 95 percent confidence level in HFC-23 emissions and the uncertainty of the Tier 3 (proxy) result may be similar. In both cases, the uncertainty may be calculated statistically from the uncertainties of the input parameters and, because these methods do not rely on emission factors or activities, the concept of subdividing uncertainty has no validity.

Uncertainty of the estimate is expressed as a coefficient of variance (percent) and, for each of these streams, there will be an uncertainty as a consequence of uncertainties in measured concentration and flowrate and uncertainty in the duration of the flow. The combined uncertainty can be determined analytically and should be calculated using the standard methodology described in Chapter 3 of Volume 1.

## 3.10.1.4 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this sub-source category are outlined below:

#### Comparison of emissions estimates using different approaches

Inventory compilers should compare reported plant emissions estimates against those determined using the Tier 1 default factor and production data. If only national production data are available, they should compare aggregated plant emissions to a national default estimate. If significant differences are found in the comparison, they should answer the following questions:

1. Are there inaccuracies associated with any of the individual plant estimates (e.g., an extreme outlier may be accounting for an unreasonable quantity of emissions)?
2. Are the plant-specific emission factors significantly different from one another?
3. Are the plant-specific production rates consistent with published national level production rates?
4. Is there any other explanation for a significant difference, such as the effect of controls, the manner in which production is reported or possibly undocumented assumptions?

#### Direct emission measurement check

- Inventory compilers should confirm that internationally recognised, standard methods were used for plant measurements. If the measurement practices fail this criterion, then the use of these emissions data should be carefully evaluated. It is also possible that, where a high standard of measurement and QA/QC is in place at sites, the uncertainty of the emissions estimates may be revised downwards.
- Each plant's QA/QC process should be evaluated to assess if the number of samples and the frequency of sample collection is appropriate given the variability in the process itself.
- Where possible, inventory compilers should verify all measured and calculated data through comparison with other systems of measurement or calculation. For example, emissions measurement within the process itself can be verified periodically with measurement of the vent stream. Inventory compilers should verify abatement system utilisation and efficiency.
- With a periodic external audit of the plant measurement techniques and results, it is also possible to compare implied emission factors across plants and account for major differences.

### 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, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

- To provide for completely transparent reporting, emissions of HFC-23 from HCFC-22 production should be reported as a separate item, rather than included with other HFC emissions.
- Documentation should also include:
  - (i) Methodological description;
  - (ii) Number of HCFC-22 plants;
  - (iii) HCFC-22 production (if multiple producers);
  - (iv) Presence of abatement technology;
  - (v) Process descriptions, operating parameters; and
  - (vi) Related emission factors.

**Confidentiality**

- The use of the Tiers 2 and 3 methods would mean that the plant emissions of HFC-23 are reported separately from the production of HCFC-22. By de-coupling the HFC-23 emissions and HCFC-22 production, the emission data on HFC-23 cannot be considered to be of commercial confidence as it does not reveal the levels of production of HCFC-22 without detailed and confidential knowledge of the individual manufacturing facility.
- The application of the Tier 1 method to total national production of HCFC-22 would enable this to be calculated from published emissions of HFC-23 and, if there were less than three producers, such production data could be considered confidential business information. In such cases, steps should be taken to protect confidentiality through, for example, the aggregation of all HFC emissions. For transparency reasons, whenever there is aggregation, a qualitative discussion of HCFC-22 production should be included.
- When national emissions are calculated as the sum from individual facilities and these have been calculated using different methodologies, it is not possible to recalculate the HCFC-22 production from these data alone and there should be no problems concerning confidentiality.

## 3.10.2 Emissions from production of other fluorinated compounds

### 3.10.2.1 INTRODUCTION

A large number of fluorine containing greenhouse gases can be produced as by-products of fluorochemical manufacture and emitted into the atmosphere. For example, in a recent national inventory, significant by-product emissions of $SF_6$, $CF_4$, $C_2F_6$, $C_3F_8$, $C_4F_{10}$, $C_5F_{12}$ and $C_6F_{14}$ were reported for a fluorochemical plant (UNFCCC, 2005). Other examples include the release of by-product $CF_4$ from the production of CFC-11 and 12 or of $SF_6$ from the production of uranium hexafluoride in the nuclear fuel cycle.

Emissions of a chemical occur during its production and distribution or as a by-product during the production of a related chemical (HFC-23 from HCFC-22 production is covered specifically in Section 3.10.1 above). There may also be emissions of the material that is being produced; the so-called ‘fugitive emissions’. Both by-product and fugitive emissions are calculated in the same way. In this section, emissions associated with use are not addressed specifically, being counted in the emissions related to consumption (see Chapters 4.5, 6, 7 and 8 in this volume). Typically, fluorochemicals may be released from chemical processes involving a broad range of technologies and processes[5]:

- Telomerization Process used in the production of fluorochemicals fluids and polymers
- Photooxidation of tetrafluoroethylene to make fluorochemical fluids
- Direct Fluorination often used in $SF_6$ production
- Halogen Exchange Processes to make low boiling PFCs like $C_2F_6$ and $CF_4$, HFC 134a and 245fa
- $NF_3$ manufacturing by direct fluorination
- Production of uranium hexafluoride

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[5] This list is illustrative.

- Production of fluorinated monomers like tetrafluoroethylene and hexafluoropropylene
- Production of fluorochemical agrochemcials
- Production of fluorochemical anesthetics

Halogen exchange processes are extensively used for HFC manufacture, while most PFCs and $SF_6$ require elemental fluorine, generated electrochemically. In 'electrochemical fluorination' processes, the fluorine is not separated but makes the desired product in the electrochemical cell. In other processes it is separated and subsequently used, either as the elemental gas or as a component of a carrier system, such as $CoF_3$. Each process will have a different spectrum of emissions, in terms of both chemical nature and quantities, and so a common default emission function is of relatively little value. It is essential that the existence of potentially emissive plants is identified within each country, hence this step is first in the decision tree (Figure 3.17). The common factor for these plants is the use of anhydrous hydrogen fluoride, which is the source of fluorine in halogen exchange processes and in processes that use elemental fluorine. The production and importation of anhydrous hydrogen fluoride can therefore be used as a means of tracing significant producers of fluorochemicals. Further enquiries (see Figure 3.17) can then elucidate whether or not there are significant fluorochemical greenhouse gas emissions.

### 3.10.2.2 METHODOLOGICAL ISSUES

#### CHOICE OF METHOD

It is *good practice* to choose the method using the decision tree shown in Figure 3.17. If the Category 2B9 Fluorochemical Production is identified as *key* and this subcategory is judged to be significant, inventory compilers should consider whether or not emissions are dominated by the production of a sub-set of chemicals, and focus more sophisticated data collection efforts on production of these chemicals. The number of major producers of these fluorinated greenhouse gases is quite small: in the case of $SF_6$, there are globally about 6 companies with about 10 production facilities world-wide (Preisegger, 1999). The number of smaller producers may grow in the near future, particularly in developing economies. However, a survey of national producers should not be difficult to compile.

#### Tier 1

In the Tier 1 methodology, a default emission factor, or a similar number derived for the particular country's circumstances, can be used to estimate national production-related emissions of individual HFCs, PFCs, $SF_6$ and other fluorinated greenhouse gases.

**EQUATION 3.41**
**TIER 1 CALCULATION OF PRODUCTION-RELATED EMISSIONS**

$$E_k = EF_{default,k} \bullet P_k$$

Where:

$E_k$ = production-related emissions of fluorinated greenhouse gas *k*, kg

$EF_{default,\,k}$ = default emission factor, kg/kg

$P_k$ = total production of fluorinated greenhouse gas *k*, kg

Problems of confidentiality arising from reporting specific component data can be circumvented by providing a single number for total national emissions of each HFC, PFC and $SF_6$. This may be facilitated if data are collected by a third party and reported only as this total.

#### Tier 2

The method based on process efficiencies, which works for HFC-23 emissions from HCFC-22 plants, is of less value for other types of plants. This is due in part to the lower inefficiency expected from these other by-product emissions; the uncertainty in measurement of efficiencies is likely to be much greater than the by-product emission factor. Furthermore, a range of by-products may be responsible for process inefficiency (unlike the case for HCFC-22 where one by-product predominates). However, production efficiency data should exist for each process and, in the absence of a more rigorous estimate, the quantity of emissions estimated from process inefficiencies may be used in a qualitative decision as to whether or not these emissions are a significant subcategory under a *key category* (in which case, Tier 3 methodology is specified).

### Tier 3

The Tier 3 methodology is potentially the most accurate estimate and is the sum of factory specific emissions of *each* by-product fluorinated greenhouse gas determined using standard methods to estimate the composition and flowrate of gas streams actually vented to atmosphere after any abatement technology. In this case:

**EQUATION 3.42**
**TIER 3 DIRECT CALCULATION OF PRODUCTION-RELATED EMISSIONS**

$$E_k = \sum_i \sum_j \int_t C_{ijk} \bullet f_{ijk} \qquad [\textstyle\int_t \text{ means the quantity should be summed over time.}]$$

Where:

$E_k$ = total production-related emissions of fluorinated greenhouse gas *k*: the sum over all *i* plants, over all *j* streams in each plant of the emitted mass flows **f** and concentrations **C** integrated over time *t*.

or, where proxy methodology is used, for example where the emission rate of the by-product is normalised to a more easily (or accurately) measurable parameter, such as feedstock flow rate, as described in Equation 3.35 in Section 3.10.1:

**EQUATION 3.43**
**TIER 3 PROXY CALCULATION OF PRODUCTION-RELATED EMISSIONS**

$$E_k = \sum_i \sum_j \int_t E_{ijk} \qquad [\textstyle\int_t \text{ means the quantity should be summed over time.}]$$

Where:

$E_k$ = total production-related emissions of fluorinated greenhouse gas *k*: $\mathbf{E_{ijk}}$ = the emissions of fluorinated greenhouse gas *k* from each plant and stream determined by the proxy methods, described in Equations 3.38 and 3.39 in Section 3.10.1

Note that, generally, flows are measured volumetrically and should be converted into mass flow (kg/hour) based on the ideal gas law, temperature, pressure and composition, similarly concentration should be converted into compatible units (e.g., kg/kg).

In this case, the flowrates, concentrations and duration should be calculated separately for the periods when the abatement technology is or is not operating and only those that lead to actual emissions should be summed and reported.

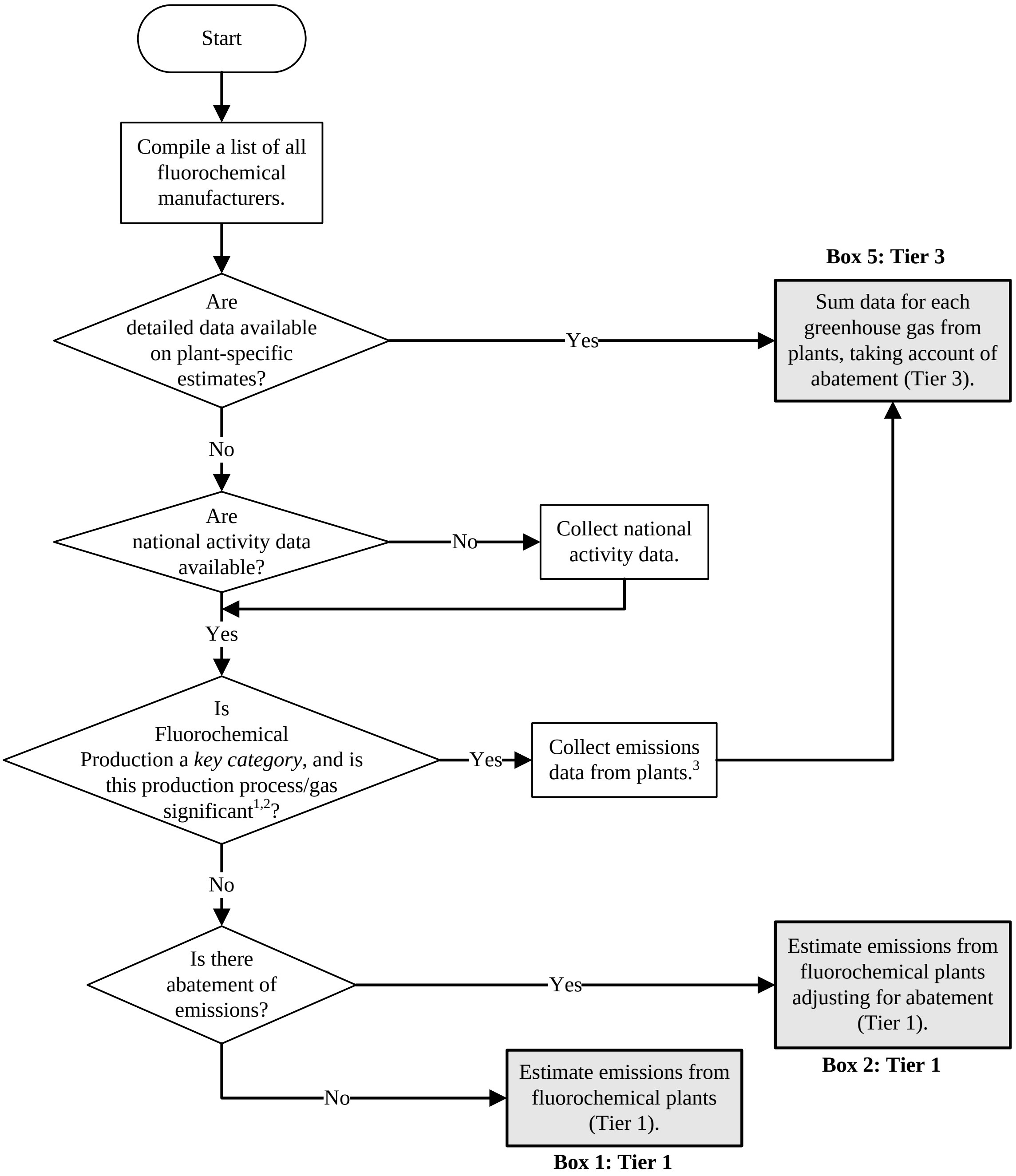
## CHOICE OF EMISSION FACTORS

Tier 3 relies on measurements of the quantities of individual materials that are released into the atmosphere and neither Tier 2 nor Tier 3 relies on emission factors. For Tier 1, in the absence of abatement measures, a default emission factor of 0.5 percent of production, not counting losses in transport and transfer of materials, is suggested for HFCs and PFCs, based on data supplied to AFEAS (2004). There is a wide range of substances that may potentially be released. However, the AFEAS data showed that the components that were lost during production of a particular fluorochemical had, in general, radiative forcing properties similar to those of the desired fluorochemical. Consequently, for sources that are not significant subcategories under *key category*, fugitive and by-product emissions are the same and are included in the 0.5 percent emission factor.

In the case of $SF_6$, based on German experience, a default emission factor of 0.2 percent of the total quantity of $SF_6$ produced is suggested for those countries in which the predominant end use does not require highly purified $SF_6$ gas (e.g., electrical equipment, insulated windows) (Preisegger, 1999). Based on experience in Japan, in countries where the major uses require highly purified $SF_6$ gas (e.g., semiconductor manufacturing), the default value should be 8 percent because of handling losses during disposal of residual gas (i.e., the ‘heel’ that is not used or recycled) in returned cylinders (Suizu, 1999). If national data are available, these should be used, particularly for other materials not specifically listed here.

The default emission factors are based on situations where no abatement measures are employed. If the quantity of gas emitted to the atmosphere is reduced by, for example, thermal oxidation of the vent stream, the quantity emitted should be adjusted to account for the destruction efficiency of the oxidiser and the length of time that it is in service. Based on the experience in the destruction of HFC-23, a default destruction efficiency of 100 percent is suggested but the on-line time of the destruction process will have a greater effect on emissions and should be recorded.

**Figure 3.17** **Decision tree for emissions of fluorinated greenhouse gases from production processes, applicable to both fugitive and by-product emissions**



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.
2. Tier 2 methodology may be used at this point to establish whether or not this is a *key category* but, as explained in Section 3.10.2.2, this is the only use for Tier 2.
3. Data may be collected as a country study by a third party in order to preserve confidentiality.

## CHOICE OF ACTIVITY DATA

Again, activity data has no role in the Tiers 3 and 2 estimates, which are based on measurements. For Tier 1, the activity is the annual mass of the desired fluorochemical that is produced.

### Recycling

Recycling of used gas may be done by the producers of new gas or by other recycling firms. Emissions may occur during handling and purification of old gas and handling of recycled gas. Specific emission factors are not available. Thus, *good practice* is to use the same default factor as for new production.

### COMPLETENESS

For some inventory compilers, identifying smaller producers and, in particular, recycling firms may be a difficult task. However, initial estimates based on the national mass balance of these fluorinated greenhouse gases should identify if production related emissions from such entities provide a sizeable contribution to total national emissions.

### DEVELOPING A CONSISTENT TIME SERIES

Both by-product and fugitive emissions of fluorocompounds from production processes should be estimated using the same method for the entire time series and appropriate emission factors. If data for any years in the time series are unavailable for the Tier 3 method, these gaps should be filled according to the guidance provided in Volume 1, Chapter 5.

## 3.10.2.3 UNCERTAINTY ASSESSMENT

For Tier 1, the uncertainty in activity data needs to be determined for the reporting country and statistically combined with the uncertainty in the default emission factor. Typically, in a well operated facility, the default uncertainty in activity data should be in the region of 1 percent, assuming that rigorous accounting records are maintained and that production is monitored by weight. The actual emission factor may range from well in excess of the default value to zero. The default uncertainty of the default emission factors is therefore set at 100 percent, for example 0.5±0.5 (%).

For Tier 3 emissions, the uncertainty of the measurements should be determined individually and combined (using standard statistical methods) to provide a total uncertainty for the estimate. The methodology is identical to that described for HFC-23 from HCFC-22. In the Tier 2 methodology, the uncertainty both of the measurements of efficiencies and the assignment of losses to individual compounds should be assessed. Because these are liable to produce a much larger uncertainty than that from Tier 3, the utility of Tier 2 is likely to be limited to assessing whether or not by-product fluorochemical emissions are a significant subcategory under *key category*.

## 3.10.2.4 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of emissions estimates using different approaches

Inventory compilers should compare the estimate based on aggregated producer-level data to an estimate based on national production data and the suggested default emission factors. They should investigate significant discrepancies in cooperation with the producers to determine if there are unexplained differences.

### REPORTING AND DOCUMENTATION

Confidentiality issues may arise where there are limited numbers of manufacturers. In these cases more aggregate reporting of total national emissions may be necessary. If survey responses cannot be released as public information, third-party review of survey data may be necessary to support data verification efforts.

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. 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.

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## SECTION 3.9

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# CHAPTER 4

# METAL INDUSTRY EMISSIONS

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# 4 METAL INDUSTRY EMISSIONS

## 4.1 INTRODUCTION

The following sections 4.2 through 4.7 give guidance for estimating greenhouse gas emissions that result from the production of metals.

- Section 4.2 covers emissions from iron and steel, and metallurgical coke production;
- Section 4.3 covers emissions from ferroalloy production;
- Section 4.4 covers emissions from aluminium production;
- Section 4.5 covers emissions from magnesium production;
- Section 4.6 covers emissions from lead production;
- Section 4.7 covers emissions from zinc production.

Care should be exercised to avoid double counting of carbon dioxide ($CO_2$) emissions in both this chapter and in Volume 2 on Energy Sector, or, in omitting $CO_2$ emissions since $CO_2$ emissions resulting from carbon's role as process reactant and as a heat source to drive the chemical reactions involved in the metallurgical processes are closely related in many cases. Should $CO_2$ capture technology be installed at a metals production facility, the $CO_2$ captured should be deducted in a higher tier emissions calculation. Any methodology taking into account $CO_2$ capture should consider that $CO_2$ emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately, e.g., for iron and steel production, inventory compilers should ensure that the same quantities of $CO_2$ are not double counted. In these cases the total amount of $CO_2$ captured should preferably be reported in the corresponding energy combustion and IPPU source categories in proportion to the amounts of $CO_2$ generated in these source categories. The default assumption is that there is no $CO_2$ capture and storage (CCS) taking place. For additional information on $CO_2$ capture and storage refer to Volume 3, Section 1.2.2 and for more details to Volume 2, Section 2.3.4.

# 4.2 IRON & STEEL AND METALLURGICAL COKE PRODUCTION

The production of iron and steel leads to emissions of carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$). This chapter provides guidance for estimating emissions of $CO_2$ and $CH_4$.[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 $CO_2$ and $CH_4$ 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).

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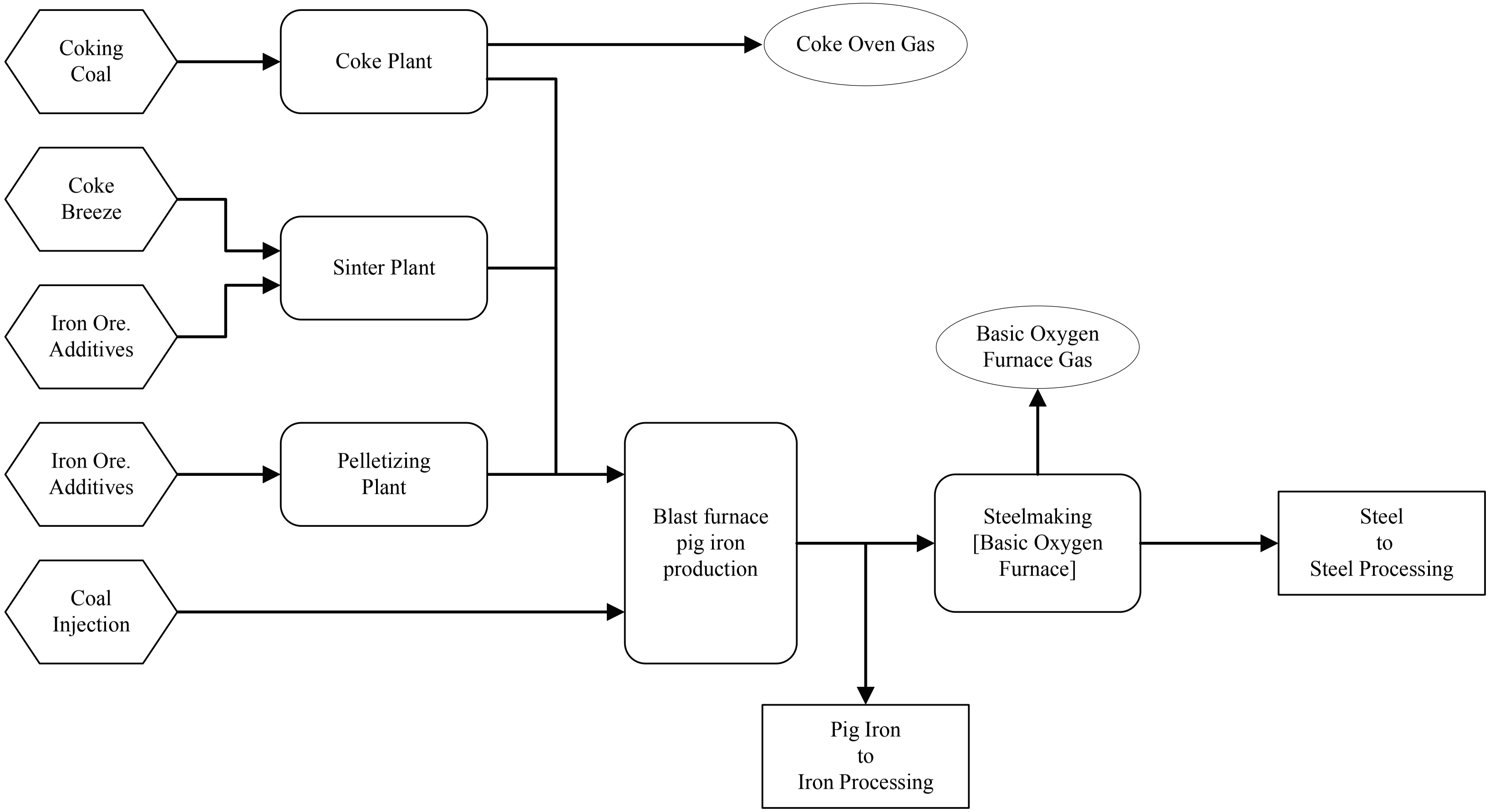
[1] No methodologies are provided for $N_2O$ emissions. These emissions are likely to be small, but countries can calculate estimates provided they develop country-specific methods based on researched data.

**Figure 4.1 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

### METALLURGICAL COKE PRODUCTION

Metallurgical coke is primarily used in the blast furnace to make iron. Coke is also used in other metallurgical processes, such as the manufacture of cast iron, ferroalloys, lead, and zinc, and in kilns to make lime and magnesium. Metallurgical coke is the solid product obtained from the carbonisation of coal, principally coking coal, at high temperature. It is low in moisture content and volatile matter. Coking coal refers to bituminous coal with a quality that allows the production of a coke suitable to support a blast furnace charge. Its gross calorific value is greater than 23 865 kJ/kg (5 700 kcal/kg) on an ash-free but moist basis. Coke oven gas is a by-product of the manufacture of metallurgical coke for the production of iron and steel. Figure 4.2 illustrates the coke production process and associated sources of $CH_4$ and $CO_2$ emissions.

Note that coke oven gas may be burned to heat coke ovens or transferred onsite in an integrated iron and steel plant and used in sinter production or iron production processes. Coke oven gas may also be transferred off site (e.g., into the natural gas distribution system) and used as an energy source. The combustion of coke in blast furnaces during the iron and steel-making process produces blast furnace gas, which may then be recovered and transferred from the iron and steel mill to the onsite coke plant and burned to heat coke ovens or used in sinter production. The combustion of blast furnace gas and coke oven gas is the main sources of $CO_2$ and $CH_4$ emissions in coke production.

### SINTER PRODUCTION

Iron ore and other iron-containing materials may be agglomerated in sinter plants at integrated iron and steel plants prior to introduction into the blast furnace. Feedstock to sinter plants may include fine iron ores, additives (e.g., lime, olivine), and iron-bearing recycled materials from downstream iron and steelmaking processes (e.g., dust from blast-furnace gas cleaning). Coke breeze (small-grade coke oven coke with particle sizes of < 5 mm) is the most commonly used process material in sinter plants. The coke breeze may be produced from the onsite coke ovens in integrated iron and steel plants, or may be purchased from offsite coke producers. Blast furnace gas or coke oven gas produced onsite during integrated iron and steel production may be used in sinter plants. Operation of sinter plants produces carbon dioxide emissions from oxidation of the coke breeze and other inputs. Off gas from sinter production also contains methane and other hydrocarbons. Figure 4.3 illustrates the sinter production process.

### PELLET PRODUCTION

Pellets are formed from iron-containing raw materials (i.e., fine ore and additives) into 9-16 mm spheres in a very high temperature process. The process includes grinding, drying, balling, and thermal treatment of the raw materials. Pelletisation plants are principally located at iron mines or at shipping ports, but can also be located onsite as part of an integrated iron and steel facility. Natural gas or coal may be used as fuel for pelletisation plants; for pelletisation plants located onsite at an integrated iron and steel facility, coke oven gas may be used as a fuel. Energy consumption for the process and the associated $CO_2$ emissions will depend in part on the quality of the iron ore and other raw materials used in the process. The $CO_2$ emissions will also depend upon the carbon contents and heating values of fuels used in the process.

### IRONMAKING AND THE ROLE OF COKE

Most $CO_2$ emitted by the iron and steel industry is associated with the production of iron, more specifically the use of carbon to convert iron ore to iron. Figure 4.4 describes the iron-making process and associated sources of emissions. Carbon is supplied to the blast furnace mainly in the form of coke produced from metallurgical grade coking coal (but can also be in the form charcoal made from wood or other forms of carbon.). Carbon serves a dual purpose in the iron making process, primarily as a reducing agent to convert iron oxides to iron, but also as an energy source to provide heat when carbon and oxygen react exothermically. Blast furnace gas is produced during the combustion of coke in blast furnaces. It is typically recovered and used as a fuel partly within the plant and partly in other steel industry processes, or in power stations equipped to burn it. Blast furnace gas may also be recovered and transferred from the iron and steel mill to the onsite coke plant and burned for energy within the coke ovens. Blast furnace gas may also be transferred offsite and used as an energy source both within the furnace and when blast furnace gas is combusted to heat blast air. Oxygen steel furnace gas is obtained as a by-product of the production of steel in a basic oxygen furnace (BOF) and is recovered on leaving the furnace. All carbon used in blast furnaces should be considered process-related IPPU emissions.

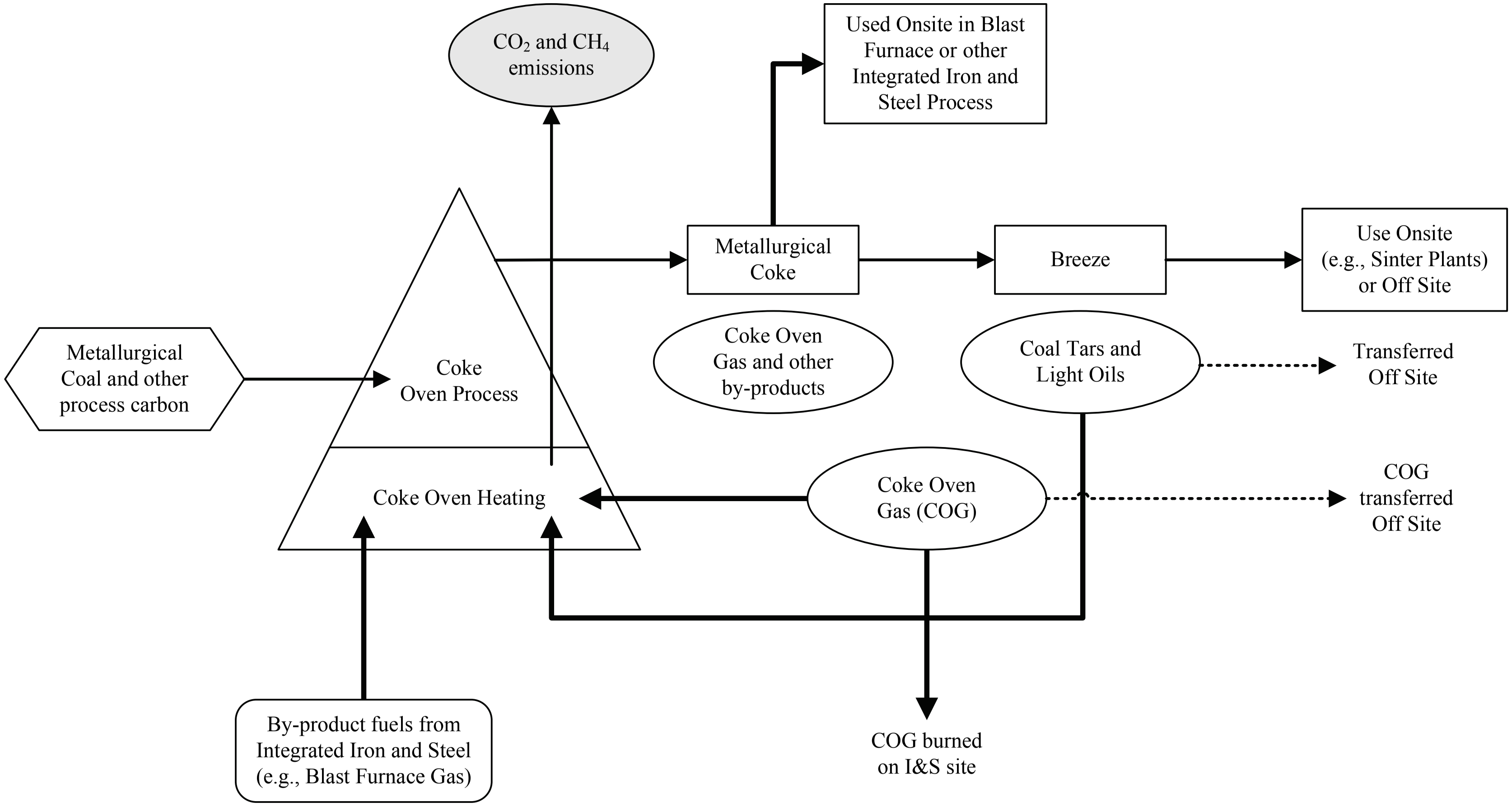
Additionally, iron can be produced through a direct reduction process. Direct reduction involves the reduction of iron ore to metallic iron in the solid state at process temperatures less than 1 000°C. A solid product referred to as direct reduced iron (DRI) is produced by the direct reduction process. DRI has a carbon content of < 2 percent. DRI is normally used as a replacement for scrap metal in the electric arc furnace steelmaking route, but may also be used as a feedstock for blast furnace iron making. DRI may also be melted into briquettes, referred to as hot briquetted iron (HBI), when the product has to be stored or transported. Inventory preparers can estimate the $CO_2$ emissions from these processes from the energy consumption and carbon content of the fuel (e.g., natural gas, coal).

### STEELMAKING

Steel production in a BOF begins by charging the vessel with 70-90 percent molten iron and 10-30 percent steel scrap. High purity oxygen then combines with the carbon in the iron to create an exothermic reaction that melts the charge while lowering the carbon content. Iron from the blast furnace usually contains 3-4 percent carbon, which must be reduced to less than 1 percent, refined, and alloyed to produce the desired grade of steel.

Steel production in an EAF typically occurs by charging 100 percent recycled steel scrap, which is melted using electrical energy imparted to the charge through carbon electrodes and then refined and alloyed to produce the desired grade of steel. Although EAFs may be located in integrated plants, typically they are stand-alone operations because of their fundamental reliance on scrap and not iron as a raw material. Since the EAF process is mainly one of melting scrap and not reducing oxides, carbon’s role is not as dominant as it is in the blast furnace/BOF process. In a majority of scrap-charged EAF, $CO_2$ emissions are mainly associated with consumption of the carbon electrodes. All carbon used in EAFs and other steelmaking processes should be considered process-related IPPU emissions. Figure 4.5 illustrates the steel making process and associated sources of emissions.

**Figure 4.2** **Illustration of coke production process (emissions reported in Category 1A of the Energy Sector)**



Note:
Bold lines apply only to Onsite Coke Production at Integrated Iron and Steel Mill. Dashed lines apply to transfers of materials to ‘Off Site processes.’ ‘Off Site process’ does not include Integrated Iron and Steel production processes, which are categorised as Onsite.

**Figure 4.3** **Illustration of sinter production process**

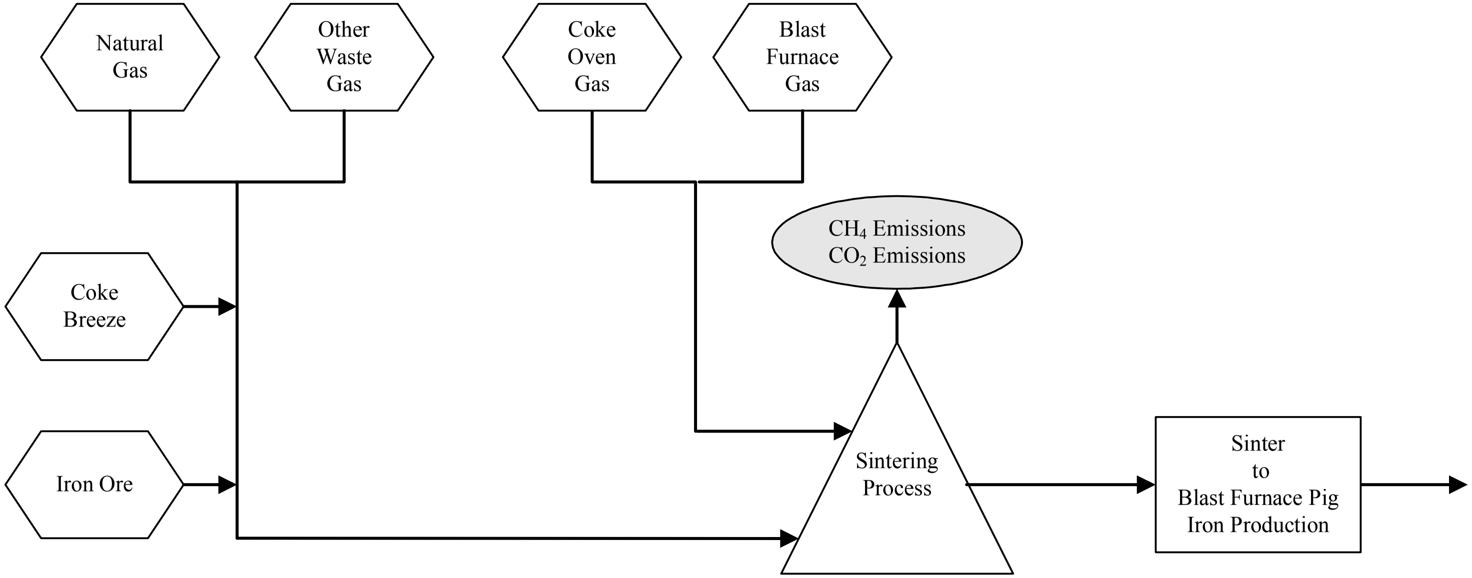


**Figure 4.4** **Illustration of pig iron production processes**

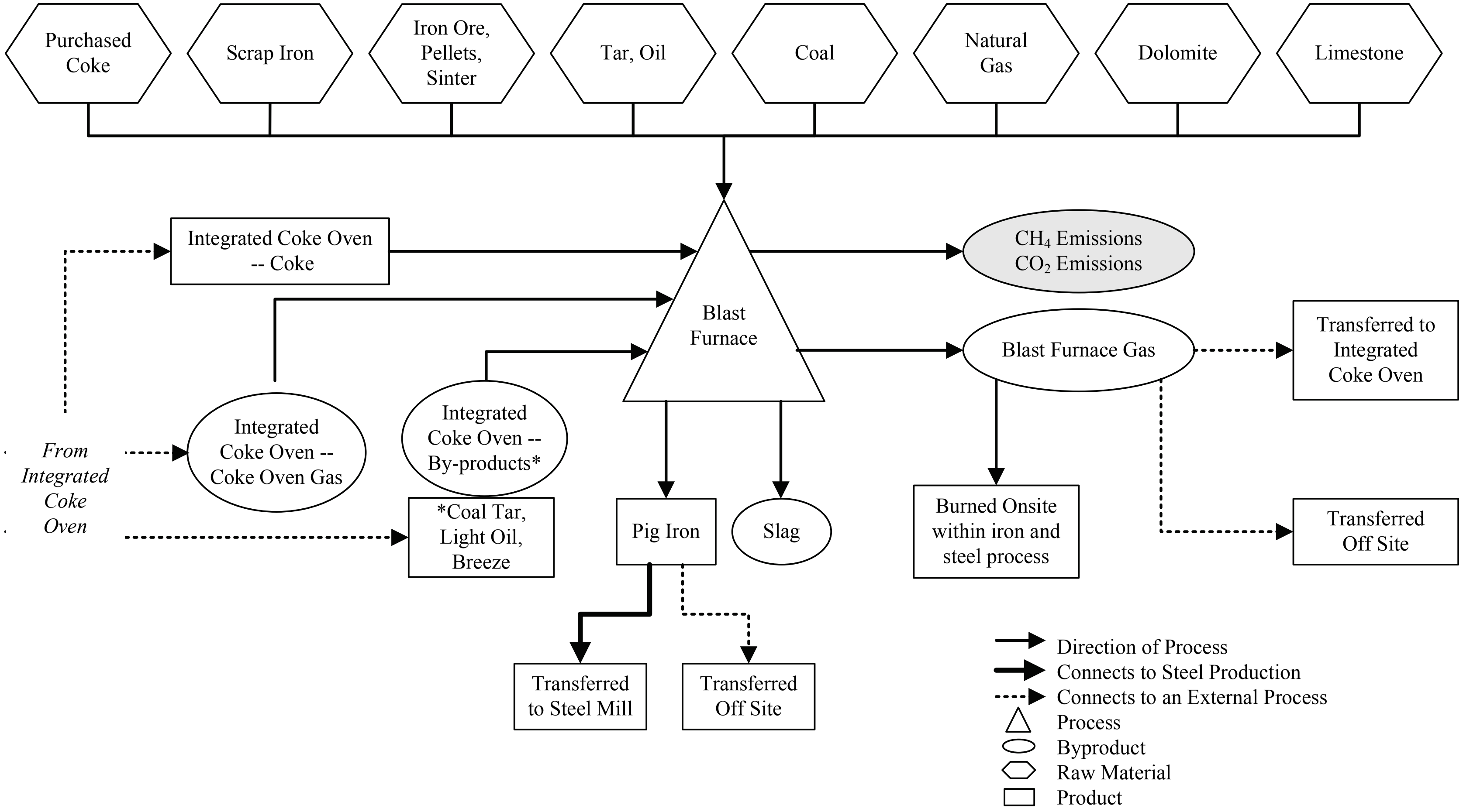
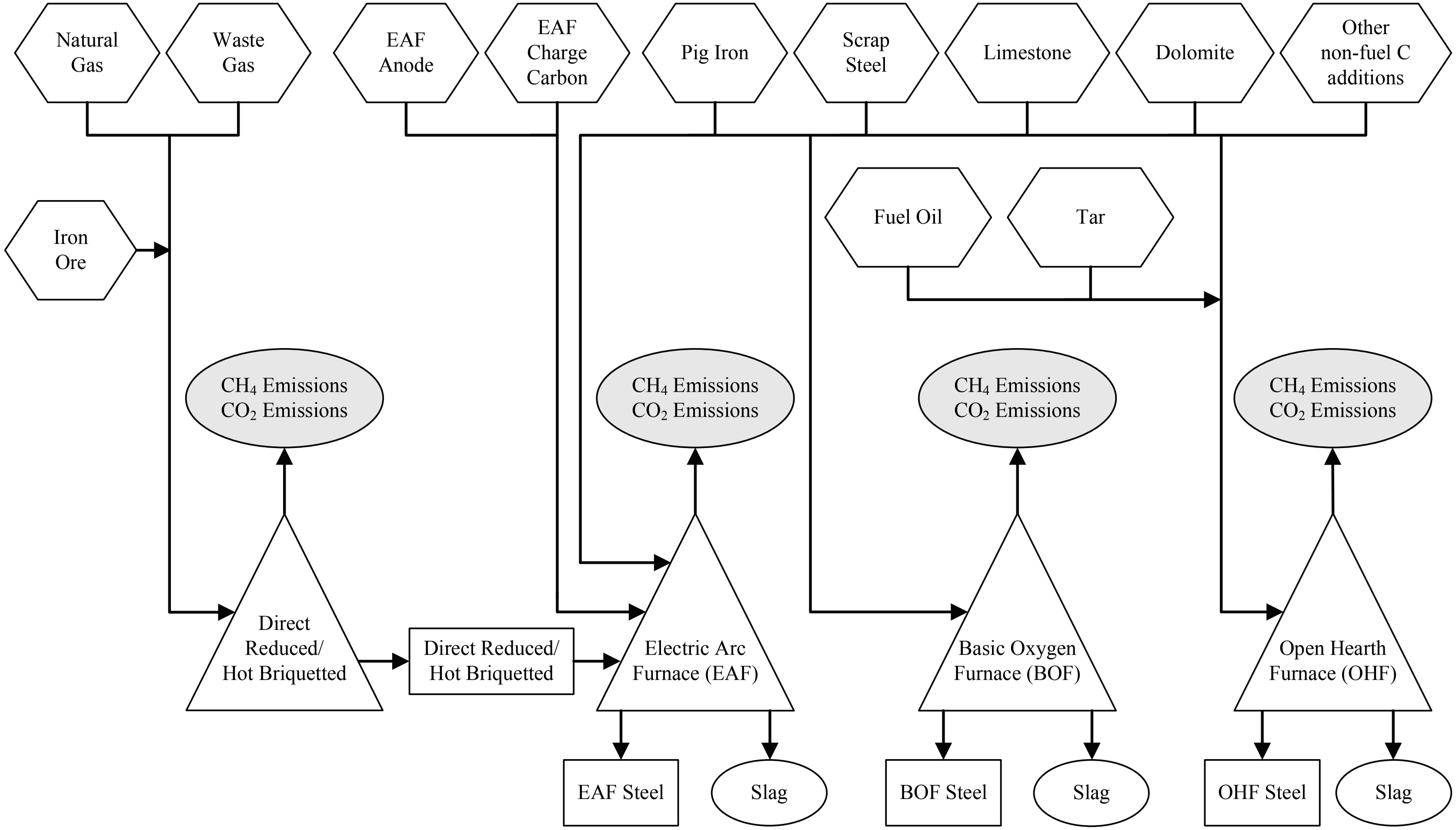


**Figure 4.5 Illustration of steel production processes**



## 4.2.2 Methodological issues

### 4.2.2.1 CHOICE OF METHOD: METALLURGICAL COKE PRODUCTION

The *IPCC Guidelines* outline three tiers for calculating $CO_2$ emissions and two tiers for calculating $CH_4$ emissions from coke production. The choice of a *good practice* method for estimation of $CO_2$ emissions depends on national circumstances as shown in the decision tree in Figure 4.6 Estimation of $CO_2$ Emissions from Metallurgical Coke Production. For $CH_4$ emissions, use the decision tree in Figure 4.8.

Metallurgical coke is produced either at the iron and steel facility ('onsite') or at separate facilities ('offsite').The Tier 1 method calculates emissions from all coke production using default emission factors applied to national coke production.

The Tier 2 method for estimating $CO_2$ emissions distinguishes between onsite and offsite coke production. It uses national activity data for the consumption and production of process materials (e.g., coking coal consumed, coke produced, and coal tar products produced). As discussed above, the Tier 2 method is not applicable to estimating $CH_4$ emissions. The Tier 3 method requires plant-specific $CO_2$ emissions data and plant-specific $CH_4$ emissions data, or plant-specific activity data.

### TIER 1 METHOD – PRODUCTION-BASED EMISSION FACTORS

Equation 4.1 calculates emissions from all coke production. The Tier 1 method assumes that all coke made onsite at iron and steel production facilities is used onsite. The Tier 1 method is to multiply default emission factors by tonnes of coke produced. Emissions should be reported in the Energy Sector.

**EQUATION 4.1**
**EMISSIONS FROM COKE PRODUCTION (TIER 1)**

$$E_{CO2} = Coke \bullet EF_{CO2} \text{ and } E_{CH4} = Coke \bullet EF_{CH4} \quad \text{(To be reported in Energy Sector)}$$

Where:

$E_{CO2}$ or $E_{CH4}$ = emissions of $CO_2$ or $CH_4$ from coke production, tonnes $CO_2$ or tonnes $CH_4$

Coke = quantity of coke produced nationally, tonnes

EF= emission factor, tonnes $CO_2$/tonne coke production or tonnes $CH_4$/tonne coke production

Note: The Tier 1 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.

### TIER 2 METHOD

The Tier 2 method is appropriate if national statistics on process inputs and outputs from integrated and non-integrated coke production processes are available. Tier 2 will produce a more accurate estimate than Tier 1 because it takes into account the actual quantity of inputs into and outputs rather than making assumptions.

As expressed in Equations 4.2 and 4.3, Tier 2 estimates $CO_2$ emissions from onsite coke production separately from off-site production. This separation is due to overlapping data requirements when estimating emissions from onsite coke production and emissions from iron and steel production.

**EQUATION 4.2**
**$CO_2$ EMISSIONS FROM ONSITE COKE PRODUCTION (TIER 2)**

$$E_{CO2,\, energy} = \left[ CC \bullet C_{CC} + \sum_a \left( PM_a \bullet C_a \right) + BG \bullet C_{BG} - CO \bullet C_{CO} - COG \bullet C_{COG} - \sum_b \left( COB_b \bullet C_b \right) \right] \bullet \frac{44}{12}$$

Where:

$E_{CO2,\, energy}$ = emissions of $CO_2$ from onsite coke production to be reported in Energy Sector, tonnes

CC = quantity of coking coal consumed for coke production in onsite integrated iron and steel production facilities, tonnes

$PM_a$ = quantity of other process material *a*, other than those listed as separate terms, such as natural gas, and fuel oil, consumed for coke and sinter production in onsite coke production and iron and steel production facilities, tonnes

BG = quantityof blast furnace gas consumed in coke ovens, $m^3$ (or other unit such as tonnes or GJ. Conversion of the unit should be consistent with Volume 2: Energy)

CO = quantity of coke produced onsite at iron and steel production facilities, tonnes

COG = quantity of coke oven gas transferred offsite , $m^3$ (or other unit such as tonnes or GJ. Conversion of the unit should be consistent with Volume 2: Energy)

$COB_b$ = quantity of coke oven by-product *b*, transferred offsite either to other facilities, tonnes

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

For offsite coke production, the inventory compiler should use Equation 4.3. Total emissions are the sum of emissions from all plants using both Equations 4.2 and 4.3.

**EQUATION 4.3**
**$CO_2$ EMISSIONS FROM OFFSITE COKE PRODUCTION (TIER 2)**

$$E_{CO2,energy} = \left[ CC \bullet C_{CC} + \sum_a \left( PM_a \bullet C_a \right) - NIC \bullet C_{NIC} - COG \bullet C_{COG} - \sum_b \left( COB_b \bullet C_b \right) \right] \bullet \frac{44}{12}$$

Where:

$E_{CO2,\ energy}$ = emissions of $CO_2$ from offsite coke production to be reported in Energy Sector, tonnes

CC = quantity of coking coal used in non-integrated coke production facilities, tonnes

$PM_a$ = quantity of other process material *a*, other than coking coal, such as natural gas, and fuel oil consumed nationally in non-integrated coke production, tonnes

NIC = quantity of coke produced offsite in non-integrated coke production facilities nationally, tonnes

COG = quantity of coke oven gas produced in offsite non-integrated coke production facilities nationally that is transferred to other facilities, $m^3$ (or other unit such as tonnes or GJ. Conversion of the unit should be consistent with Volume 2: Energy)

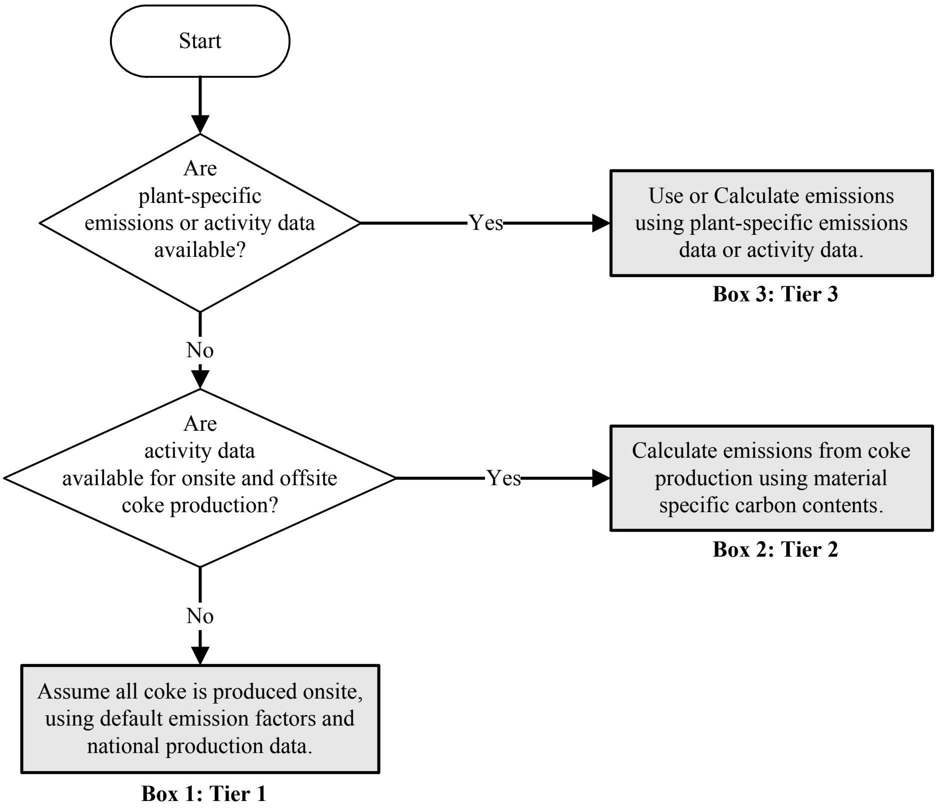
$COB_b$= quantity of coke oven by-product *b*, produced nationally in offsite non-integrated facilities and transferred offsite to other facilities, tonnes

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

## TIER 3 METHOD

Unlike the Tier 2 method, the Tier 3 method uses plant specific data because plants can differ substantially in their technology and process conditions. If actual measured $CO_2/CH_4$ emissions data are available from onsite and offsite coke production plants, these data can be aggregated and used directly to account for national emissions from metallurgical coke production using the Tier 3 method. Total national emissions will equal the sum of emissions reported from each facility. If facility-specific $CO_2$ emissions data are not available, $CO_2$ emissions can be calculated from plant-specific activity data applying the Tier 2 method, Equations 4.2 and 4.3. Total national emissions will equal the sum of emissions reported from each facility.

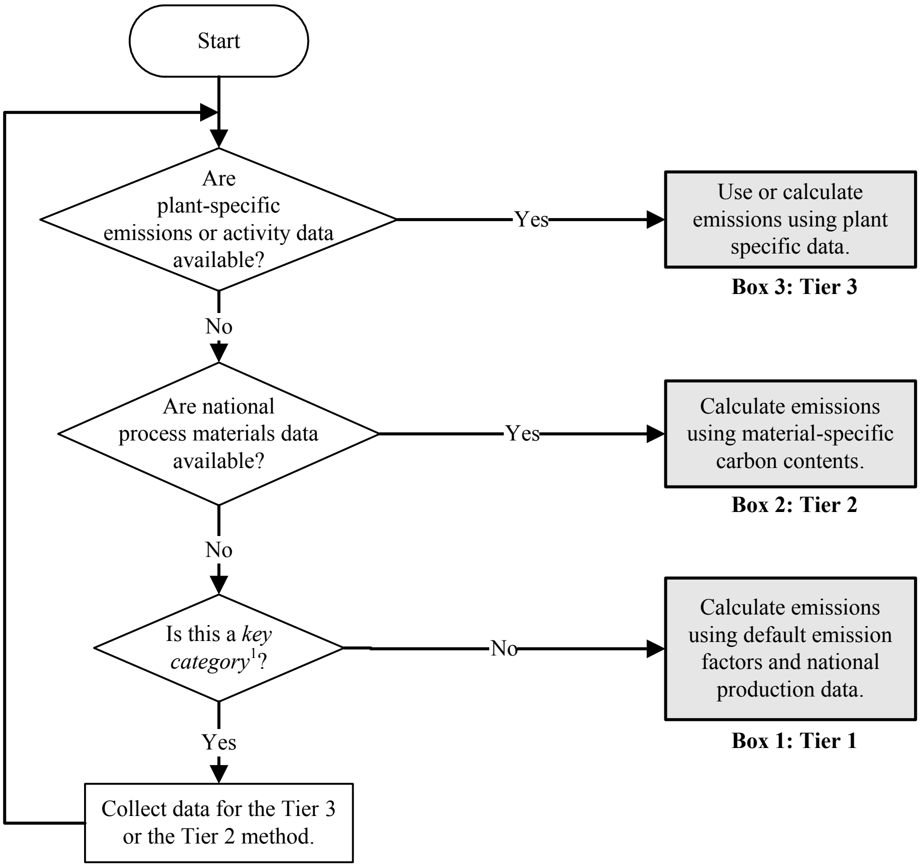
**Figure 4.6 Estimation of $CO_2$ emissions from metallurgical coke production**



#### 4.2.2.2 CHOICE OF METHOD: IRON AND STEEL PRODUCTION

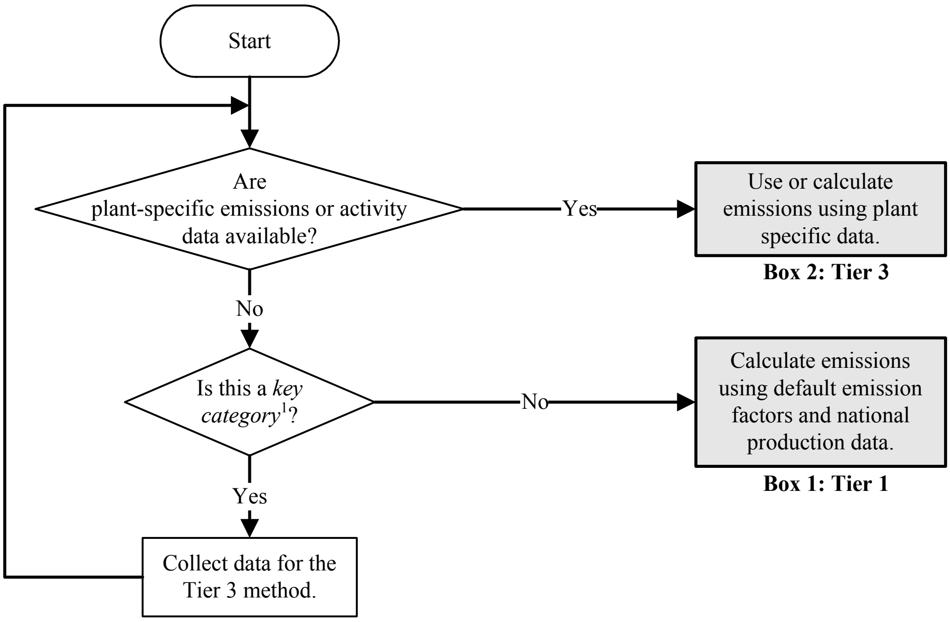
These *Guidelines* outline three tiers for calculating $CO_2$ emissions and two tiers for calculating $CH_4$ emissions from iron and steel production. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 4.7 for $CO_2$ emissions and Figure 4.8 for $CH_4$ emissions: Decision Tree for Estimation of $CO_2$ Emissions from Iron & Steel Production and Decision Tree for Estimating of $CH_4$ Emissions from Iron and Steel Production. The Tier 1 method is based on national production data and default emission factors. It may lead to errors due to its reliance on assumptions rather than actual data for the quantity of inputs into the sinter production and iron and steel production sector that contribute to $CO_2$ emissions. Therefore, the Tier 1 is appropriate only if iron and steel production is not a *key category*. Default emission factors are provided for sinter production, blast furnace iron making, direct reduced iron production, pellet production, and each method of steelmaking. The primary sources of emissions are the blast furnace iron making, and steelmaking. The Tier 2 method for estimating $CO_2$ emissions from iron and steel production is based on data for the known consumption of raw materials, including reducing agents, and industry-wide data. It uses a mass balance approach and material-specific carbon contents. The Tier 2 method is not applicable to estimating $CH_4$ emissions. The Tier 3 method requires plant-specific emissions or activity data aggregated to the national level for estimating $CO_2$ and $CH_4$ emissions.

**Figure 4.7 Decision tree for estimation of $CO_2$ emissions from iron and steel 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.

**Figure 4.8 Decision tree for estimation of $CH_4$ emissions from iron and steel 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.

## METHODOLOGY FOR ESTIMATING $CO_2$ 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 pig iron production 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 steps.

Equation 4.6 calculates $CO_2$ emissions from production of Direct Reduced Iron (DRI) for the Tier 1 method using a $CO_2$ emission factor.

It is also *good practice* to estimate separately the emissions from sinter production and national pellet production, using Equations 4.7 and 4.8. Equations 4.7 and 4.8 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.

Total emissions are the sum of Equations 4.4 to 4.8.

**EQUATION 4.4**
**$CO_2$ EMISSIONS FROM IRON AND STEEL PRODUCTION (TIER 1)**

$$\text{Iron \& Steel: } E_{CO2,\, non-energy} = BOF \bullet EF_{BOF} + EAF \bullet EF_{EAF} + OHF \bullet EF_{OHF}$$

**EQUATION 4.5**
**$CO_2$ EMISSIONS FROM PRODUCTION OF PIG IRON NOT PROCESSED INTO STEEL (TIER 1)**

$$\text{Pig Iron Production: } E_{CO2,\, non-energy} = IP \bullet EF_{IP}$$

**EQUATION 4.6**
**$CO_2$ EMISSIONS FROM PRODUCTION OF DIRECT REDUCED IRON (TIER 1)**

$$\text{Direct Reduced Iron: } E_{CO2,\, non-energy} = DRI \bullet EF_{DRI}$$

**EQUATION 4.7**
**$CO_2$ EMISSIONS FROM SINTER PRODUCTION (TIER 1)**

$$\text{Sinter Production: } E_{CO2,\, non-energy} = SI \bullet EF_{SI}$$

**EQUATION 4.8**
**$CO_2$ EMISSIONS FROM PELLET PRODUCTION (TIER 1)**

$$\text{Pellet Production: } E_{CO2,\, non-energy} = P \bullet EF_{P}$$

Where:

$E_{CO2,\, non-energy}$ = emissions of $CO_2$ 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 $CO_2$/tonne *x* produced

### Tier 2 method

The Tier 2 method is appropriate if 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 a number of other process inputs and outputs that could be considered under Tier 2. 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. The Tier 2 method will produce a more accurate estimate than the Tier 1 method because it takes into account the actual quantity of inputs that contribute to $CO_2$ emissions.

In calculating pellet production emissions, energy consumption and heating value and carbon content of the fuel can be used similarly to the other methodologies.

**EQUATION 4.9**
**$CO_2$ EMISSIONS FROM IRON & STEEL PRODUCTION (TIER 2)**

$$E_{CO2,non-energy} = \Big[ PC \bullet C_{PC} + \sum_{a} (COB_a \bullet C_a) + CI \bullet C_{CI} + L \bullet C_L + D \bullet C_D + CE \bullet C_{CE} + \sum_{b} (O_b \bullet C_b) + COG \bullet C_{COG} - S \bullet C_S - IP \bullet C_{IP} - BG \bullet C_{BG} \Big] \bullet \frac{44}{12}$$

**EQUATION 4.10**
**$CO_2$ EMISSIONS FROM SINTER PRODUCTION (TIER 2)**

$$E_{CO2,non-energy} = \Big[ CBR \bullet C_{CBR} + COG \bullet C_{COG} + BG \bullet C_{BG} + \sum_{a} (PM_a \bullet C_a) - SOG \bullet C_{SOG} \Big] \bullet \frac{44}{12}$$

Where, for iron and steel production:

$E_{CO2,\ non\text{-}energy}$ = emissions of $CO_2$ 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

$O_b$ = 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 blast furnace in iron and steel production, $m^3$ (or other unit such as tonnes or GJ. Conversion of the unit should be consistent with Volume 2: Energy)

S = quantity of steel produced, tonnes

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

BG = quantity of blast furnace gas transferred offsite, $m^3$ (or other unit such as tonnes or 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:

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

CBR = quantity of purchased and onsite produced coke breeze used for sinter production, tonnes

COG= quantity of coke oven gas consumed in blast furnace in sinter production, $m^3$ (or other unit such as tonnes or GJ. Conversion of the unit should be consistent with Volume 2: Energy)

BG = quantity of blast furnace gas consumed in sinter production, $m^3$ (or other unit such as tonnes or GJ. Conversion of the unit should be consistent with Volume 2: Energy)

$PM_a$ = quantity of other process material *a*, other than those listed as separate terms, such as natural gas, and fuel oil, consumed for coke and sinter production in integrated coke production and iron and steel production facilities, tonnes

SOG = quantity of sinter off gas transferred offsite either to iron and steel production facilities or other facilities, $m^3$ (or other unit such as tonnes or 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]

Equation 4.11 calculates $CO_2$ emissions from production of direct reduced iron for the Tier 2 method based on fuel consumption and fuel carbon content. Emissions from DRI production are derived from combusting fuel, coke breeze, metallurgical coke or other carbonaceous materials, and are to be reported as IPPU emissions.

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

$$E_{CO2,non-energy} = \left(DRI_{NG} \bullet C_{NG} + DRI_{BZ} \bullet C_{BZ} + DRI_{CK} \bullet C_{CK}\right) \bullet \frac{44}{12}$$

Where:

$E_{CO2,\ non\text{-}energy}$ = 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

### 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 $CO_2$ emissions data are available from iron and steelmaking facilities, these data can be aggregated to account for national $CO_2$ emissions. If facility-specific $CO_2$ emissions data are not available, $CO_2$ emissions can be calculated from plant-specific activity data for individual reducing agents, exhaust gases, and other process materials and products. 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 $CH_4$

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 $CO_2$ above the charge, in the hood and off-gas channels, but some will remain un-reacted as $CH_4$ and non-methane volatile organic compounds (NMVOC). The amounts depend on the operation of the furnace. Sprinkle-charging will reduce the amounts of $CH_4$ compared to batch-wise charging. Increased temperature in the hood (less false air) will reduce the content of $CH_4$ further.

This section describes a Tier 1 default method and a more advanced Tier 3 facility-level method for $CH_4$ from sinter production or iron production, both of which are similar to the approaches described for estimating $CO_2$ emissions. There is no Tier 2 method. $CH_4$ may be emitted from steel–making processes as well, however those emissions are assumed to be negligible. Therefore $CH_4$ emissions from steel-making processes are not discussed here.

The Tier 1 methodology for $CH_4$ is based on emission factors and national production statistics.

**EQUATION 4.12**

**$CH_4$ EMISSIONS FROM SINTER PRODUCTION (TIER 1)**

$$\text{Sinter Production: } E_{CH4,\, non-energy} = SI \bullet EF_{SI}$$

**EQUATION 4.13**

**$CH_4$ EMISSIONS FROM BLAST FURNACE PRODUCTION OF PIG IRON (TIER 1)**

$$\text{Pig Iron Production: } E_{CH4, non-energy} = PI \bullet EF_{PI}$$

**EQUATION 4.14**

**$CH_4$ EMISSIONS FROM DIRECT REDUCED IRON PRODUCTION (TIER 1)**

$$\text{Direct Reduced Iron Production: } E_{CH4, non-energy} = DRI \bullet EF_{DRI}$$

Where:

$E_{CH4,\ non\text{-}energy}$ = emissions of $CH_4$ 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

DRI = quantity of direct reduced iron produced nationally, tonnes

$EF_x$ = emission factor, kg $CH_4$/tonne *x* produced

The Tier 3 method uses plant specific emissions data. If actual measured $CH_4$ emissions data are available for coke production, these data can be aggregated to account for national $CH_4$ emissions. Total national emissions will equal the sum of emissions reported from each facility.

## 4.2.2.3 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

### *Carbon dioxide emission factors*

Table 4.1 provides default emission factors for coke, sinter, pellet, iron, and steel production. The emission factors for the three steelmaking methods are based on expert judgment using typical practice for the different steel production scenarios listed. The default emission factors account for all carbon input into the blast furnace. It is assumed based on the Integrated Pollution Prevention and Control (IPPC) Reference Document on Production of Iron and Steel (European IPPC Bureau, 2001) (referred to in this section as 'IPPC I&S BAT Document') that most of the carbon input to the blast furnace is from coke (60 -90 percent).

The default $CO_2$ emission factor for coke production is derived by averaging plant-specific $CO_2$ emissions data for 11 European coke plants reported in the IPPC I&S BAT Document. Emissions of $CO_2$ are reported in Table 6.2 of the IPPC I&S BAT Document in units of kilograms of $CO_2$ per tonne of liquid steel produced. The $CO_2$ emissions range from 175 to 200 kg $CO_2$ per tonne liquid steel. The conversion factors provided in Table 6.2 of the IPPC Document are 940 kg pig iron per tonne liquid steel and 358 kg coke per tonne pig iron. Based on these conversion factors the average $CO_2$ emissions from the 11 European coke plants is 0.56 tonne $CO_2$ per tonne coke produced.

The $CO_2$ emission factor for sinter plants is derived by averaging plant-specific $CO_2$ emissions data for four European sinter plants reported in the IPPC I&S BAT Document. Emissions of $CO_2$ are reported in Table 4.1 of the IPPC I&S BAT Document in units of kilograms of $CO_2$ per tonne of liquid steel produced. The $CO_2$ emissions range from 205 to 240 kg $CO_2$ per tonne liquid steel. The conversion factors provided in Table 4.1 of the IPPC I&S BAT Document are 940 kg pig iron per tonne liquid steel and 1160 kg sinter per tonne pig iron. Based on these conversion factors the average $CO_2$ emissions from the four European sinter plants is 0.2 kg $CO_2$ per kg sinter produced.

The $CO_2$ emission factor for blast furnace iron making is derived by averaging plant-specific $CO_2$ emissions data for European sinter plants reported in the IPPC I&S BAT Document. The $CO_2$ and CO content of blast furnace gas produced by the iron making process is reported in Tables 7.2 and 7.3 of the IPPC I&S BAT Document in units of kilograms of $CO_2$ per tonne of pig iron produced and kilograms of CO per tonne of pig iron produced. The $CO_2$ content ranges from 400 to 900 kg $CO_2$ per tonne pig iron produced and the CO content ranges from 300 to 700 kg CO per tonne of pig iron produced. Based on the assumption that all of the blast furnace gas burned for energy recovery (and combusted to $CO_2$) within the integrated iron and steel mill and that no blast furnace gas is transferred off site, this corresponds to an emission factor of 1.35 kg $CO_2$ per kg pig iron produced.

TABLE 4.1
TIER 1 DEFAULT $CO_2$ EMISSION FACTORS FOR COKE PRODUCTION AND IRON & STEEL PRODUCTION

| **Process** | **Emission Factor** | **Source** |
|---|---|---|
| Sinter Production (tonne $CO_2$ per tonne sinter produced) | 0.20 | Sinter 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 4.1, Page 29. http://eippcb.jrc.es/pages/FActivities.htm |
| Coke Oven (tonne $CO_2$ per tonne coke produced) | 0.56 | Coke 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 6.2, Page 122. http://eippcb.jrc.es/pages/FActivities.htm |
| Iron Production (tonne $CO_2$ per tonne pig iron produced) | 1.35 | 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, Tables 7.2 and 7.3. http://eippcb.jrc.es/pages/FActivities.htm |
| 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 |
| Pellet production (tonne $CO_2$ per tonne pellet produced) | 0.03 | Pellet 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 5.1 Page 95. http://eippcb.jrc.es/pages/FActivities.htm |
| **Steelmaking Method** | | |
| Basic Oxygen Furnace (BOF) (tonne $CO_2$ per tonne of steel produced) | 1.46 | Steel Production: Consensus of experts and IISI Environmental Performance Indicators 2003 STEEL<br>(International Iron and Steel Institute, 2004) |
| Electric Arc Furnace (EAF) (tonne $CO_2$ per tonne of steel produced) ** | 0.08 | Steel Production: Consensus of experts and IISI Environmental Performance Indicators 2003 STEEL<br>(International Iron and Steel Institute, 2004) |
| Open Hearth Furnace (OHF) (tonne $CO_2$ per tonne of steel produced) | 1.72 | Steel Production: Consensus of experts and IISI Environmental Performance Indicators 2003 STEEL<br>(International Iron and Steel Institute, 2004) |
| Global Average Factor (65% BOF, 30% EAF, 5% OHF)* (tonne $CO_2$ per tonne of steel produced) | 1.06 | Steel Production: Consensus of experts and IISI Environmental Performance Indicators 2003 STEEL<br>(International Iron and Steel Institute, 2004) |

* Factor based on 2003 international data where BOFs accounted for approximately 63 percent of world steel production and EAFs approximately 33 percent; OHF production accounted for the remaining 4 percent but is declining.

** The emission factor for EAF steelmaking does not include emissions from iron production. The emission factors for BOF and OHF steelmaking do include emissions from blast furnace iron production.

Note that the $CO_2$ emission factor for EAF steelmaking in this table is based on production of steel from scrap metal, and therefore the EAF emission factor does not account for any $CO_2$ emissions from blast furnace iron making. The Tier 1 $CO_2$ emission factor for EAFs in this table is therefore not applicable to EAFs that use pig iron as a raw material.

The emission factor for pellet production is based on the IPPC I&S BAT Document which provides an emission factor range of 15.6 to 31.8 kg $CO_2$ per tonne product. However, the $CO_2$ emission factor for a specific process will depend on the characteristic of the raw materials and fuels used in the process. The emission factor would vary depending upon whether coal, natural gas, or coke oven gas was used as the primary fuel. The 'default' emission factor provided is at the high end of the range, 30 kg $CO_2$ per tonne product, and should be used if the inventory compiler does not know anything about the fuels or raw materials used. If the inventory compiler knows the inputs used, $CO_2$ emissions should be calculated using the Tier 2 method, accounting for the fuel consumption, heating value and carbon content of the fuel.

For the purposes of Tier 1 emission calculations, it is assumed that the default fuel for production of Direct Reduced Iron is natural gas. Natural gas-based processes account for the vast majority of installed direct reduced iron (DRI) production capacity worldwide, with 63 percent of that capacity being the MIDREX process. Fuel consumption for production of direct reduced iron using the MIDREX process is typically 10.5 - 14.5 GJ natural gas/metric tonne solid DRI assuming 100 percent lump iron ore operation. Fuel consumption for production of hot briquetted iron from iron fines was reported to be 12.5 GJ natural gas per tonne of product for the FINMET process and 14 GJ natural gas per tonne of product for the CIRCORED process. The default energy consumption of 12.5 GJ natural gas per tonne of DRI produced and the default carbon content of natural gas of 15.3 kg carbon per GJ natural gas correspond to a $CO_2$ emission factor of 191.3 kg carbon per tonne DRI produced (0.7 tonnes $CO_2$ per tonne DRI produced).

### *Methane emission factors*

Default $CH_4$ emission factors are provided in Table 4.2 below. The Tier 1 $CH_4$ emission factor for coke production is derived by averaging plant-specific $CH_4$ emissions data for 11 European coke plants reported in the IPPC I&S BAT Document. Emissions of $CH_4$ are reported in Table 6.2 and Table 6.3 of the IPPC I&S BAT Document in units of grams of $CH_4$ per tonne of liquid steel produced. The $CH_4$ emissions reported range from 27 to 32 grams $CH_4$ per tonne liquid steel. Based on the conversion factors the average $CH_4$ emissions from the 11 European coke plants is 0.1 grams $CH_4$ per tonne coke produced.

The Tier 1 $CH_4$ emission factor for sinter production is derived by averaging plant-specific $CH_4$ emissions data for European sinter plants reported in the EMEP/CORINAIR Emissions Inventory Guidebook (EEA, 2005) and in other emission inventory reports. Emissions of $CH_4$ are reported in Table 8.2a of the EMEP/CORINAIR Emission Inventory Guidebook for sinter and palletising plants. For sinter plants using coke breeze an emission factor of 50 mg $CH_4$ per MJ was reported and a range of coke input of 38 to 55 kg coke per tonne sinter was reported. This corresponds to an average emission factor of 0.07 kg $CH_4$ per tonne sinter using the default value of 28.2 TJ/Gg coke. An emission factor of 0.05 kg $CH_4$ per tonne sinter was reported for sinter plants operating in Finland. (Pipatti, 2001)

**TABLE 4.2**
**TIER 1 DEFAULT $CH_4$ EMISSION FACTORS FOR COKE PRODUCTION AND IRON & STEEL PRODUCTION**

| Process | Emission Factor | Source |
|---|---|---|
| Coke Production | 0.1 g per tonne of coke produced | Coke 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 6.2-3, Page 122. http://eippcb.jrc.es/pages/FActivities.htm |
| Sinter Production | 0.07 kg per tonne of sinter produced | EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005). Processes With Contact: *Sinter and Pelletizing Plants: Sinter and Pelletizing Plants (Except Combustion 030301)* Table 8.2a Emission factors for gaseous compounds |
| DRI Production | 1 kg /TJ (on a net calorific basis) | Energy Volume default emission factor for $CH_4$ Emissions from natural gas combustion. [See Table 2.3 of Volume 2, Chapter 2.] |

## TIER 2 METHOD

The default carbon contents in Table 4.3 should be used if an inventory compiler does not have information on conditions in iron and steel-making facilities and coke production facilities, but has detailed activity data for the process materials and offsite transfers. The Tier 2 method, as described in Equation 4.2 for integrated coke production, Equations 4.9 to 4.11 for iron and steel production and Equation 4.3 for non-integrated coke production includes the major material flows in iron and steel-making and coke production that lead to emissions. Carbon contents in Table 4.3 are based on those provided in Table 1.2 and 1.3 in Volume 2, Chapter 1.

TABLE 4.3
TIER 2 MATERIAL-SPECIFIC CARBON CONTENTS FOR IRON & STEEL AND COKE PRODUCTION (kg C/kg )

| Process Materials | Carbon Content |
|---|---|
| Blast Furnace Gas | 0.17 |
| Charcoal* | 0.91 |
| Coal[1] | 0.67 |
| Coal Tar | 0.62 |
| Coke | 0.83 |
| Coke Oven Gas | 0.47 |
| Coking Coal | 0.73 |
| Direct Reduced Iron (DRI) | 0.02 |
| Dolomite | 0.13 |
| EAF Carbon Electrodes[2] | 0.82 |
| EAF Charge Carbon[3] | 0.83 |
| Fuel Oil[4] | 0.86 |
| Gas Coke | 0.83 |
| Hot Briquetted Iron | 0.02 |
| Limestone | 0.12 |
| Natural Gas | 0.73 |
| Oxygen Steel Furnace Gas | 0.35 |
| Petroleum Coke | 0.87 |
| Purchased Pig Iron | 0.04 |
| Scrap Iron | 0.04 |
| Steel | 0.01 |

Source: Default values are consistent with the those provided in Vol 2 and have been calculated with the assumptions below. Complete references for carbon content data are included in Table 1.2 and 1.3 in Volume 2, Chapter 1.

Notes:

[1] Assumed other bituminous coal

[2] Assumed 80 percent petroleum coke and 20 percent coal tar

[3] Assumed coke oven coke

[4] Assumed gas/diesel fuel

* 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.)

### TIER 3 METHODS

The Tier 3 method is based on aggregated plant-specific emission estimates or the application of the Tier 2 equations at a 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 rates for all of the process materials and off-site transfers such as those listed in Table 4.3. While Table 4.3 provides default carbon contents, it is *good practice* under Tier 3 to adjust these values to reflect variations at the plant level from default values represented in the table. The default factors 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.

### 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 assume 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 ingots, 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 $CO_2$ 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 $CO_2$ emissions) or on plant-specific direct emissions monitoring data (for both $CO_2$ and $CH_4$ emissions) . 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 $CO_2$ 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

In estimating emissions from this source category: coke production (Energy) and iron and steel production (IPPU), there is a risk of double counting or omission in either the Industrial Processes or the Energy Sector. Since the primary use of carbon sources (predominantly coke, but also coal, oil, natural gas, limestone, etc.) is to produce pig iron, the $CO_2$ and $CH_4$ emissions from iron and steel production including sinter production are considered industrial process emissions and should be reported as such. The $CO_2$ and $CH_4$ emissions from coke production (both fuel consumption and conversion losses) are categorised as energy production and should be reported as such. However, for integrated production and iron and steel with onsite coke production, there may be flows of by-products (e.g., coke oven gas, blast furnace gas, coke oven by-products) between the coke production facility and the iron and steel production facility, creating potential double counting issues. Carbon consumed in the from of coke oven gas at an iron and steelmaking facility and the resulting $CO_2$ and $CH_4$ emissions would be categorized as IPPU emissions and reported as such. Carbon consumed in the form of blast furnace gas at an onsite coke production facility and the resulting $CO_2$ and $CH_4$ emissions would be categorized as Energy emissions and should reported as such Tracking of such carbon flows will require good knowledge of the inventory in that source category.

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 a carbon balance at an iron and steelmaking facility to assure that $CO_2$ emissions are not double-counted. $CO_2$ and $CH_4$ emissions associated with onsite and offsite coke making are to be reported under Energy Sector (see Volume 2).

### OTHER FORMS OF CARBON

Although the dominant means of producing crude iron, or pig iron, is the blast furnace 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, these 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 vessels besides blast furnaces, often using natural gas or coal instead of coke, and these carbon sources should be accounted for in the same manner as coke because they are serving 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 $CO_2$ and $CH_4$ emissions. If the coke fines are produced at a coke plant within the facility and the $CO_2$ and $CH_4$ emissions are accounted for in the coal entering the facility, or if the coke breeze is otherwise accounted for as purchased coke, the $CO_2$ and $CH_4$ 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 not to double count the use of blast-furnace-derived by-product gases such as blast furnace gas, or recovered BOF off-gas as energy in the energy sector as sources of $CO_2$, 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 and 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 necessary to make adjustments for blast furnace gas, or iron that may be sold or transferred offsite. The process flow of exhaust gases are clearly illustrated in Figures 4.1-4.5.

### 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, $CO_2$ and $CH_4$ 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 $CO_2$ or $CH_4$ emissions from this steelmaking process.

### OHF PROCESS

Although the OHF is no longer prevalent, it may be necessary to inventory $CO_2$ and $CH_4$ 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

Emissions from coke production, sinter production, and iron and steel and production should be calculated using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, these gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5, Time Series Consistency and Recalculation.

## 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 ± 25 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
UNCERTAINTY RANGES

| Method | Data Source | Uncertainty Range |
|---|---|---|
| Tier 1 | Default Emission Factors<br>National Production Data | ± 25%<br>± 10% |
| Tier 2 | Material-Specific Default Carbon Contents<br>National Reducing Agent & Process Materials Data | ± 10%<br>± 10% |
| Tier 3 | Company-Derived = Process Materials Data<br>Company-Specific Measured $CO_2$ and $CH_4$ Data<br>Company-Specific Emission Factors | ± 5%<br>± 5%<br>± 5% |

For Tier 1 the most important type of activity data is the amount of steel produced using each method. National statistics should be available and likely have an uncertainty of ± 10 percent. For Tier 2, the total amount of reducing agents and process materials used for iron and steel production would likely be within 10 percent. Tier 3 requires plant-specific information on the amounts of reducing agents and process materials (about 5 percent uncertainty). Also actual emissions data for Tier 3 would be expected to have ± 5 percent uncertainty. Tier 3 uncertainty may be more accurately derived based on an analysis of the actual data received.

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

### 4.2.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventories agencies are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this source category are outlined below.

**Review of emission factors and carbon contents**

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

**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 conditions or technology.

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

#### Expert review

Inventory compilers should include key industrial trade organisations associated with iron and steel production in a review process. This process should begin early in the inventory development process to provide input to the development and review of methods and data acquisition

Third party reviews are also useful for this source category, particularly related to initial data collection, measurement work, transcription, calculation and documentation.

#### Activity data check

For all tier levels, inventory compilers should check with Volume 2, Chapter 2 (Stationary Combustion of Energy Sector) to ensure that emissions from reducing agents and process materials (coal, coke, natural gas, etc.) are not double-counted or omitted.

Inventory compilers should examine any inconsistency between data from different plants to establish whether these reflect errors, different measurement techniques or result from real differences in emissions, operational conditions or technology. This is particularly relevant to the plant-specific estimates of amounts of reducing agents or reported carbon content of process materials.

Inventory compilers should compare aggregated plant-level estimates to industry totals for process materials consumption where such trade data are available.

## 4.2.4.2 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, Section 6.11. 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.

### TIER 1 METHOD

Besides reporting of estimated emissions, it is *good practice* to report the total steel production by process and corresponding emission factors used and to report the amount of iron produced that is not processed into steel. In the corresponding table, it should be noted that reported emissions are only part of total emissions from the sector and that coke production emissions are categorized as energy emissions and are reported in Volume 2, Chapter 2, Stationary Combustion of Energy Sector.

### TIER 2 METHODS

*Good practice* is to document the estimated or calculated emissions, all activity data, and corresponding emission factors and any assumptions or data justifying alternative emission factors. There should be a clear explanation of the linkage with the source category 1A (Fuel Combustion) estimate for integrated coke production emissions to demonstrate that double counting or missing emissions have not occurred.

### TIER 3 METHOD

*Good practice* is to document the calculated emissions and source of all data, taking into account the need to protect the confidentiality of data for specific facilities if the data are business-sensitive or of a proprietary nature. In addition, inventory compilers should for all tiers, document all information needed to reproduce the estimate, as well as the QA/QC procedures.

# 4.3 FERROALLOY PRODUCTION

## 4.3.1 Introduction

Ferroalloy is the term used to describe concentrated alloys of iron and one or more metals such as silicon, manganese, chromium, molybdenum, vanadium and tungsten. Silicon metal production is usually included in the ferroalloy group because silicon metal production process is quite similar to the ferrosilicon process. These alloys are used for deoxidising and altering the material properties of steel. Ferroalloy facilities manufacture concentrated compounds that are delivered to steel production plants to be incorporated in alloy steels. Silicon metal is used in aluminium alloys, for production of silicones and in electronics. Ferroalloy production involves a metallurgical reduction process that results in significant carbon dioxide emissions.

In ferroalloy production, raw ore, carbon materials and slag forming materials are mixed and heated to high temperatures for reduction and smelting. The carbonaceous reductants are usually coal and coke, but bio-carbon (charcoal and wood) is also commonly used as a primary or secondary carbon source. Carbon dioxide ($CO_2$) and methane ($CH_4$) emissions from coke production are estimated in Section 4.2 and reported within the Energy Sector. Electric submerged arc furnaces with graphite electrodes or consumable Søderberg electrodes are used. The heat is produced by the electric arcs and by the resistance in the charge materials. The furnaces may be open, semi-covered or covered. A commonly used technology is the submerged-arc open-top electric furnace (EAF). In the EAF, passing current through graphite electrodes suspended in a cup-shaped, refractory-lined steel shell accomplishes heating. Carbon reduction of the metallic oxides occurs as both coke and graphite electrodes are consumed. The carbon in the electrodes captures the oxygen from the metal oxides to form CO, while the ores are reduced to molten base metals. The component metals then combine in the solution.

In addition to emissions originating from reducing agents and electrodes, the calcination of carbonate fluxes such as limestone or dolomite, when used, contribute to the emission of greenhouse gases.

Primary emissions in covered arc furnaces consist almost entirely of CO as opposed to $CO_2$, due to the strong reducing environment. This CO is either utilised for energy production in boilers, or it is flared. The energy produced is assumed to be used internally at the site and the carbon content of the CO subsequently converted to $CO_2$ in-plant.

The CO gas produced in open or semi-closed furnaces is burnt to $CO_2$ above the charge level. Any CO emitted to the atmosphere is assumed to be converted to $CO_2$ within days afterwards. While $CO_2$ is the main greenhouse gas from ferroalloy production, recent research has shown that $CH_4$, and $N_2O$ account for an equivalent greenhouse emission of up to 5 percent of the $CO_2$ emissions from ferrosilicon (FeSi) and silicon-metal (Si-metal) production. Methodologies are presented for $CO_2$ and $CH_4$ emissions in this section. These emissions should be better investigated for all ferroalloy production, and more measurements of these emissions should be done from FeSi and Si-metal production.

## 4.3.2 Methodological issues

### 4.3.2.1 CHOICE OF METHOD

#### METHODOLOGY FOR $CO_2$

The *IPCC Guidelines* outline several approaches for calculating $CO_2$ emissions from ferroalloy production. For practical purposes, this section adopts a mass balance approach where all CO emitted is reported as emitted $CO_2$. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 4.9. The Tier 1 method calculates emissions from general emission factors applied to a country's total ferroalloy production. The Tier 1 method is very simple, and it may lead to errors due to its reliance on assumptions rather than actual data. Therefore it is appropriate only when ferroalloy production is not a *key category*. The Tier 2 method calculates emissions from a known consumption of reducing agents, preferably from plant-specific consumption data, but alternatively from industry-wide data using emission factors similar to those used to estimate combustion emissions. The Tier 3 method is based on facility-specific emissions data.

**Tier 1 method: production-based emission factors**

The simplest estimation method is to multiply default emission factors by ferroalloy product type as shown in Equation 4.15.

**EQUATION 4.15**
**$CO_2$ EMISSIONS FOR FERROALLOY PRODUCTION BY THE TIER 1 METHOD**

$$E_{CO2} = \sum_i \left( MP_i \bullet EF_i \right)$$

Where:

$E_{CO2}$ = $CO_2$ emissions, tonnes

$MP_i$ = production of ferroalloy type *i*, tonnes

$EF_i$ = generic emission factor for ferroalloy type *i*, tonnes $CO_2$/tonne specific ferroalloy product

### Tier 2 method: production-based, raw material specific emission factors

An alternate approach is to use emission factors for the reducing agents. For the other raw materials and products carbon contents should be considered.

**BOX 4.1**
**DEFINITIONS FOR WORDS/SYMBOLS USED IN EQUATIONS IN THIS SECTION**

Content means weight-fraction in all equations

$\sum$ means the sum of all *i*, *h*, *j*, *k* or *l*

**EQUATION 4.16**
**$CO_2$ EMISSIONS FOR FERROALLOY PRODUCTION BY TIER 2 METHOD**

$$\begin{aligned}E_{CO2} = {} & \sum_i \left( M_{reducing\ agent,i} \bullet EF_{reducing\ agent,i} \right) + \sum_h \left( M_{ore,h} \bullet CContent_{ore,h} \right) \bullet \frac{44}{12} \\ & + \sum_j \left( M_{slag\ forming\ material,j} \bullet CContent_{slag\ forming\ material,j} \right) \bullet \frac{44}{12} \\ & - \sum_k \left( M_{product,k} \bullet CContent_{product,k} \right) \bullet \frac{44}{12} \\ & - \sum_l \left( M_{non-product\ outgoing\ stream,l} \bullet CContent_{non-product\ outgoing\ stream,l} \right) \bullet \frac{44}{12}\end{aligned}$$

Where:

$ECO_2$ = $CO_2$ emissions frm ferroalloy production, tonnes

$M_{\text{reducing agent, i}}$ = mass of reducing agent *i*, tonnes

$EF_{\text{reducing agent, i}}$ = emission factor of reducing agent *i*, tonnes $CO_2$/tonne reducing agent

$M_{\text{ore, h}}$ = mass of ore *h*, tonnes

$CContent_{\text{ore, h}}$ = carbon content in ore *h*, tonnes C/tonne ore

$M_{\text{slag forming material, j}}$ = mass of slag forming material *j*, tonnes

$CContent_{\text{slag forming material, j}}$ = carbon content in slag forming material *j*, tonnes C/tonne material

$M_{\text{product, k}}$ = mass of product *k*, tonnes

$CContent_{\text{product, k}}$ = carbon content in product *k*, tonnes C/tonne product

$M_{\text{non-product outgoing stream, l}}$ = mass of non-product outgoing stream *l*, tonnes

$CContent_{\text{non-product outgoing stream, l}}$ = carbon content in non-product outgoing stream *l*, tonnes C/tonne

The constant 44/12 is the multiplication factor for the mass of $CO_2$ emitted from each mass unit of total carbon used.

### Tier 3 method: calculations based on amounts and analyses of reducing agents

The producers use coal and coke with different contents of ash, fixed carbon and volatiles. Further, the amounts of carbon in carbonate ores and slag forming materials will vary. The most accurate method is therefore to calculate the $CO_2$ emissions from the total amount of carbon in reducing agents, electrode paste, ores, slag forming materials and products, and this calculation is carried out for each ferroalloy produced.

**EQUATION 4.17**

**$CO_2$ EMISSIONS FOR FERROALLOY PRODUCTIION BY TIER 3 METHOD**

$$\begin{aligned}
E_{CO2} = & \sum_i \left( M_{reducing\ agent,i} \bullet CContent_{reducing\ agent,i} \right) \bullet \frac{44}{12} \\
& + \sum_h \left( M_{ore,h} \bullet CContent_{ore,h} \right) \bullet \frac{44}{12} \\
& + \sum_j \left( M_{slag\ forming\ material,j} \bullet CContent_{slag\ forming\ material,j} \right) \bullet \frac{44}{12} \\
& - \sum_k \left( M_{product,k} \bullet CContent_{product,k} \right) \bullet \frac{44}{12} \\
& - \sum_l \left( M_{non-product\ outgoing\ stream,l} \bullet CContent_{non-product\ outgoing\ stream,l} \right) \bullet \frac{44}{12}
\end{aligned}$$

Where:

$ECO_2$ = $CO_2$ emissions frm ferroalloy production, tonnes

$M_{\text{reducing agent, i}}$ = mass of reducing agent *i*, tonnes

$CContent_{\text{reducing agent, i}}$ = carbon content in reducing agent *i*, tonnes C/tonne reducing agent

$M_{\text{ore, h}}$ = mass of ore *h*, tonnes

$CContent_{\text{ore, h}}$ = carbon content in ore *h*, tonnes C/tonne ore

$M_{\text{slag forming material, j}}$ = mass of slag forming material *j*, tonnes

$CContent_{\text{slag forming material, j}}$ = carbon content in slag forming material *j*, tonnes C/tonne material

$M_{\text{product, k}}$ = mass of product *k*, tonnes

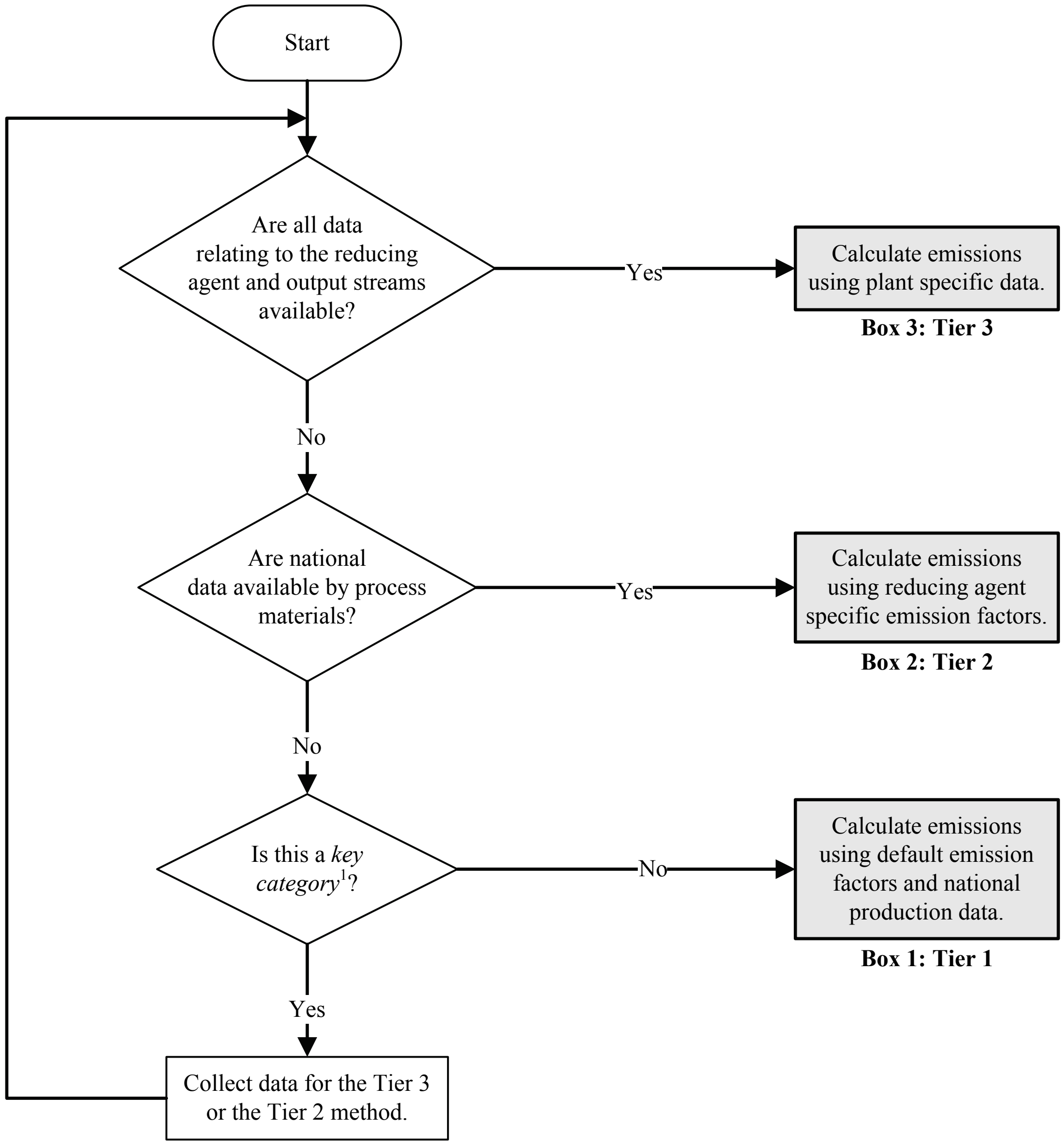
$CContent_{\text{product, k}}$ = carbon content in product *k*, tonnes C/tonne product

$M_{\text{non-product outgoing stream, l}}$ = mass of non-product outgoing stream *l*, tonnes

$CContent_{\text{non-product outgoing stream, l}}$ = carbon content in non-product outgoing stream *l*, tonnes C/tonne

The constant 44/12 is the multiplication factor for the mass of $CO_2$ emitted from each mass unit of total carbon used. The calculation will have good accuracy if analyses of total carbon in all reducing agents are available.

**Figure 4.9** **Decision tree for estimation of $CO_2$ emissions from ferroalloy 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.

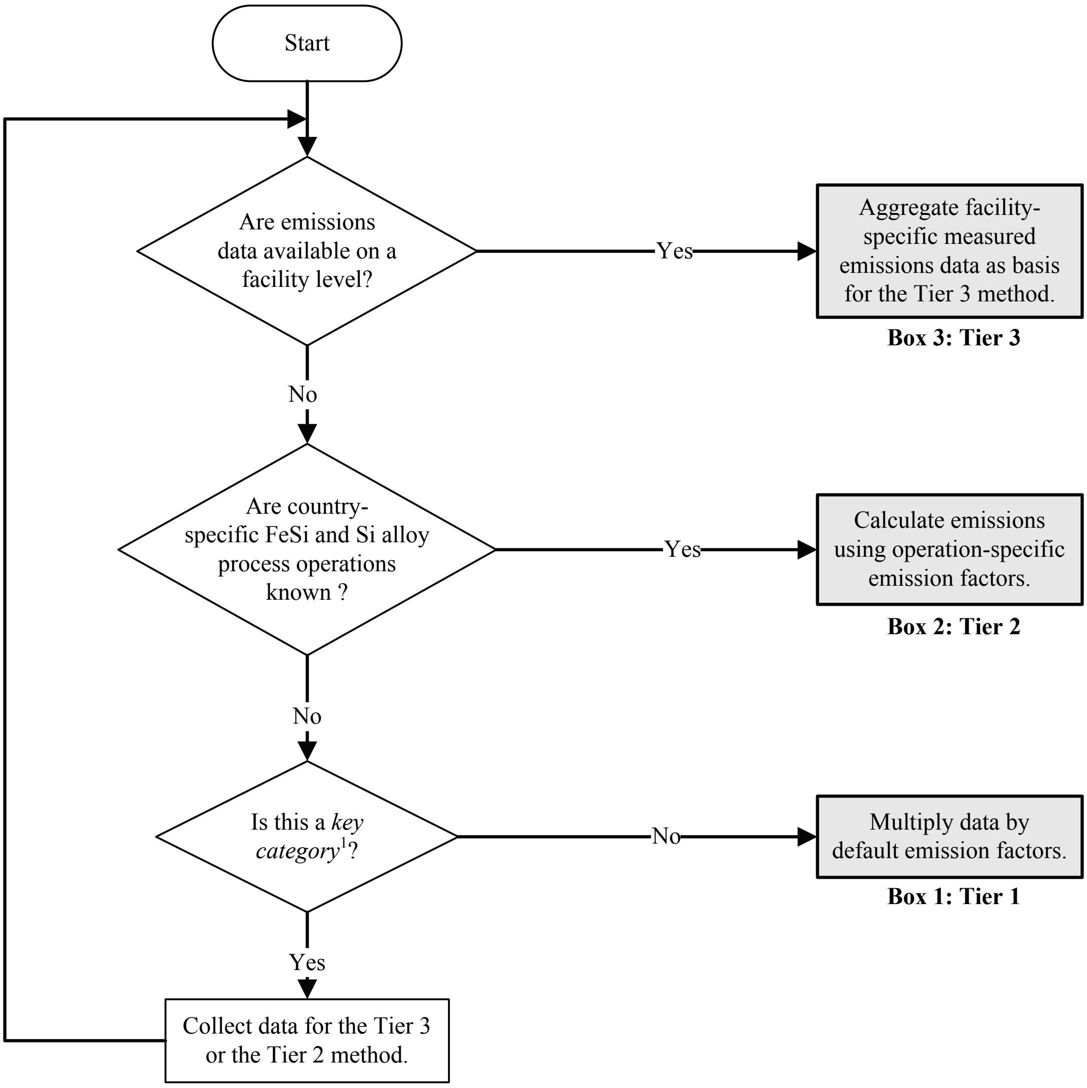
## METHODOLOGY FOR $CH_4$ AND DISCUSSION OF $N_2O$ EMISSIONS

The heating of carbon materials in the furnace releases volatiles including methane. With open or semi-covered furnaces – predominantly used for FeSi and Si ferroalloy production - most of the volatiles will burn to $CO_2$ above the charge, in the hood and off-gas channels, but some will remain un-reacted as $CH_4$ and NMVOC. The amounts depend on the operation of the furnace. Sprinkle-charging will reduce the amounts of $CH_4$ compared to batch-wise charging. Increased temperature in the hood (less false air) will reduce the content of $CH_4$ further.

The *IPCC Guidelines* outline several approaches for calculating $CH_4$ emissions from FeSi- and Si- ferroalloy production. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 4.10. The Tier 1 method calculates emissions from general emission factors applied to a country's total ferroalloy production. The Tier 1 method is very simple, and it may lead to errors due to its reliance on assumptions rather than actual data. Therefore it should only be used when ferroalloy production is not a *key category*. The Tier 2 method calculates emissions from operation-specific emission factors. The Tier 3 method uses facility-specific emissions data.

The errors associated with estimates or measurements of $N_2O$ emissions from the ferroalloys industry are very large and thus, a methodology is not provided.

**Figure 4.10** **Decision tree for estimation of $CH_4$ emissions from FeSi and Si alloy 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 1 method: FeSi and Si alloy production-based emission factors

The simplest estimation method is to multiply default emission factors by Si-alloy product type.

Total emissions are calculated according to:

**EQUATION 4.18**
**$CH_4$ EMISSIONS FOR FERROALLOY PRODUCTION BY THE TIER 1 METHOD**

$$E_{CH4} = \sum_i \left( MP_i \bullet EF_i \right)$$

Where:

$E_{CH4}$ = $CH_4$ emissions, kg

$MP_i$ = production of Si-alloy *i*, tonnes

$EF_i$ = generic emission factor for Si-alloy *i*, kg $CH_4$/ tonne specific Si-alloy product

### Tier 2 method: FeSi and Si alloy production-based, operation specific emission factors

The Tier 2 method is also based on emission factors but unlike the Tier 1 method, these are operation specific.

### Tier 3 method: Direct measurements

Inventory compilers are strongly encouraged to measure $CH_4$ emissions where emissions from ferroalloys industry is a *key category*.

## 4.3.2.2 CHOICE OF EMISSION FACTORS

### EMISSION FACTORS FOR $CO_2$

### Tier 1 method: production-based emission factors

When the only data available are national ferroalloy production statistics, it is *good practice* to use default emission factors. However, because of widely disparate factors depending on the type of ferroalloy production, it is necessary to determine how much tonnage is produced by which method and then to sum the product of the factors shown in Table 4.5 and the appropriate production tonnages. These factors are based on expert judgement using typical practice for the ferroalloy production scenarios listed. If any bio-carbon, except some woodchips for FeSi and Si-metal production, is used, the factors cannot be employed.

TABLE 4.5
GENERIC $CO_2$ EMISSION FACTORS FOR FERROALLOY PRODUCTION
(tonnes $CO_2$/tonne product)

| **Type of Ferroalloy** | **Emission Factor** |
|---|---|
| Ferrosilicon 45% Si | 2.5 |
| Ferrosilicon 65 % Si | 3.6 |
| Ferrosillicon 75% Si | 4.0 |
| Ferrosillicon 90% Si | 4.8 |
| Ferromanganeses (7% C) | 1.3 |
| Ferromanganeses (1% C) | 1.5 |
| Silicomanganese | 1.4 |
| Silicon metal | 5.0 |
| Ferrochromium | 1.3 (1.6 with sinter plant) |
| Source: IPCC (1997), IPCC (2000), Olsen (2004) and Lindstad (2004) | |

These default emission factors have been assessed by Olsen (2004) for the manganese alloys, Lindstad (2004) for the silicon alloys and by Olsen, Monsen and Lindstad (1998) for FeCr.

For FeMn alloys the emission factors are based on production where the Mn containing raw materials are a mixture of oxide ores, carbonate ores and imported Mn-sinter. If the sinter is produced abroad it will not give any contribution to the national greenhouse gas inventory. Emission from sinter production must be reported where the production is located.

The factor for FeSi90 and Si-metal is based on a Fix C consumption of 110 percent of the stoichiometric amount needed for reduction of $SiO_2$. For the other FeSi-alloys the factor is based on 114 percent of the stoichiometric amount of Fix C.

### Tier 2 method: production-based, raw material specific emission factors

The emission factors for the reducing agents used in production of manganese and silicon alloys are given in Table 4.6. The factors have been assessed by Olsen (2004) for use in manganese alloys production and by Lindstad (2004) for use in silicon alloys.

**TABLE 4.6**
**$CO_2$ EMISSION FACTORS FOR FERROALLOY PRODUCTION**
**(tonnes $CO_2$/tonne reducing agent)**

| **Reducing agent (usage)** | **Emission Factor** |
|---|---|
| Coal (for FeSi and Si-metal) | 3.1 |
| Coal (for other ferroalloys) | * (See below) |
| Coke (for FeMn and SiMn) | 3.2-3.3 |
| Coke (for Si and FeSi) | 3.3-3.4 |
| Coke (for other ferroalloys) | * (See below) |
| Prebaked electrodes | 3.54 |
| Electrode paste | 3.4 |
| Petroleum coke | 3.5 |

*: Inventory compilers are encouraged to use producer-specific values based on average blend of coal and/or coke for each ferroalloy producer.

Source: Olsen (2004), Lindstad (2004)

### Tier 3 method: calculations based on amounts and analyses of reducing agents

For the Tier 3 method, it is necessary to determine the carbon contents of the reducing agents used in the production processes. But most ferroalloys producers analyse only on the basis of percentage of ash and volatiles, and calculate:

Fix C % = 100 % – % Ash – % Volatiles.

In that case, the total C-contents of reducing agents. is calculated by the following equation.

**EQUATION 4.19**
**CARBON CONTENTS OF FERROALLOY REDUCTING AGENTS**

$$CContent_{reducing\ agent,i} = F_{FixC,i} + F_{volatiles,i} \bullet C_v$$

Where:

$CContent_{reducing\ agent,\ i}$ = carbon content in reducing agent *i*, tonnes C/tonne reducing agent

$F_{FixC,i}$ = mass fraction of Fix C in reducing agent *i*, tonnes C/ tonne reducing agent

$F_{volatiles,i}$ = mass fraction of volatiles in reducing agent *i*, tonnes volatiles/ tonne reducing agent

$C_v$ = carbon content in volatiles, tonnes C/tonne volatiles
(Unless other information is available, Cv = 0.65 is used for coal and 0.80 for coke.)

## EMISSION FACTORS FOR $CH_4$

### Tier 1 method: FeSi and Si alloy production-based emission factors

When the only data available are national ferroalloy production statistics, it is *good practice* to use default emission factors. However, because of the disparate factors depending on the type of ferroalloy production, it is necessary to determine how much tonnage is produced by which method and then to sum the product of the factors shown in Table 4.7 and the appropriate production tonnages. The default emission factors for $CH_4$ is based on the averages of a small number of operation-specific measurements (shown in Table 4.7 for Tier 2) carried out by SINTEF and DNV mainly in 1995 and 1998 (FFF (2000)).

TABLE 4.7
DEFAULT EMISSION FACTORS FOR $CH_4$ (kg $CH_4$/tonne product)

| Emission | Alloy | Emission Factor |
|---|---|---|
| $CH_4$ | Si-metal | 1.2 |
| | FeSi 90 | 1.1 |
| | FeSi 75 | 1.0 |
| | FeSi 65 | 1.0 |

Source: FFF (2000)

### Tier 2 method: FeSi and Si alloy production-based, operation specific emission factors

The Tier 2 method is also based on emission factors but unlike the Tier 1 method, these factors are operation specific. The procedure is otherwise the same as that outlined in Equation 4.18, using values in Table 4.8.

TABLE 4.8
EMISSION FACTORS FOR $CH_4$ (kg $CH_4$/tonne product)

| Emission | Alloy | Operation of Furnace | | |
|---|---|---|---|---|
| | | Batch-charging | Sprinkle-charging [1)] | Sprinkle-charging and >750$^0$C [2)] |
| $CH_4$ | Si-metal | 1.5 | 1.2 | 0.7 |
| | FeSi 90 | 1.4 | 1.1 | 0.6 |
| | FeSi 75 | 1.3 | 1.0 | 0.5 |
| | FeSi 65 | 1.3 | 1.0 | 0.5 |

[1] Sprinkle-charging is charging intermittently every minute.

[2] Temperature in off-gas channel measured where the thermocouple cannot ‘see’ the combustion in the furnace hood.

### Tier 3 method: Direct measurements

Tier 3 is based on measurements rather than emission factors. The inventory compiler should consult guidance on plant-level measurements outlined in Volume 1, Chapter 2, and on QA/QC of measurements in Volume 1, Chapter 6.

## 4.3.2.3 CHOICE OF ACTIVITY DATA

### TIER 1 METHOD

The Tier 1 method requires only the amount of ferroalloy produced in the country by product type. These data may be available from governmental agencies responsible for manufacturing statistics, business or industry trade associations, or individual ferroalloy companies. These tonnages can then be multiplied by the corresponding emission factors in Table 4.5 to estimate $CO_2$ emissions from the sector and Table 4.7 to estimate $CH_4$ emissions from the sector.

### TIER 2 METHOD

The Tier 2 method requires the total amount of reducing agent and other process materials used for ferroalloy production in the country, and knowledge of processes used. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual ferroalloy companies. These amounts can then be multiplied by the appropriate generic emission factors in Tables 4.6 and 4.8 and summed to determine total $CO_2$ and $CH_4$ emissions from the sector. However, activity data collected at the plant-level is preferred.

### TIER 3 METHOD

The Tier 3 method requires collection, compilation, and aggregation of facility-specific emissions data. These data may be available directly from companies.

#### 4.3.2.4 COMPLETENESS

In estimating emissions from this source category, there is a risk of double-counting or omission in either the Industrial Processes or the Energy Sector. Since the primary use of carbon sources (coal, coke, limestone, dolomite etc.) is to produce ferroalloys, the emissions are considered to be industrial process emissions and should be reported as such. It should be noted that the risk of double counting is particularly high for the Tier 1 approach. Any deviation from reporting emissions as originating from an industrial process should be explicitly mentioned in the inventory, and a double-counting/completeness check should be performed.

#### 4.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from ferroalloy production should be calculated using the same method for every year in the time series. Where data are unavailable to support a Tier 3 method for all years in the time series, these gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5.

### 4.3.3 Uncertainty assessment

Uncertainties for ferroalloy production result predominantly from uncertainties associated with activity data, and to a lesser extent from uncertainty related to the emission factor. Although some ferroalloys may be produced using wood or other biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood or other biomass would not be counted under this source because wood-based carbon is of biogenic origin. Emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, but may generate differing amounts of $CO_2$ per unit of ferroalloy produced compared to the use of petroleum coke.

#### 4.3.3.1 EMISSION FACTOR UNCERTAINTIES

For Tier 3, actual emissions data would be expected to have less than 5 percent uncertainty. For Tier 2, the material-specific emission factors would be expected to be within 10 percent, which would provide less uncertainty overall than for Tier 1. Emission factors would be expected to be within 10 percent or less than 5 percent if plant-specific carbon content data are available. The default emission factors used in Tier 1 may have an uncertainty of 25 to 50 percent.

#### 4.3.3.2 ACTIVITY DATA UNCERTAINTIES

For Tier 1 the most important type of activity data is the amount of ferroalloy production by product type. National statistics should be available and likely have an uncertainty less than 5 percent. Tier 2 applied with plant-specific information on the amounts of reducing agents and process materials as applied in Tier 2 method should not exceed 5 percent uncertainty.

TABLE 4.9
UNCERTAINTY RANGES

| Method | Data Source | Unertainty Range |
|---|---|---|
| Tier 1 | National Production Data<br>Default Emission Factors | < 5%<br>< 25 % |
| Tier 2 | Company-Derived Reducing Agent & Process Materials<br>National Reducing Agent & Process Materials Data<br>Company-Specific Emission Factors<br>Material-Specific Default Emission Factors | < 5%<br>< 5%<br>< 5%<br>< 10% |
| Tier 3 | Company-Specific Measured $CO_2$ Data | < 5% |

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

### 4.3.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventories agencies are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this source category are outlined below.

**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.

**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 conditions or technology. For ferroalloy production, inventory compilers should compare plant data with other plants.

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

**Expert review**

Inventory compilers should include key industrial trade organisations associated with ferroalloy production in a review process. This process should begin early in the inventory development process to provide input to the development and review of methods and data acquisition

Third party reviews are also useful for this source category, particularly related to initial data collection, measurement work, transcription, calculation and documentation.

**Activity data check**

For all tier levels, inventory compilers should check with Volume 2, Chapter 2, Stationary Combustion of Energy Sector, to ensure that emissions from reducing agents and process materials (coal, coke, natural gas, etc.) are not double-counted or omitted.

Inventory compilers should examine any inconsistency between data from different plants to establish whether these reflect errors, different measurement techniques or result from real differences in emissions, operational conditions or technology. This is particularly relevant to the plant-specific estimates of amounts of reducing agents or reported carbon content of process materials.

Inventory compilers should compare aggregated plant-level estimates to industry totals for process materials consumption where such trade data are available.

### 4.3.4.2 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, Section 6.11. 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.

## TIER 1 METHOD

Besides reporting of estimated emissions, it is *good practice* to report the total ferroalloy production by process and corresponding emission factors used. In the corresponding table, it should be noted that reported emissions are only part of total emissions from the sector and the rest are reported elsewhere Volume 2, Chapter 2, Stationary Combustion of Energy Sector.

## TIER 2 METHODS

*Good practice* is to document the estimated or calculated emissions, all activity data, and corresponding emission factors and any assumptions or data justifying alternative emission factors. There should be a clear explanation of the linkage with the Fuel Combustion Sub-Sector estimate to demonstrate that double counting or missing emissions have not occurred.

## TIER 3 METHOD

*Good practice* is to document the calculated emissions and source of all data, taking into account the need to protect the confidentiality of data for specific facilities if the data are business-sensitive or of a proprietary nature. In addition, inventory compilers should for all tiers, document all information needed to reproduce the estimate, as well as the QA/QC procedures.

# 4.4 PRIMARY ALUMINIUM PRODUCTION

## 4.4.1 Introduction

This section covers process emissions from primary aluminium production[2]. Worldwide, primary aluminium is produced exclusively by the Hall-Heroult electrolytic process. In this process, electrolytic reduction cells differ in the form and configuration of the carbon anode and alumina feed system and belong to one of four technology types: Centre-Worked Prebake (CWPB)[3], Side-Worked Prebake (SWPB), Horizontal Stud Søderberg (HSS) and Vertical Stud Søderberg (VSS).

The most significant process emissions are:

(i) Carbon dioxide ($CO_2$) emissions from the consumption of carbon anodes in the reaction to convert aluminium oxide to aluminium metal;

(ii) Perfluorocarbons (PFCs) emissions of $CF_4$ and $C_2F_6$ during anode effects.

Also emitted are smaller amounts of process emissions, CO, $SO_2$, and NMVOC. $SF_6$ is not emitted during the electrolytic process and is only rarely used in the aluminium manufacturing process, where small quantities are emitted when fluxing specialized high magnesium aluminium alloys[4].

The decision trees in Figures 4.11 and 4.12 provide guidance for selecting a methodology estimating emissions from aluminium production. All inventory compilers in countries with aluminium production should be able to implement at a minimum level the Tier 1 method and thereby ensure completeness of reporting. Although this chapter presents default emission factors for both $CO_2$ and PFC emissions, 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. Aluminium smelters routinely collect the process data needed for calculation of Tier 2 emissions factors.

## 4.4.2 Methodological issues

### 4.4.2.1 CHOICE OF METHOD FOR $CO_2$ EMISSIONS FROM PRIMARY ALUMINIUM PRODUCTION

During normal operations, aluminium is produced at the cathode and carbon is consumed at the anode per the electrolytic reduction reaction:

$$\boxed{2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2}$$

Most carbon dioxide emissions result from the electrolysis reaction of the carbon anode with alumina ($Al_2O_3$). The consumption of prebaked carbon anodes and Søderberg paste is the principal source of process related carbon dioxide emissions from primary aluminium production. Other sources of process related carbon dioxide emissions associated with Prebake anode baking account for less than 10 percent of the total non-energy related carbon dioxide emissions.

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

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

[3] Including Point Feed Prebake and Bar Broken Prebake cells.

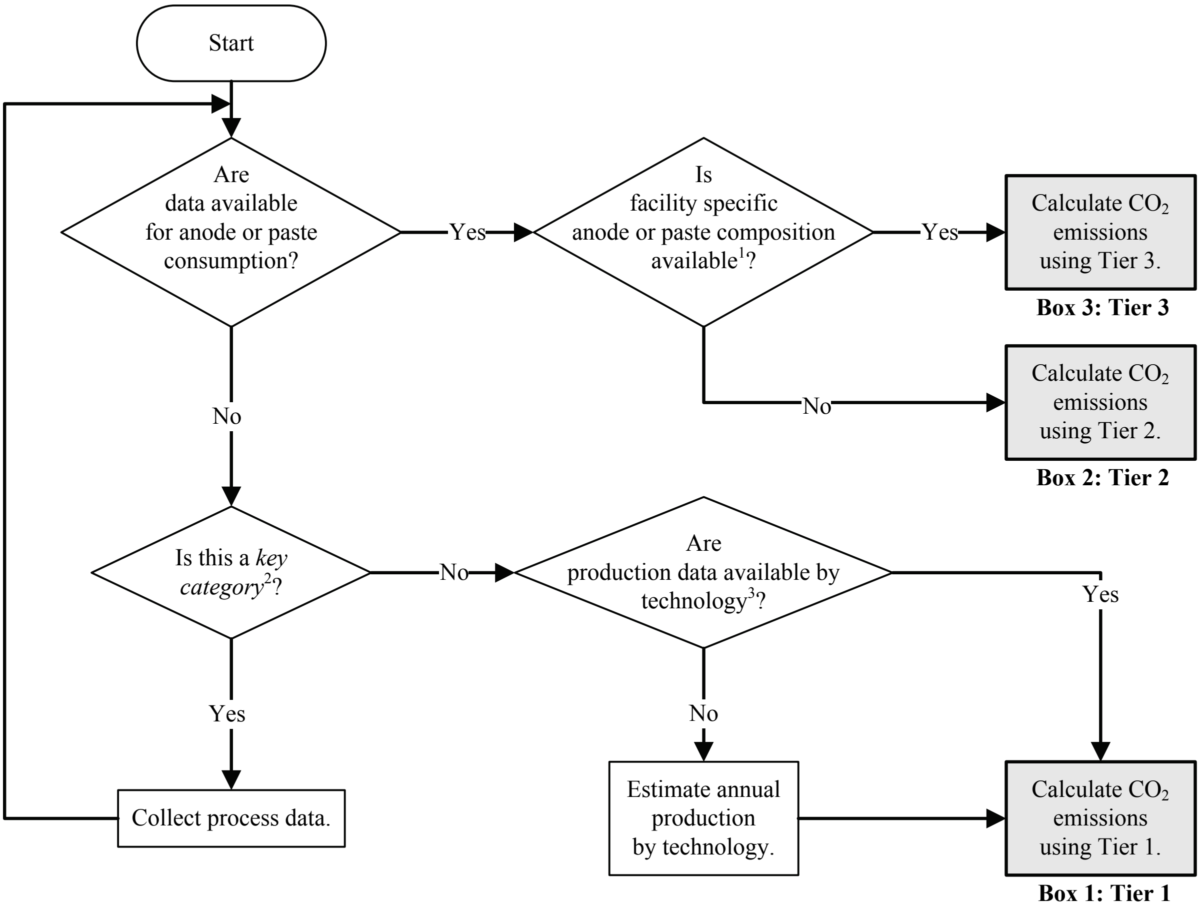
[4] A 2004 IAI survey found no evidence of $SF_6$ being emitted from primary aluminium smelting through the Hall-Heroult electrolytic production process.

producing carbon dioxide are included in process parameters routinely monitored at the production facilities, the net anode carbon consumed for Prebake facilities, or anode paste consumption for Søderberg facilities.

For the $CO_2$ emissions calculation, production data require technology differentiation as Søderberg or Prebake.There is no need for further differentiation as to the specific type of Søderberg or Prebake technology.

The decision tree shown in Figures 4.11 describes *good practice* in choosing the $CO_2$ inventory methodology appropriate for national circumstances.

**Figure 4.11 Decision tree for calculation of $CO_2$ emissions from primary aluminium production**



Note:
1. See International Aluminium Institute, The Aluminium Sector Greenhouse Gas Protocol, 2005.
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.
3. For $CO_2$ emissions calculation, the production data requires technology differentiation as Søderberg or Prebake. There is no need for further differentiation as to the specific type of Søderberg or Prebake technology.

### Tier 1 method for $CO_2$ emissions

The Tier 1 method for calculating $CO_2$ emissions uses only broad cell technology characterizations (Prebake or Søderberg) as a lower order estimate of $CO_2$ emissions from aluminium production. Given the uncertainty associated with the Tier 1 method, it is *good practice* to use higher tier methods if $CO_2$ from primary aluminium is a *key category*.

Total $CO_2$ emissions are calculated according to Equation 4.20.

**EQUATION 4.20**
**PROCESS $CO_2$ EMISSIONS FROM ANODE AND/OR PASTE CONSUMPTION (TIER 1 METHOD)**

$$E_{CO2} = EF_P \bullet MP_P + EF_S \bullet MP_S$$

Where:

$E_{CO2}$ = $CO_2$ emissions from anode and/or paste consumption, tonnes $CO_2$

$EF_P$ = Prebake technology specific emission factor (tonnes $CO_2$/tonne aluminium produced)

$MP_P$ = metal production from Prebake process (tonnes Al)

$EF_S$ = Søderberg technology specific emission factor (tonnes $CO_2$/tonne aluminium produced)

$MP_S$ = metal production from Søderberg process (tonnes Al)

### Tier 2 or Tier 3 methods for $CO_2$ emissions

For both the Prebake and Søderberg processes $CO_2$ emissions are calculated using a mass balance approach that assumes that the carbon content of net anode consumption or paste consumption is ultimately emitted as $CO_2$. The Tier 2 methods for both Prebake and Søderberg processes make use of typical industry values for impurities while the Tier 3 methods uses actual concentrations of impurities. The choice of method between the Tier 2 and Tier 3 method will depend on whether anode or paste composition data are available at the individual plant level.

#### *$CO_2$ emissions for Prebake cells (CWPB and SWPB)*:

The $CO_2$ emissions for the Tier 2 and the Tier 3 method for Prebake cells are calculated according to Equation 4.21. Tier 3 requires specific operating facility data for all the components in Equation 4.21, whereas Tier 2 is based on default values for some of the components. Section 4.4.2.2 below provides more details on using these parameters.

**EQUATION 4.21**
**$CO_2$ EMISSIONS FROM PREBAKED ANODE CONSUMPTION (TIER 2 AND TIER 3 METHODS)**

$$E_{CO2} = NAC \bullet MP \bullet \frac{100 - S_a - Ash_a}{100} \bullet \frac{44}{12}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from prebaked anode consumption, tonnes $CO_2$

MP = total metal production, tonnes Al

NAC = net prebaked anode consumption per tonne of aluminium, tonnes C/ tonne Al

$S_a$ = sulphur content in baked anodes, wt %

$Ash_a$ = ash content in baked anodes, wt %

44/12 = $CO_2$ molecular mass: carbon atomic mass ratio, dimensionless

Equation 4.21 should be applied to each Prebake smelter in the country and the results summed to arrive at total national emissions. It is possible to use a hybrid Tier 2/3 approach if data on ash or sulphur content are not available for each smelter.

Emissions from the combustion of fossil fuels used in the production of baked anodes are covered in Volume 2: Energy. However, two other sources of $CO_2$ emissions are associated with anode baking furnaces – the combustion of volatile matter released during the baking operation and the combustion of baking furnace packing material (coke). Equations 4.22 and 4.23 can be used for the calculation of such emissions.[5]

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[5] For additional information on the application of these equations to estimate emissions from combustion of volatile matter, see the IAI Greenhouse Gas Protocol (IAI, 2005a).

**EQUATION 4.22**
**$CO_2$ EMISSIONS FROM PITCH VOLATILES COMBUSTION (TIER 2 AND TIER 3 METHODS)**

$$E_{CO2} = \left(GA - H_w - BA - WT\right) \bullet \frac{44}{12}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from pitch volatiles combustion, tonnes $CO_2$

GA = initial weight of green anodes, tonnes

$H_w$ = hydrogen content in green anodes, tonnes

BA = baked anode production, tonnes

WT = waste tar collected, tonnes

**EQUATION 4.23**
**$CO_2$ EMISSIONS FROM BAKE FURNACE PACKING MATERIAL (TIER 2 AND TIER 3 METHODS)**

$$E_{CO2} = PCC \bullet BA \bullet \frac{100 - S_{pc} - Ash_{pc}}{100} \bullet \frac{44}{12}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from bake furnace packing material, tonnes $CO_2$

PCC = packing coke consumption, tonnes/tonne BA

BA = baked anode production, tonnes

$S_{pc}$ = sulphur content in packing coke, wt %

$Ash_{pc}$ = ash content in packing coke, wt %

### *$CO_2$ emissions for Søderberg cells (VSS and HSS)*:

The $CO_2$ emissions for the Tier 2 and the Tier 3 method for Søderberg cells are calculated according to Equation 4.24. Tier 3 requires specific operating facility data for all the components in Equation 4.24, whereas Tier 2 is based on default values for some of the components. Section 4.4.2.2 below provides details on parameters to be used:.

**EQUATION 4.24[6]**
**$CO_2$ EMISSIONS FROM PASTE CONSUMPTION (TIER 2 AND TIER 3 METHODS)**

$$E_{CO2} = \left( PC \bullet MP - \frac{CSM \bullet MP}{1000} - \frac{BC}{100} \bullet PC \bullet MP \bullet \frac{S_p + Ash_p + H_p}{100} \right.$$
$$\left. - \frac{100 - BC}{100} \bullet PC \bullet MP \bullet \frac{S_c + Ash_c}{100} - MP \bullet CD \right) \bullet \frac{44}{12}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from paste consumption, tonnes $CO_2$

MP = total metal production, tonnes Al

PC = paste consumption, tonnes/tonne Al

CSM = emissions of cyclohexane soluble matter, kg/tonne Al

BC = binder content in paste, wt %

$S_p$ = sulphur content in pitch, wt %

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[6] An acceptable alternative method is to use the parameter of 'pitch coking' in lieu of deducting measured or default values for $S_p$, $H_p$, $Ash_p$ and CSM from Equation 4.24. The pitch coking value is a commonly determined parameter for many facilities with Søderberg cells and standard methodology for performing the pitch coking test is described in ASTM D2416.

$Ash_p$ = ash content in pitch, wt %

$H_p$ = hydrogen content in pitch, wt %

$S_c$ = sulphur content in calcined coke, wt %

$Ash_c$ = ash content in calcined coke, wt %

CD = carbon in skimmed dust from Søderberg cells, tonnes C/tonne Al

44/12 = $CO_2$ molecular mass : carbon atomic mass ratio, dimensionless

Equation 4.24 should be applied to each smelter in the country using the Søderberg process and the results summed to arrive at total national emissions. It is possible to use a hybrid Tier 2/3 approach if data on ash or sulphur content are not available for each smelter.

### 4.4.2.2 CHOICE OF EMISSION FACTORS FOR $CO_2$ EMISSIONS FROM PRIMARY ALUMINIUM PRODUCTION

#### Tier 1 method for $CO_2$ emissions

Table 4.10 lists the default emission factors for $CO_2$ per tonne of aluminium. The emission factors of 1.6 and 1.7 for Prebake and Søderberg technologies are based on International Aluminium Institute (IAI) global survey data (International Aluminium Institute, Life Cycle Assessment of Aluminium, 2000).

**TABLE 4.10**
**TIER 1 TECHNOLOGY SPECIFIC EMISSION FACTORS FOR CALCULATING CARBON DIOXIDE EMISSIONS FROM ANODE OR PASTE CONSUMPTION**

| Technology | Emission Factor (tonnes $CO_2$/tonne Al) | Uncertainty (+/-%) |
|---|---|---|
| Prebake[7] | 1.6 | 10 |
| Søderberg | 1.7 | 10 |

Source: International Aluminium Institute, Life Cycle Assessment of Aluminium (IAI, 2000).

#### Tier 2 and Tier 3 emission factors for $CO_2$ emissions

***$CO_2$ emissions for Prebake cells (CWPB and SWPB)*:**

The most significant factors in Equation 4.21 are metal production and net anode consumption for Prebake technology. Both these parameters should be collected from individual operating facilities for use with the Tier 2 or the Tier 3. Other terms in the equation make minor adjustments for non-carbon components of the anodes (for example, sulphur and ash) and thus are not as critical. Tier 3 is based on the use of specific operating facility data for these minor components, whereas Tier 2 is based on default values listed in Tables 4.11 to 4.13. Tier 3 improves the accuracy of the results, but the improvement in accuracy is not expected to exceed 5 percent. Carbon consumed per tonne of aluminium produced is typically recorded by primary aluminium production facilities given its economic significance. Facilities using prebake cells refer to this consumption as 'net anode or net carbon consumption,' and those using Søderberg cells refer to it as 'anode paste consumption.'

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[7] The emission factor for Prebake cells includes $CO_2$ emissions from the combustion of pitch volatiles and packing coke from baking anodes.

TABLE 4.11
DATA SOURCES AND UNCERTAINTIES FOR PARAMETERS USED IN TIER 2 OR 3 METHOD FOR $CO_2$ EMISSIONS FROM PREBAKE CELLS (CWPB AND SWPB), SEE EQUATION 4.21

| Parameter | Tier 2 Method | | Tier 3 Method | |
|---|---|---|---|---|
| | **Data Source** | **Uncertainty (+/-%)** | **Data Source** | **Uncertainty (+/-%)** |
| MP: total metal production (tonnes aluminium per year) | Individual facility records | 2 | Individual facility records | 2 |
| NAC: net anode consumption per tonne of aluminium (tonnes per tonne Al) | Individual facility records | 5 | Individual facility records | 5 |
| $S_a$: sulphur content in baked anodes (wt %) | Use industry typical value, 2 | 50 | Individual facility records | 10 |
| $Ash_a$: ash content in baked anodes (wt %) | Use industry typical value, 0.4 | 85 | Individual facility records | 10 |
| Source: IAI (2005b). | | | | |

TABLE 4.12
DATA SOURCES AND UNCERTAINTIES FOR PARAMETERS USED IN TIER 2 OR 3 METHOD FOR $CO_2$ EMISSIONS FROM PITCH VOLATILES COMBUSTION (CWPB AND SWPB), SEE EQUATION 4.22

| Parameter | Tier 2 Method | | Tier 3 Method | |
|---|---|---|---|---|
| | **Data Source** | **Uncertainty (+/-%)** | **Data Source** | **Uncertainty (+/-%)** |
| GA: initial weight of green anodes processed (tonnes green anode per year) | Individual facility records | 2 | Individual facility records | 2 |
| $H_w$: Hydrogen content in green anodes (tonnes) | Use industry typical value, 0.005 • GA | 50 | Individual facility records | 10 |
| BA: Baked anode production (tonnes per year) | Individual facility records | 2 | Individual facility records | 2 |
| WT: Waste tar collected (tonnes)<br>a) Riedhammer furnaces<br>b) All other furnaces | Use industry typical value,<br>a) 0.005 • GA<br>b) insignificant | 50 | Individual facility records | 20 |
| Source: IAI (2005b). | | | | |

TABLE 4.13
DATA SOURCES AND UNCERTAINTIES FOR PARAMETERS USED IN TIER 2 OR 3 METHOD FOR $CO_2$ EMISSIONS FROM BAKE FURNACE PACKING MATERIAL (CWPB AND SWPB), SEE EQUATION 4.23

| Parameter | Tier 2 Method | | Tier 3 Method | |
|---|---|---|---|---|
| | **Data Source** | **Uncertainty (+/-%)** | **Data Source** | **Uncertainty (+/-%)** |
| PCC: Packing coke consumption (tonnes per tonne BA) | Use industry typical value, 0.015 | 25 | Individual facility records | 2 |
| BA: Baked anode production (tonnes per year) | Individual facility records | 2 | Individual facility records | 2 |
| $S_{pc}$: Sulphur content in packing coke (wt %) | Use industry typical value, 2 | 50 | Individual facility records | 10 |
| $Ash_{pc}$: Ash content in packing coke (wt %) | Use industry typical value, 2.5 | 95 | Individual facility records | 10 |
| Source: IAI (2005b). | | | | |

***$CO_2$ emissions for Søderberg cells (VSS and HSS):***

The binder content in paste, BC, typically varies by less than 1 percent and is part of operation practice by facility. It is an important term in Equation 4.24 because the carbon content of the pitch, which acts as a binder, is lower than that of the coke, which makes up the remainder of the paste. As was noted previously for Prebake anode consumption, the most important components of Equation 4.24 are the metal production and paste consumption. The other terms in Equation 4.24 make small corrections based on impurities and minor differences in carbon content of paste materials. Tier 3 is based on the use of specific operating facility data for these minor components, whereas Tier 2 is based on default values listed in Table 4.14. Tier 3 improves the accuracy of the results; however, the impact can be expected to be less than 5 percent on the result.

**TABLE 4.14**
**DATA SOURCES AND UNCERTAINTIES FOR PARAMETERS USED IN TIER 2 OR 3 METHOD FOR $CO_2$ EMISSIONS FROM SØDERBERG CELLS (VSS AND HSS)**

| **Parameter** | **Tier 2 Method** | | **Tier 3 Method** | |
|---|---|---|---|---|
| | **Data Source** | **Data Uncertainty (+/-%)** | **Data Source** | **Data Uncertainty (+/-%)** |
| MP: total metal production (tonnes Al/year) | Individual facility records | 2 | Individual facility records | 2 |
| PC : paste consumption (tonnes per tonne Al) | Individual facility records | 2-5 | Individual facility records | 2-5 |
| CSM: emissions of cyclohexane soluble matter (kg per tonne Al) | Use industry typical value,<br>HSS – 4.0<br>VSS – 0.5 | 30 | Individual facility records | 15 |
| BC: binder content in paste (wt %) | Use industry typical value,<br>Dry Paste – 24<br>Wet Paste – 27 | 25 | Individual facility records | 5 |
| $S_p$: sulphur content in pitch (wt %) | Use industry typical value, 0.6 | 20 | Individual facility records | 10 |
| $Ash_p$: ash content in pitch (wt %) | Use industry typical value, 0.2 | 20 | Individual facility records | 10 |
| $H_p$: hydrogen content in pitch (wt %) | Use industry typical value, 3.3 | 50 | Individual facility records | 10 |
| $S_c$: sulphur content in calcined coke (wt %) | Use industry typical value, 1.9 | 20 | Individual facility records | 10 |
| $Ash_c$: ash content in calcined coke (wt %) | Use industry typical value, 0.2 | 50 | Individual facility records | 10 |
| CD: carbon in dust from anode (tonnes of carbon in skim per tonne Al) | Use industry typical value, 0.01 | 99 | Individual facility records | 30 |

## 4.4.2.3 CHOICE OF METHOD FOR PFCS

During electrolysis, alumina ($Al_2O_3$) is dissolved in a fluoride melt comprising about 80 weight percent cryolite ($Na_3AlF_6$). Perfluorocarbons ($CF_4$ and $C_2F_6$ collectively referred to as PFCs) are formed from the reaction of the carbon anode with the cryolite melt during a process upset condition known as an 'anode effect'. An anode effect occurs when the concentration of alumina in the electrolyte is too low to support the standard anode reaction.

**BOX 4.2**

**ANODE EFFECT DESCRIPTION**

An anode effect is a process upset condition where an insufficient amount of alumina is dissolved in the electrolyte, causing voltage to be elevated above the normal operating range, resulting in the emission of PFC-containing gases.

Both Tier 2 and Tier 3 for PFCs are based on plant-specific process data for anode effects, which are regularly collected. In choosing a method for PFCs, it should be noted that the uncertainty associated with higher tier methodologies is significantly lower than that for Tier 1, and therefore Tier 2 and Tier 3 are strongly recommended if this is a *key category*. Depending on the production technology type, the uncertainty of the methods for PFCs ranges from several hundred percent for the Tier 1 method to less than twenty percent for the Tier 3 method. The Tier 3 methodology for PFC inventory should be utilized with slope or overvoltage coefficients calculated from measurement data obtained using good measurement practices (U.S. EPA and IAI, 2003). Communication with primary aluminium producers will determine the availability of process data, which, in turn dictates the method used to calculate emissions. Plants routinely measure anode effect performance as anode effect minutes per cell-day or anode effect overvoltage. PFC emissions are directly related to anode effect performance via a coefficient, either the slope coefficient or the overvoltage coefficient.

The decision tree shown in Figure 4.12 describes *good practice* in choosing the PFC inventory methodology appropriate for national circumstances. For high performing facilities that emit very small amounts of PFCs, the Tier 3 method will likely not provide a significant improvement in the overall facility GHG inventory in comparison with the Tier 2 Method.[8] Consequently, it is *good practice* to identify these facilities prior to selecting methods in the interest of prioritising resources. The parameters that identify these high performing facilities depend on the type of process data collected by the facility. High performing facilities are those that operate with less than 0.2 anode effect minutes per cell day when anode effect minutes are measured. When overvoltage is recorded, high performing facilities operate with less than 1.4 mV overvoltage. In addition, for these high performing facilities accurate measurement of the Tier 3 PFC coefficient is difficult because the very low frequency of anode effects requires an extended time to obtain statistically robust results. The status of a facility as a high performing facility should be assessed annually because economic factors, such as the restarts of production lines after a period of inactivity, or, process factors, such as periods of power curtailments might cause temporary increases in anode effect frequency. In addition, over time, facilities that might not at first meet the requirements for high performers may become high performing facilities through implementation of new technology or improved work practices. Note that in all cases, applying different Tiers for different years will require careful implementation to ensure time series consistency.

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

### Tier 1 method: Use of technology based default emission factors

The Tier 1 method uses technology-based default emission factors for the four main production technology types (CWPB, SWPB, VSS and HSS). 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, are not directly taken into account. Tier 1 can be consistent with *good practice* only when PFCs from primary aluminium is not a *key category* and when pertinent process data are not available from operating facilities.

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[8] The levels for the process parameters that define high performing facilities for PFC emissions are the combined result of the magnitude of, and, the uncertainty in the Tier 2 coefficient. The levels are calculated by using the positive and negative extremes of the 95% confidence limits for the Tier 2 coefficient as a proxy for the range of likely values for Tier 3 coefficients for these facilities. The potential difference is then assessed on the overall greenhouse gas emissions from a production facility considering both PFC and $CO_2$ emissions. When facilities operate at or below the anode effect process parameter levels noted here for high performing facilities, the impact of moving from the Tier 2 method for PFCs to the Tier 3 method would not result in a change greater than 5% in overall GWP weighted GHG emissions. PFC emissions from high performing facilities account for less than 3% of global PFC emissions based on IAI 2004 anode effect survey data.

**EQUATION 4.25**
**PFC EMISSIONS (TIER 1 METHOD)**

$$E_{CF4} = \sum_i \left( EF_{CF4,i} \bullet MP_i \right)$$

*and*

$$E_{C2F6} = \sum_i \left( EF_{C2F6,i} \bullet MP_i \right)$$

Where:

$E_{CF4}$ = emissions of $CF_4$ from aluminium production, kg $CF_4$

$E_{C2F6}$ = emissions of $C_2F_6$ from aluminium production, kg $C_2F_6$

$EF_{CF4,i}$ = default emission factor by cell technology type *i* for $CF_4$, kg $CF_4$/tonne Al

$EF_{C2F6,i}$ = default emission factor by cell technology type *i* for $C_2F_6$, kg $C_2F_6$/tonne Al

$MP_i$ = metal production by cell technology type *i*, tonnes Al

### Tier 2 and Tier 3 methods: based on anode effect performance

There are two different equations for estimating individual plant $CF_4$ emissions, which are both based on the relationship between anode effect and performance. These are the slope and overvoltage coefficient equations. Both types of coefficients are based on direct measurements of PFCs. Tier 2 makes use of an average coefficient from measurements at numerous facilities while Tier 3 is based on measurements at the individual facility. Because the process mechanisms that produce PFC emissions 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 all the 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. The choice between the two estimation relationships depends on the process control technology in use. Equation 4.26 should be used when anode effect minutes per cell day are recorded and Equation 4.27 should be used when overvoltage data are recorded.

**Slope Coefficient:** The slope coefficient represents the kg of $CF_4$ per tonne of aluminium produced, divided by anode effect minutes per cell-day[9]. 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 slope method for both $CF_4$ and $C_2F_6$.

**EQUATION 4.26**
**PFC EMISSIONS BY SLOPE METHOD (TIER 2 AND TIER 3 METHODS)**

$$E_{CF4} = S_{CF4} \bullet AEM \bullet MP$$

*and*

$$E_{C2F6} = E_{CF4} \bullet F_{C2F6/CF4}$$

Where:

$E_{CF4}$ = emissions of $CF_4$ from aluminium production, kg $CF_4$

$E_{C2F6}$ = emissions of $C_2F_6$ from aluminium production, kg $C_2F_6$

$S_{CF4}$ = slope coefficient for $CF_4$, (kg $CF_4$/tonne Al)/(AE-Mins/cell-day)

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

MP = metal production, tonnes Al

$F_{C2F6/CF4}$ = weight fraction of $C_2F_6/CF_4$, kg $C_2F_6$/kg $CF_4$

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[9] The term ‘cell-day’ refers to the number of cells operating multiplied by the number of days of operation.

**Overvoltage Coefficient:** Some process control systems characterize anode effects by calculating an Anode Effect Overvoltage[10] (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 many 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.

**EQUATION 4.27**
**PFC EMISSIONS BY OVERVOLTAGE METHOD (TIER 2 AND TIER 3 METHODS)**

$$E_{CF4} = OVC \bullet \frac{AEO}{CE/100} \bullet MP$$

*and*

$$E_{C2F6} = E_{CF4} \bullet F_{C2F6/CF4}$$

Where:

$E_{CF4}$ = emissions of $CF_4$ from aluminium production, kg $CF_4$

$E_{C2F6}$ = 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

$F_{C2F6/CF4}$ = weight fraction of $C_2F_6/CF_4$, kg $C_2F_6$/kg $CF_4$

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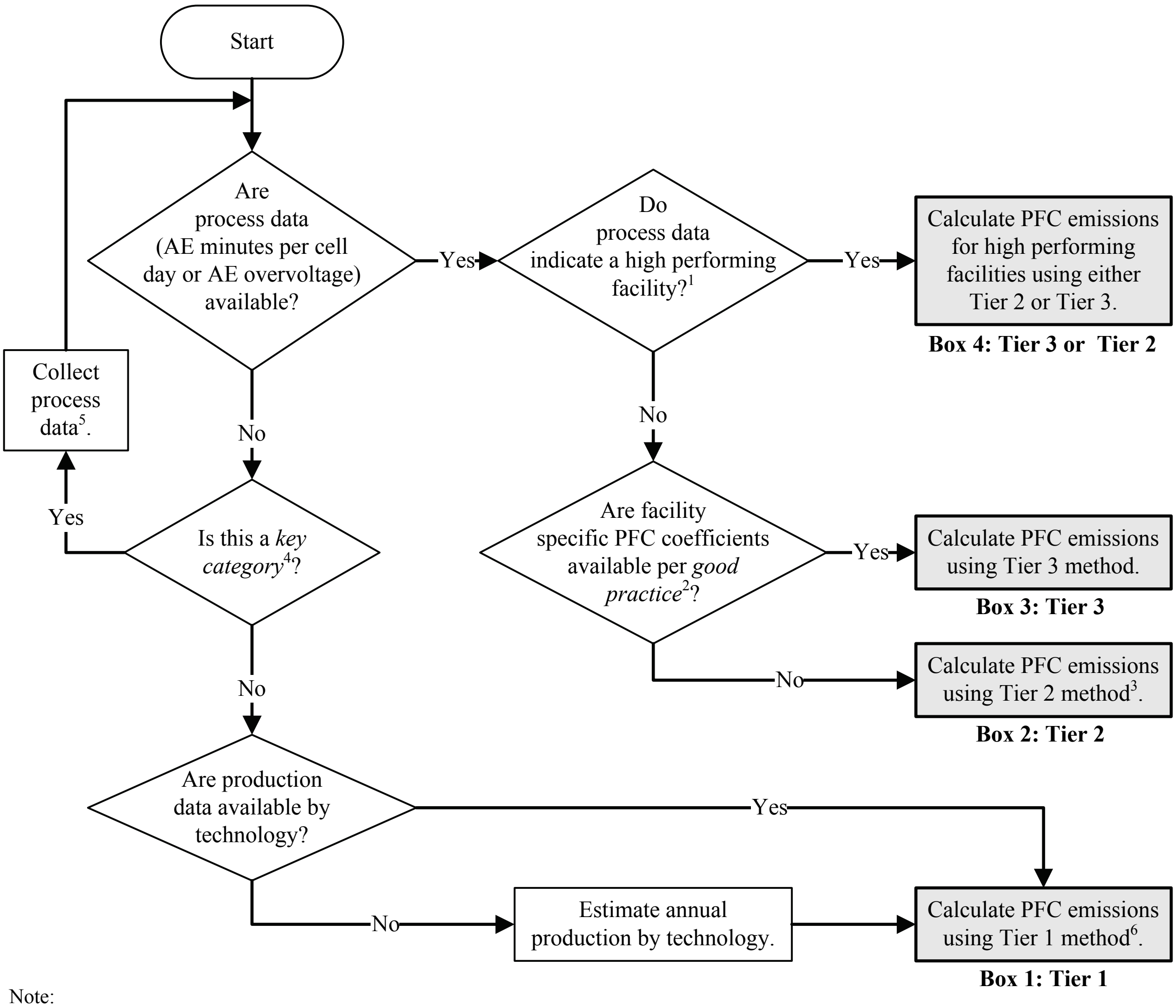
[10] Computer control systems report either ‘positive’ or ‘algebraic’ overvoltage depending on the version of software used. Use of the expression ‘overvoltage’ should not be confused with the classical electrochemical terminology, which usually means the extra voltage needed for an electrochemical reaction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

**Figure 4.12 Decision tree for calculation of PFC emissions from primary aluminium production**



Note:

1. High performing facilities emit so little PFCs that no significant improvement can be expected in the overall facility GHG inventory by using the Tier 3 method rather than the Tier 2 method. High performing facilities are defined, based on what process data are collected, as those that operate with less than 0.2 anode effect minutes per cell day, or, less than 1.4 mV overvoltage. In such facilities the improvement in accuracy in facility GHG inventory is less than 5% when moving from Tier 2 to Tier 3 methods for PFCs.
2. *Good practices* for obtaining facility specific PFC equation coefficients are detailed in the IAI GHG Protocol (IAI, 2005).
3. In this case, Tier 2 method should be used until site-specific Tier 3 coefficients become available and the Tier 3 method employed unless PFC emissions become immaterial, in which case facilities can choose to use either the Tier 2 or Tier 3 method.
4. 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.
5. For *key categories*, it is *good practice* to collect anode effect process data and production activity data at the individual production facility level.
6. Primary aluminium facilities regularly record activity data including metal production and anode effect process data facilitating, at a minimum, Tier 2 calculation method. Errors of magnitude of x10 can result from use of Tier 1 methods for PFCs.

## 4.4.2.4 CHOICE OF EMISSION FACTORS FOR PFCS

### Tier 1: Technology based default emission factors

Default emission factors for Tier 1 method are provided in Table 4.15.

**TABLE 4.15**
**DEFAULT EMISSION FACTORS AND UNCERTAINTY RANGES FOR THE CALCULATION OF PFC EMISSIONS FROM ALUMINIUM PRODUCTION BY CELL TECHNOLOGY TYPE (TIER 1 METHOD)**

| Technology | $CF_4$ | | $C_2F_6$ | |
|---|---|---|---|---|
| | $EF_{CF4}$ (kg/tonne Al)[a] | Uncertainty Range (%)[b] | $EF_{C2F6}$ (kg/tonne Al)[c] | Uncertainty Range (%)[d] |
| CWPB | 0.4 | -99/+380 | 0.04 | -99/+380 |
| SWPB | 1.6 | -40/+150 | 0.4 | -40/+150 |
| VSS | 0.8 | -70/+260 | 0.04 | -70/+260 |
| HSS | 0.4 | -80/+180 | 0.03 | -80/+180 |

[a] Default $CF_4$ values calculated from median anode effect performance from 1990 IAI survey data (IAI, 2001).

[b] Uncertainty based on the range of calculated $CF_4$ specific emissions by technology from 1990 IAI anode effect survey data (IAI, 2001).

[c] Default $C_2F_6$ values calculated from global average $C_2F_6$:$CF_4$ ratios by technology, multiplied by the default $CF_4$ emission factor.

[d] Uncertainty range based on global average $C_2F_6$:$CF_4$ ratios by technology, multiplied by calculated minimum and maximum specific $CF_4$ emissions from 1990 IAI survey data (IAI, 2001).

Note: These default emission factors should only be used in the absence of Tier 2 or Tier 3 data.

### Tier 2: PFC emission factor based on a technology specific relationship between anode effect performance and PFC emissions.

The Tier 2 method is based on using either technology specific slope or overvoltage coefficients for the applicable reduction cell and process control technology as listed in Table 4.16.[11]

**TABLE 4.16**
**TECHNOLOGY SPECIFIC SLOPE AND OVERVOLTAGE COEFFICIENTS FOR THE CALCULATION OF PFC EMISSIONS FROM ALUMINIUM PRODUCTION (TIER 2 METHOD)**

| Technology[a] | Slope Coefficient [b, c] [(kg $_{PFC}$/$t_{Al}$) / (AE-Mins/cell-day)] | | Overvoltage Coefficient[b, c, d] [(kg $_{CF4}$/$t_{Al}$) / (mV)] | | Weight Fraction $C_2F_6$ / $CF_4$ | |
|---|---|---|---|---|---|---|
| | $CF_4$ | Uncertainty (+/-%) | $CF_4$ | Uncertainty (+/-%) | $C_2F_6$/$CF_4$ | Uncertainty (+/-%) |
| CWPB | 0.143 | 6 | 1.16 | 24 | 0.121 | 11 |
| SWPB | 0.272 | 15 | 3.65 | 43 | 0.252 | 23 |
| VSS | 0.092 | 17 | NR | NR | 0.053 | 15 |
| HSS | 0.099 | 44 | NR | NR | 0.085 | 48 |

[a] Centre Worked Prebake (CWPB), Side Worked Prebake (SWPB), Vertical Stud Søderberg (VSS), Horizontal Stud Søderberg (HSS).

[b] Source: Measurements reported to IAI, US EPA sponsored measurements and multiple site measurements (U.S. EPA and IAI, 2003).

[c] Embedded in each Slope and Overvoltage coefficient is an assumed emissions collection efficiency as follows: CWPB 98%, SWPB 90%, VSS 85%, HSS 90%. These collection efficiencies have been assumed based on measured PFC collection fractions, measured fluoride gas collection efficiencies and expert opinion.

[d] The noted coefficients reflect measurements made at some facilities recording positive overvoltage and others recording algebraic overvoltage. No robust relationship has yet been established between positive and algebraic overvoltage. Positive overvoltage should provide a better correlation with PFC emissions than algebraic overvoltage. Overvoltage coefficients are not relevant (NR) to VSS and HSS technologies.

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[11] These slope coefficients were derived from measurement of PFCs and correlating the measured PFC emissions to anode effect minutes per cell day at over one-hundred aluminium smelters. The values in Table 4.16 are the technology specific factors from measurement data available as of March 2005 when this document was developed. It is important to note Tier 2 slope coefficients are based on the anode-effect minutes per cell-day statistic as defined in the IAI GHG Protocol (IAI, 2005a). It is *good practice* to refer to the most current data for calculation of PFC emissions as noted in the IAI GHG Protocol and to the IPCC Emission Factor Database.

#### Tier 3: PFC emission factor based on a facility specific relationship between anode effect performance and PFC emissions

The Tier 3 method is based on a facility specific slope or anode effect overvoltage PFC coefficient. This coefficient characterizes the relationship between facility anode effect performance and measured PFC emissions from periodic or continuous measurements that are consistent with established measurement practices (U.S. EPA and IAI, 2003) and the International Aluminium Institute GHG Protocol (IAI, 2005a).

### 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 $CO_2$ and PFC emissions. Uncertainty in the tonnes 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.

*Good practice* methods for PFC emissions require accurate anode effect minutes per cell day data or accurate overvoltage (AEO) data for all cell types. Annual statistics should be based on the production-weighted average of monthly anode effect data. Both Tier 2 and Tier 3 utilize anode effect minutes per cell day or anode effect overvoltage, and aluminium production data. Individual aluminium companies or industry groups, national aluminium associations or the International Aluminium Institute, should be consulted to ensure that the data are available and in a useable format for inventory estimation.

For $CO_2$ emissions, all aluminium smelters collect data to support Tier 2 or Tier 3 methods. Søderberg 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 $CO_2$ 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.

### 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. Anode effect process data 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.

### 4.4.2.7 DEVELOPING A CONSISTENT TIME SERIES

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.

A complete time series of PFC related activity data such as anode effect 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 anode effect frequency data are available and anode effect duration data are unavailable, it is *good practice* to splice or backcast PFC emissions per tonne aluminium based on anode effect frequency data. 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 whether any technology upgrades have been implemented at the facility, whether there have been substantial changes in work practices, whether any changes in the calculation of underlying process data have occurred, and the quality of the measurements made to establish the Tier 3 coefficients. 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 helpful information on splicing methods and details regarding constructing a time series for primary aluminium is available from IAI (IAI, 2005). Expert advice is also available from the International Aluminium Institute (London, UK) regarding greenhouse gas emissions and typical industry emissions from aluminium production.

## 4.4.3 Uncertainty assessment

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

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 Søderberg 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.

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. The high level of uncertainty in the Tier 1 method results directly from the large variability in anode effect performance among operators using similar production technology. 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 method over the Tier 2 method; however, the level of uncertainty reduction depends on the cell technology type. The uncertainty for industry average coefficients ranges from +/-6 percent for CWPB, the most widely measured and used technology, to +/-44 percent for HSS. Both Tier 2 and Tier 3 methods are based on direct PFC measurements that establish a relationship between anode effect performance and PFC specific emissions. The Tier 2 method uses an industry average equation coefficient while the Tier 3 method uses a facility specific coefficient based on direct PFC measurements made at the facility. As more facility measurements are made, especially in those facilities operating with Søderberg technologies, the uncertainty in the average coefficients should be reduced. The lowest uncertainty for PFC emissions calculations is from the use of the Tier 3 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 (USEPA/IAI, 2003). When properly established these Tier 3 coefficients will have an uncertainty of +/-15 percent at the time the coefficients are measured.

### 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. The other component of calculated facility specific emissions using Tier 2 or Tier 3 methods is the anode effect activity data, i.e., either anode effect minutes per cell day or anode effect overvoltage. 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.

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

### 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 Søderberg 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 $CO_2$ 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 in Table 4.15. 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 primary aluminium, the EPA/IAI Protocol for Measurement of Tetrafluoromethane ($CF_4$) and Hexafluoroethane ($C_2F_6$) Emissions from Primary Aluminum Production is the internationally recognized standard (U.S. EPA and IAI, 2003). Inventory compilers should encourage plants to use this method for developing Tier 3 PFC equation coefficients. Significant differences between calculated coefficients based on PFC measurements and the industry average Tier 2 coefficients for similar reduction technology should elicit further review and checks on calculations. Large differences should be explained and documented. An international data set of anode effect performance, which can be used to identify outlier data, is available from the International Aluminium Institute. 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.

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 PFCs 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 $CF_4$ and $C_2F_6$ 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.

TABLE 4.17
GOOD PRACTICE REPORTING INFORMATION FOR CALCULATING $CO_2$ AND PFC EMISSIONS FROM ALUMINIUM PRODUCTION BY TIER

| **Data** | **Tier 3** | **Tier 2** | **Tier 1** |
|---|---|---|---|
| **PFCs** | | | |
| Annual national production (by CWPB, SWPB, HSS, or VSS technology) | | | X |
| Annual production by smelter (by CWPB, SWPB, HSS, or VSS technology) | X | X | |
| Anode Effect minutes per cell-day or Anode Effect Overvoltage (mV) | X | X | |
| Facility specific emission coefficients linked to anode effect performance | X | | |
| Technology specific emission coefficients linked to anode effect performance | | X | |
| Default technology emission coefficients | | | X |
| Supporting documentation | 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 | | |

# 4.5 MAGNESIUM PRODUCTION

## 4.5.1 Introduction

In the magnesium industry, there are a number of potential emission sources and gases. The amount and type of emission from the magnesium industry will reflect the raw material used for primary magnesium metal production and/or the type of cover gas mixture used in the casting and recycling foundries to prevent oxidation of molten magnesium. It is *good practice* to consider, in a disaggregated way if possible, all segments of the magnesium industry and their related emissions. A list of possible greenhouse gas emissions, which may be associated with primary, and secondary magnesium metal production and casting operations, is provided in Table 4.18.

Primary magnesium refers to metallic magnesium derived from mineral sources. Primary magnesium can be produced either by electrolysis or a thermal reduction process. The raw materials used for primary magnesium production are dolomite, magnesite, carnalite, serpentine, brines or seawater. Processing of carbonate raw materials (magnesite and dolomite) will release $CO_2$ during manufacturing. The $CO_2$ is released during calcination of carbonate-based ores (dolomite/magnesite) - a 'pre-treatment' step to the main electrolytic/thermal reduction processes. This process is similar to the generation of $CO_2$ in the mineral industry (see Chapter 2).

Secondary magnesium production includes the recovery and recycling of metallic magnesium from a variety of magnesium containing scrap materials e.g., post consumer parts, machine cuttings, casting scraps, furnace residues, etc. Magnesium casting processes may involve metal from both primary production and secondary magnesium production. Magnesium casting processes involve handling of molten pure magnesium and/or molten high magnesium content alloys. Molten magnesium (also understood to mean high magnesium content alloys) maybe cast by a variety of methods including gravity casting, sand casting, die casting and others.

All molten magnesium spontaneously burns in the presence of atmospheric oxygen. Production and casting of all magnesium metal requires a protection system to prevent burning. Among the various protection systems commonly used are those that use gaseous components with high GWP values, such as $SF_6$, which typically escape to the atmosphere. Metallic magnesium cast from the various processes and sources all require protection methods and will therefore have similar potentials for GHG emissions.

TABLE 4. 18
POSSIBLE GHG EMISSIONS RELATED TO PRODUCTION AND PROCESSING OF MAGNESIUM

| **PROCESS** | **POTENTIAL ASSOCIATED PROCESS GHG EMISSION** | | | |
|---|---|---|---|---|
| | ***$SF_6$*** | ***HFC's*** | ***$CO_2$*** | ***Others**** |
| **Raw Materials Preparation for Primary Production** | | | | |
| Dolomite/Magnesite Based | - | - | X | - |
| Other Raw Materials | - | - | - | - |
| **Casting (primary & secondary)** | | | | |
| Primary ingot casting | X | X | X | X |
| Die casting | X | X | X | X |
| Gravity casting | X | X | X | X |
| Other casting methods | X | X | X | X |
| **Secondary Mg Production**** | X | X | X | X |

*Others include fluorinated ketone and various fluorinated decomposition products e.g., PFCs

** Includes processes involving the recycle/recovery of metallic magnesium

Secondary magnesium production (recycling), handling, melting, and casting, molten metal is protected against oxidation throughout the process by using protection systems such as $SF_6$ or $SO_2$ containing cover gases (a carrier gas (commonly air and/or $CO_2$) and $SF_6$ or $SO_2$[12]) or, in some cases, flux. High-magnesium content alloys are also commonly protected using $SF_6$ containing cover gases. Due to recent technological developments and a push towards the replacement of $SF_6$, the magnesium industry has introduced alternative cover gases. It is foreseen that the two most common alternatives to $SF_6$ in the next decade will be the fluorinated hydrocarbon HFC-134a and the fluorinated ketone FK 5-1-12 ($C_3F_7C(O)C_2F_5$), traded under the name Novec™612[13], and that the individual magnesium producer's/processor's choice of cover gas will be strongly influenced by national/regional circumstances (Tranell *et al*., 2004).

## CO$_2$ EMISSIONS FROM PRIMARY PRODUCTION

As indicated in Table 4.18, the magnesium-containing ores which release $CO_2$ during calcination are dolomite ($Mg{\bullet}Ca(CO_3)_2$) and magnesite ($MgCO_3$). For each kilogram of magnesium produced, theoretically 3.62 kg[14] (dolomite) or 1.81 kg (magnesite) respectively of $CO_2$, is emitted during calcination. The actual $CO_2$ emissions per kilogram magnesium produced will be higher than the theoretical emission due to losses of magnesium in the process chain.

## MAGNESIUM CASTING PROCESSES (PRIMARY & SECONDARY)

In magnesium casting processes, the size and type of GHG emission will depend on the chosen cover gas system used to protect liquid magnesium. In addition to emissions of the active protection compound ($SF_6$, HFC-134a or FK 5-1-12) in the cover gas itself – there may be emissions of various fluorinated decomposition products (e.g., PFCs) and potentially also the carrier gas (depending on choice of air and/or $CO_2$ or $N_2$).

### SF$_6$

It has been a common assumption that $SF_6$ in magnesium cover gas is inert and that hence, essentially all $SF_6$ used in the magnesium industry will be emitted. However, recent independent studies (Bartos *et al*., 2003 and Tranell *et al*., 2004) demonstrate that $SF_6$ does, to a certain degree, destruct in contact with liquid/gaseous magnesium at common magnesium holding/processing temperatures. The fraction of $SF_6$ destroyed in the furnace, as well as the type/amount of secondary gas products generated from the reaction with magnesium, will depend on pertaining operating conditions such as $SF_6$ concentration in cover gas, total cover gas flow-rate, size of reactive magnesium surface area, type of carrier gas used, furnace charging practises, etc.

### HFC-134a, FK 5-1-12 and decomposition products (e.g., PFCs)

Both HFC-134a and FK 5-1-12 are less thermodynamically stable (and thus have much lower GWP) than $SF_6$. It is hence expected that these gases will decompose/react extensively in the contact with liquid/gaseous magnesium, leading to the production of various fluorinated gases (e.g., PFCs). Tranell et al., 2004 found that as a general rule of thumb, when $SF_6$ is replaced by HFC-134a, less than half the amount of active fluorinated compound on a molar basis is needed to protect a given magnesium surface (under otherwise identical conditions). When $SF_6$ replaces FK 5-1-12, less than a quarter of the quantity of active compound is needed. It was reported that, as is the case for $SF_6$, the amount of active compound in the in-going cover gas destroyed in the furnace depends on conditions such as compound concentration in in-going cover gas, total cover gas flow-rate, size of reactive magnesium surface area, type of carrier gas used, charging practises etc. It should be noted that emissions of PFCs as decomposition products would be more significant in terms of $CO_2$ equivalent than FK 5-1-12 emissions, given their relative radiative effects[15].

### Carrier gases

Many cover gas systems use $CO_2$ as a carrier gas -alone or in combination with dry air- to dilute the active fluorinated compound and reduce the oxygen partial pressure in the furnace. It is a quantitatively reasonable assumption that all $CO_2$ used in the cover gas is emitted as $CO_2$. The amount of carbon dioxide cover gas used is much lower than the usual active agents in the cover gas system and can generally be disregarded.

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[12] Consistent with the scope of these Guidelines outlined in Volume 1, this chapter does not provide methods for estimating emissions of $SO_2$.

[13] FK 5-1-12 ($C_3F_7C(O)C_2F_5$), traded as Novec™612, is a fluorinated ketone produced by 3M (Milbrath, 2002).

[14] This represents a case where the ore has a stoichiometric Mg/Ca ratio of 1.

[15] The GWP value of FK 5-1-12 is not identified in the IPCC Third Assessment Report (IPCC, 2001), but it is estimated to be similar to that of $CO_2$ according to the producer of this gas.

## 4.5.2 Methodological issues

### 4.5.2.1 CHOICE OF METHOD

### $CO_2$ EMISSIONS FROM PRIMARY PRODUCTION

The choice of a *good practice* method for inventory preparation of carbon dioxide emissions from the primary magnesium (raw material) production segment will depend on national circumstances. The decision tree (see Figure 4.13, Decision Tree for Estimation of $CO_2$ Emissions from Primary Magnesium Production) describes *good practice* in adapting the methods to these country-specific circumstances.

### Tier 1

The Tier 1 method relies on national primary production data and knowledge of raw materials used in the country. National production data may not be publicly available as there are a limited number of countries producing magnesium and only a few individual producers - often only one in a country - often resulting in the designation of national production data as confidential. In the absence of national primary magnesium production statistics, industry associations, such as the International Magnesium Association (http://www.intlmag.org/), may be able to provide regional statistics. Failing other data, it may be possible to estimate primary magnesium production from annual national magnesium metal sales. This method has increased uncertainty, since it does not account for magnesium used in national product manufacturing.

$CO_2$ emissions are calculated using Equation 4.28.

**EQUATION 4.28**
**$CO_2$ EMISSIONS FROM PRIMARY MAGNESIUM PRODUCTION (TIER 1)**

$$E_{CO2} = \left(P_d \bullet EF_d + P_{mg} \bullet EF_{mg}\right) \bullet 10^{-3}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from primary magnesium production, Gg

$P_d$ = national primary magnesium production from dolomite, tonnes

$P_{mg}$ = national primary magnesium production from magnesite, tonnes

$EF_d$ = Default emission factor for $CO_2$ emissions from primary magnesium production from dolomite, tonne $CO_2$/tonne primary Mg produced

$EF_{mg}$ = Default emission factor for $CO_2$ emissions from primary magnesium production from magnesite, tonne $CO_2$/tonne primary Mg produced

### Tier 2

The Tier 2 method for determining $CO_2$ emissions from primary magnesium involves collecting company/plant-specific empirical emission factors, in addition to company specific production data. The company specific emission factors may differ substantially from the default emission factors depending on process materials handling. This collection should take place if the emissions are a *key category*.

$CO_2$ emissions are calculated using Equation 4.29.

**EQUATION 4.29**
**$CO_2$ EMISSIONS FROM PRIMARY MAGNESIUM PRODUCTION (TIER 2)**

$$E_{CO2} = \sum_i (P_i \bullet EF_i) \bullet 10^{-3}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from primary magnesium production, Gg

$P_i$ = primary magnesium produced in plant *i*, tonne

$EF_i$ = company/plant-specific emission factor for $CO_2$ emissions from primary magnesium production obtained from company/plant *i*, tonne $CO_2$ /tonne primary Mg produced

### Tier 3

If actual measured $CO_2$ emissions data are available from individual primary magnesium facilities, these data can be aggregated and used directly to account for national emissions.

## MAGNESIUM CASTING PROCESSES (PRIMARY & SECONDARY)

### $SF_6$

The choice of a *good practice* method for inventory preparation of $SF_6$ emissions from magnesium casting process segment will also depend on national circumstances. The decision tree (Figure 4.14, Decision Tree for Estimation of $SF_6$ Emissions from Magnesium Processing) describes *good practice* in adapting the methods to these country-specific circumstances.

### *Tier 1 – default emission factors*

The Tier 1 method is based on the total amount of magnesium casting or handling in the country (Equation 4.30). The underlying assumption for the Tier 1 approach is that all $SF_6$ consumption in the magnesium industry segment is emitted as $SF_6$. As described in Section 4.5.1, this assumption will potentially overestimate the GHG emissions, but the overestimate will lie within the overall uncertainty range given in Section 4.5.3. The basic Tier 1 method uses a single value as a basis for the default emission calculation when $SF_6$ is used for oxidation protection, despite the fact that $SF_6$ consumption vary substantially between different casting operations and operators (sometimes orders of magnitude). The Tier 1 method should be used only when the inventory compiler has no knowledge of type of magnesium handling- or casting operation (recycling, billet casting or die-casting etc.)

**EQUATION 4.30**
**$SF_6$ EMISSIONS FROM MAGNESIUM CASTING (TIER 1)**

$$E_{SF6} = MGc \bullet EF_{SF6} \bullet 10^{-3}$$

Where

$E_{SF6}$ = $SF_6$ emissions from magnesium casting, tonnes

MGc = total amount of magnesium casting or handling in the country, tonnes

$EF_{SF6}$ = default emission factor for $SF_6$ emissions from magnesium casting, kg $SF_6$/tonne Mg casting

### *Tier 2 – company-specific $SF_6$ consumption*

As for the Tier 1 method, the Tier 2 method also assumes that all $SF_6$ consumed is subsequentlyemitted. Instead of the amount of magnesium casting, however, the Tier 2 method uses data on national (or sub-national) consumption of $SF_6$ in the magnesium industry as reported by the industry or available through other sources such as national statistics (Equation 4.31).

The most accurate application of the method is normally collection of direct data on $SF_6$ consumption from all individual users of the gas in the magnesium industry. If no direct data are available, an alternative but a less accurate method is to estimate the share of annual national $SF_6$ consumption attributable to the magnesium industry. This requires collecting annual data on national $SF_6$ sales and assumes that all $SF_6$ gas sold to the magnesium industry is emitted within the year.

**EQUATION 4.31**
**$SF_6$ EMISSIONS FROM MAGNESIUM CASTING (TIER 2)**

$$E_{SF6} = C_{SF6}$$

Where

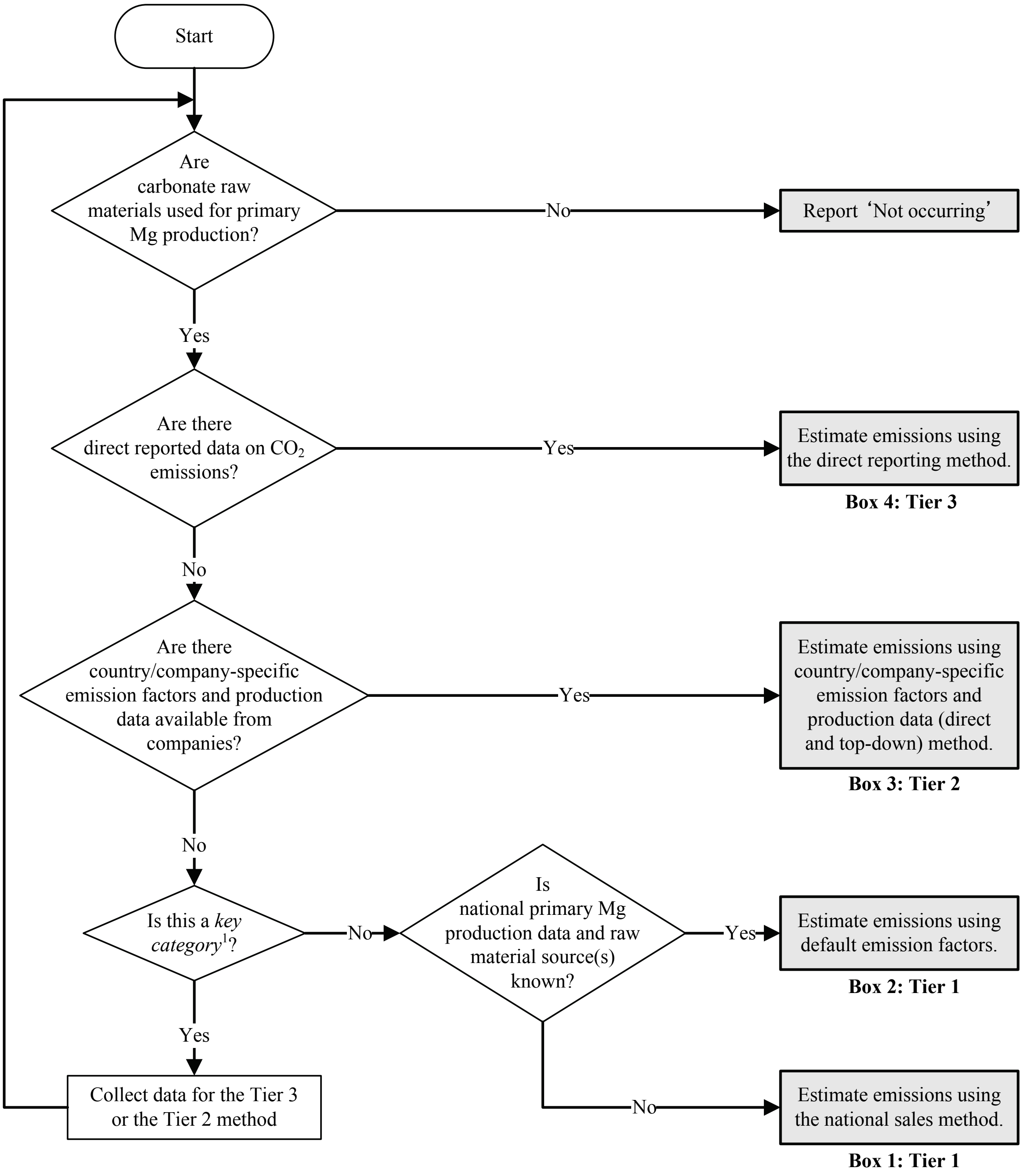
$E_{SF6}$ = $SF_6$ emissions from magnesium casting, tonnes

$C_{SF6}$ = consumption of $SF_6$ in magnesium smelters and foundries, tonnes

### *Tier 3 – direct measurement approach*

If actual measured emission data are available from individual magnesium processing facilities, these data can be aggregated and used directly to account for national emissions. In such reporting, it is *good practice* to include destruction of $SF_6$ and formation of secondary gas products.

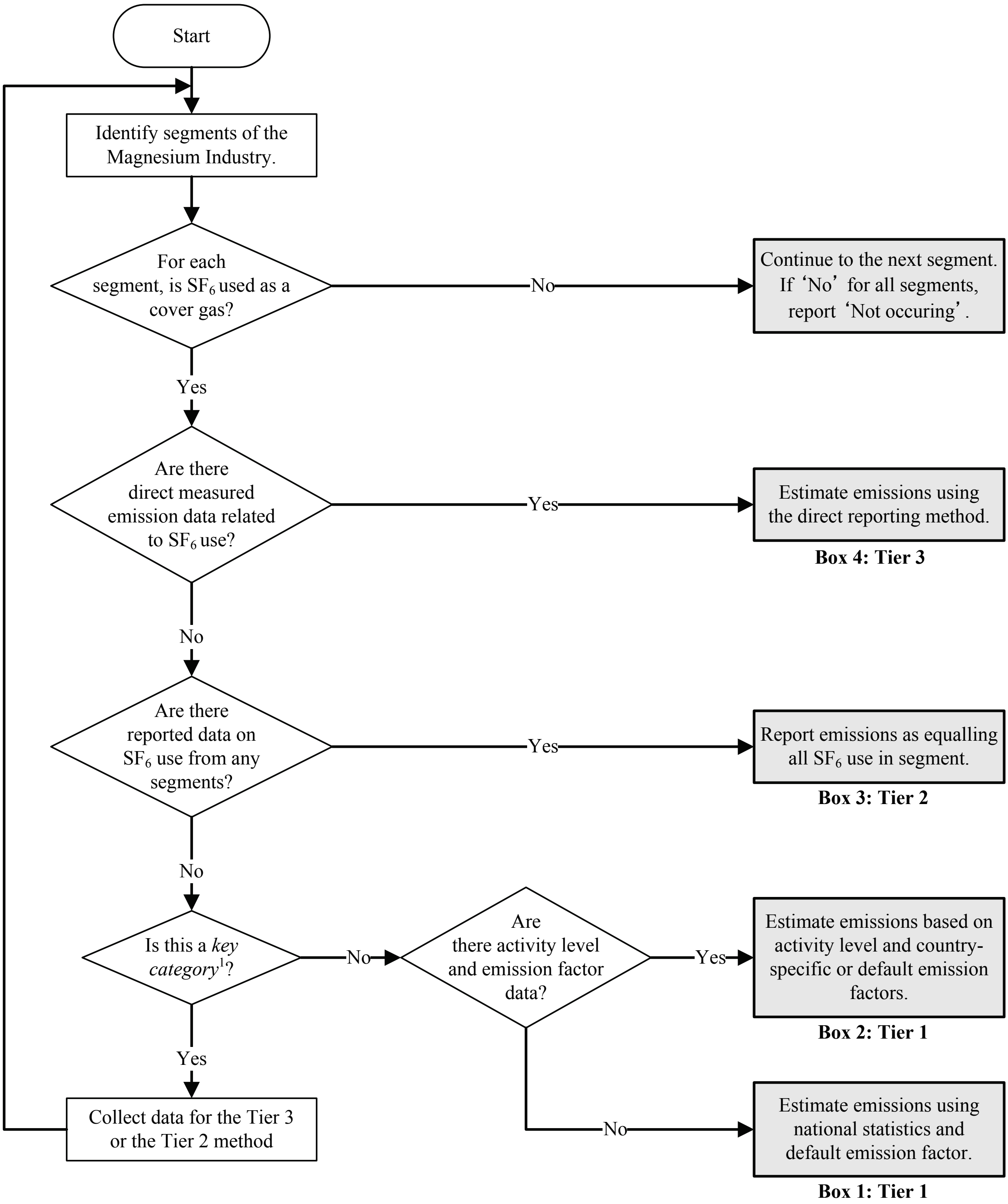
**Figure 4.13** Decision tree for estimation of $CO_2$ emissions from raw materials calcination in the primary magnesium production process



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.

**Figure 4.14 Decision tree for estimation of $SF_6$ emissions from magnesium processing**



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.

### HFC-134a, FK 5-1-12 and decomposition products (e.g., PFCs)

As described in Section 4.5.1, the industrial use of fluorinated compounds other than $SF_6$ for magnesium oxidation protection commenced in 2003-2004. As such, the industrial experience in using these compounds for magnesium protection purposes is yet very limited. Even individual plants will have little historic data, if any, on actual emissions of these other fluorinated compounds from their operations. While there is a general sense in industry that the volume use of these alternate gases will be less than $SF_6$, there are no data available at this time on which to base emission factors. Hence, it is not possible at this time to develop an emission factor-based approach (Tier 1 or 2) for reporting emissions.

However, if the GHG emission from the use of magnesium cover gases is a national *key category*, it is *good practice* to collect direct measurements or meaningful indirect measurements of GHG emissions (fugitive emissions of HFC134-a and FK 5-1-12 as well as emissions of PFCs as decomposition products) from magnesium foundries using HFC-134a or FK 5-1-12 as cover gases. This is consistent with the Tier 3 approach.

### Carrier gases

The contribution of carbon dioxide carrier gas used in protective cover gas systems is normally a small fraction of the global warming potential. In general, these emissions may be disregarded.

## 4.5.2.2 CHOICE OF EMISSION FACTORS

### $CO_2$ EMISSIONS FROM PRIMARY PRODUCTION

### Tier 1 – default emission factors

As previously mentioned, the Tier 1 method calculates emissions from default emission factors applied to a country's total primary magnesium production. The default emission factors (Table 4.19) take into account the type of material used and basic stoichiometric ratios which have been adjusted by empirical data for generic manufacturing process losses. The resulting emission of $CO_2$ per tonne magnesium produced is considerably higher than the theoretical volume described in the Section 4.5.1.

TABLE 4.19
EMISSION FACTORS FOR ORE-SPECIFIC PRIMARY Mg METAL PRODUCTION

| Raw Material | tonnes $CO_2$ emission/tonne primary Mg produced |
|---|---|
| Dolomite | 5.13 |
| Magnesite | 2.83 |

### Tier 2 – country/company-specific emission factors

The Tier 2 method for estimating $CO_2$ emissions from primary magnesium involves collecting company/plant-specific empirical emission factors. The company specific emission factors may differ substantially from the default emission factors depending on process materials handling. This collection should take place if the emissions are a *key category*.

### Tier 3 – direct measurement approach

If actual measured $CO_2$ emissions data are available from individual primary magnesium facilities, these data can be aggregated and used directly to account for national emissions.

### MAGNESIUM CASTING PROCESSES (PRIMARY & SECONDARY)

### $SF_6$

### *Tier 1 – default emission factors*

The underlying assumption for the Tier 1 approach is that all $SF_6$ consumption in this industry segment is emitted, though. as described in Section 4.5.1, this assumption will potentially overestimate the GHG emissions. The Tier 1 method also assumes no knowledge of type of magnesium handling- or casting operation (recycling, billet casting or die-casting, etc.) Under recommended conditions for die-casting, the consumption rates are about 1 kg $SF_6$ per tonne magnesium produced or smelted (Gjestland and Magers, 1996). Although the $SF_6$

consumption vary substantially between different casting operations and operators (sometimes orders of magnitude), the basic Tier 1 method uses this value as a basis for the default emission calculation when $SF_6$ is used for oxidation protection. If the national magnesium manufacturing processes are well documented, a more accurate application of the Tier 1 method is to disaggregate production data and emission factors according to the various manufacturing processes. These emission factors should relate $SF_6$ emissions to magnesium production at the same disaggregated level as the available activity data (e.g., national, sub-national). National emission factors based on plant measurements are preferable to international default factors because they reflect conditions specific to the country. Such information may be accessible through industry associations, surveys or studies.

**TABLE 4.20**
**$SF_6$ EMISSION FACTORS FOR MAGNESIUM CASTING PROCESSES (TIER 1)**

| Casting system | kg $SF_6$ emission per tonne Mg casting |
|---|---|
| All Casting Processes | 1.0 |

Source: Gjestland and Magers (1996)

### *Tier 2 – company-specific $SF_6$ consumption*

As for the Tier 1 method, the underlying principle for the Tier 2 method is that all $SF_6$ consumed is emitted. In the Tier 2 method it is, however, assumed the national (or sub-national ) consumption of $SF_6$ in the magnesium industry is reported by the industry or available through other sources such as national statistics.

The most accurate application of the method is normally collection of direct data on $SF_6$ consumption from all individual users of the gas in the magnesium industry. If no direct data are available, an alternative but a less accurate method is to estimate the share of annual national $SF_6$ consumption attributable to the magnesium industry. This requires collecting annual data on national $SF_6$ sales and assumes that all $SF_6$ gas sold to the magnesium industry is emitted within the year.

### *Tier 3 – direct measurement approach*

If actual measured emission data are available from individual magnesium processing facilities, these data can be aggregated and used directly to account for national emissions. In such reporting, it is *good practice* to include destruction of $SF_6$ and formation of secondary gas products.

### HFC-134a, FK 5-1-12 and decomposition products (e.g., PFCs)

As described above, there are little historic data upon which to base emission factors. However, if the GHG emission from the use of magnesium cover gases is a national *key category*, it is *good practice*, for inventory preparation purposes, to collect direct measurements and or reliable indirect measures of GHG emissions (fugitive emissions of HFC134-a and FK 5-1-12 as well as emissions of PFCs as decomposition products) from magnesium foundries using HFC-134a or FK 5-1-12 as cover gases. This may be considered a Tier 3 approach. Over time, it may be possible to use Tier 3 measurements as a means of developing emission factors that could be used for Tier 2.

### Carrier gases

As mentioned previously in this chapter, the contribution of carbon dioxide carrier gas used in protective cover gas systems is normally a small fraction of the global warming potential. In general it may be disregarded.

## 4.5.2.3 CHOICE OF ACTIVITY DATA

### $CO_2$ EMISSIONS FROM PRIMARY PRODUCTION

For the Tier 1 method, inventory compilers need to obtain national primary production data and knowledge of raw material type used in the country. As discussed in Section 4.5.2.1, these data may not be publicly available and therefore be difficult to obtain, in particular for small-scale (particularly thermal reduction type) production units in developing countries. Approximate national magnesium production data may be available through industry associations such as the International Magnesium Association. For the Tier 2 method, inventory compilers need to collect primary magnesium production data and data on carbonate raw materials from each company/plant. With the Tier 3 method, activity data consists of direct measured and reported emissions.

### MAGNESIUM CASTING PROCESSES (PRIMARY & SECONDARY)

#### $SF_6$

For the Tier 1 method, it is *good practice* to disaggregate production data into segments using $SF_6$, if possible, (e.g., primary production, recycling, billet casting, die casting, gravity casting, etc.) and apply available segment-specific emission factors. Where disaggregated data are not available, more aggregated production data, possibly combining output from several different processes, may be used to provide an estimate. In the absence of $SF_6$ consumption data or magnesium production data, the alternative is to collect annual national data on $SF_6$ sales to the magnesium industry. $SF_6$ producers may be able to provide these data directly, or they may be available from national statistics. It is *good practice* to consider data on consumption by other industries that use $SF_6$ (e.g., electrical equipment) when estimating the share consumed by the magnesium industry.

With the Tier 3 and 2 methods, the activity data are reported $SF_6$ (and secondary gas product) emissions or $SF_6$ consumption totals from each plant. For the Tier 1 method, national- or individual plant- magnesium production data are necessary. Where there is some direct reporting of $SF_6$ use in a segment, it is *good practice* to assess the share of production represented by the plants that directly report. For the other plants, it is *good practice* to use production-based estimates of emissions.

#### HFC-134a, FK 5-1-12 and decomposition products (e.g., PFCs)

With the Tier 3 method, activity data consists of direct measured and reported emissions. No Tier 1 or 2 method guidance is provided and hence, no activity data are necessary.

#### Carrier gases

It is *good practice* in inventory reporting that the chosen activity data for carrier gases are analogous to those of the active compound used. I.e., if $CO_2$ is used as carrier gas for $SF_6$, the activity data of $CO_2$ should reflect that of $SF_6$. If $CO_2$ is used as carrier for HFC-134a or FK 5-1-12, $CO_2$ activity data should reflect HFC-134a or FK 5-1-12 activity data.

## 4.5.2.4 COMPLETENESS

Incomplete direct reporting or incomplete activity data should not be a significant issue for primary production in developed countries. Typically, there are a small number of well-known primary magnesium producers in developed countries, and these producers are likely to keep good records. In developing countries, completeness issues generally arise in the casting segments, where facilities are more widely distributed, and have a wide range of capacities and technologies. Some plants may supply to niche markets not captured by national data sets. The inventory compiler should confirm the absence of estimates for these smaller industry segments rather than simply assuming they do not occur. It is also *good practice* to undertake periodic surveys of the industry and establish close links with international and local industry associations to check completeness of estimates.

Because alternate (non-$SF_6$) cover gas systems decompose to various fluorinated by-products, there may be some unaccounted global warming potential not described. This is not expected to be significant.

Since an increasing fraction of the world's primary production, as well as processing of magnesium, takes place in many small production units in countries with developing economies, completeness is expected to become a significant issue.

Inventory compilers should be cautious of the potential for double counting emissions from calcination of magnesium carbonate raw materials during primary magnesium production and those emissions associated with calcining limestone, dolomite, and other carboneous minerals (see Chapter 2, Other Process Uses of Carbonates, in this volume.) All emissions associated with the calcination of carbonates for primary magnesium production should be reported as GHG emissions from magnesium production.

## 4.5.2.5 DEVELOPING A CONSISTENT TIME SERIES

In terms of overall magnesium production statistics, these data will typically be available for the history of a plant. However, in some cases, historical production data may not be available due to lack of initial records or changes in the structure of the industry in the intervening period. In this case, production data from international sources may be used.

There may be issues with establishing a consistent time series for $CO_2$ emissions from primary magnesium production since these emissions may not have been reported prior to year 2006 (guidelines for reporting did not exist in the *Revised 1996 IPCC Guidelines* (IPCC, 1997)). For most primary magnesium production facilities it may, however, be assumed that the $CO_2$ emission level is relatively constant over time on a per tonne magnesium produced basis.

In terms of $SF_6$ emissions, it is *good practice* for the Tier 1 approach to multiply historic activity data by sub-national/national or default emission factor presently in use to establish consistent time series. It should be noted that plant specific emission factors would typically decrease over time due to environmental awareness, economic factors, and improved technologies and practices.

Since the magnesium industry did not use HFC-134a and FK 5-1-12 cover gases to a significant extent in any country prior to 2003, historic emissions will likely be zero. Given the level of complexity in reporting emissions related to the use of these gases, developing consistent time series will be a challenge to inventory compilers.

It is *good practice* to assess the appropriate historical emission factors following the guidance in Volume 1, Chapter 5. To ensure consistency over time, it is *good practice* to recalculate emissions estimates using previously used and new methods to ensure that any trends in emissions are real and not caused by changes in the estimation methodologies. *Good practice* is to document assumptions in all cases and archive them at the inventory compiler.

## 4.5.3 Uncertainty assessment

### $CO_2$ EMISSIONS FROM PRIMARY PRODUCTION

At the plant level, there should normally be well-documented raw material type/analysis and use, as well as tonnage magnesium produced. Directly-reported activity data, which are required for Tier 2 and 3 methods for all gases, are typically accurate to within less than 5 percent. At the national inventory level, the accuracy of magnesium production activity and emission data is comparable to that of other national production statistics (i.e., ±5 percent). Additional uncertainty is introduced through estimating the share of production not reporting directly.

### MAGNESIUM CASTING PROCESSES (PRIMARY & SECONDARY)

#### $SF_6$

In the Tier 1 approach, aggregating production from different secondary segments and using the default emission factor introduces uncertainty. For example, national data from casting operations may not be segregated into die-casting and gravity casting segments despite their potentially different $SF_6$ emission rates. Thus, this approach gives by default a very rough approximation of real emissions. Given that different handling and casting operations may use concentrations of $SF_6$ in cover gas that differ by orders of magnitude, uncertainties using the Tier 1 method may also range over orders of magnitude. For the Tier 1 and 2 methods, there is also a level of uncertainty associated with the assumption that 100 percent of the $SF_6$ used is emitted. In a typical casting operation, the uncertainty in this assumption should be within 30 percent (Bartos *et al*., 2003).

For the Tier 2 method, there is a very low uncertainty associated with $SF_6$ use on a plant level, since $SF_6$ use is measured easily and accurately from purchase data. (An uncertainty estimate of less than 5 percent is usually appropriate for directly reported data.)

For the Tier 3 method, uncertainties arise mainly from monitoring equipment calibration/accuracy. Typical gas analysis methods such as Fourier Transformed Infra Red Spectroscopy (FTIR) generally operate with an estimated accuracy of ± 10 percent. In addition to FTIR and similar analytical techniques, there will be further uncertainty caused by problems related to representative sampling and calibration that could raise the overall uncertainty of FTIR to ± 20 percent.

#### HFC-134a, FK 5-1-12 and decomposition products (e.g., PFCs)

As with the Tier 3 method for $SF_6$, main uncertainties are associated with monitoring equipment calibration/accuracy in processes using HFC-134a or FK 5-1-12 cover gases. Uncertainties are approximated to ± 10 percent.

#### Carrier gases

The largest uncertainty is associated with the Tier 1 approach of considering $CO_2$ emissions from cover gases negligible. This is particularly true if a facility uses a very $CO_2$ rich carrier gas blend. Other tiers have the same uncertainties as related for $SF_6$.

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

### 4.5.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks, as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly for higher tier methods. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

The following section outlines additional procedures specific to magnesium production:

**Comparison of emissions estimates using different approaches**

If emissions were calculated using data from individual plants, inventory compilers should compare the estimate to emissions calculated using national magnesium production data or (in the case of $SF_6$) national consumption data attributed to magnesium use. The results of the comparison should be recorded and any discrepancies should be investigated.

**Review of plant-level data**

The following plant-specific information should be archived to facilitate independent review:

- Magnesium production volumes and process types;
- Cover gas with global warming potential ($SF_6$, HFC-134a, FK 5-1-12, $CO_2$, etc.) consumption/composition or magnesium production (where factors are used);
- Plant-level QA/QC results (including documentation of sampling, measurement method, and measurement results for plant level data);
- Results of QA/QC conducted by any integrating body (e.g., industry association such as the International Magnesium Association.);
- Calculations and estimation method; and
- Where applicable, a list of assumptions in allocating national $SF_6$ usage, HFC-134a, FK 5-1-12 or other cover gases of interest or production to plant level.

Inventory compilers should determine if national or international measurement standards were used for reporting of global warming cover gas ($SF_6$, HFC-134a, FK 5-1-12, etc.) consumption or magnesium production data at the individual plants. If standard methods and QA/QC procedures were not followed, then use of these activity data should be reconsidered.

**Review of national activity data**

QA/QC activities associated with the reference to magnesium production data should be evaluated and referenced. Inventory compilers should check if the trade association or agency that compiled the national production data used acceptable QA/QC procedures. If the QA/QC procedures are deemed acceptable, inventory compilers should reference the QC activity as part of the QA/QC documentation.

**Assessment of emission factors**

Where company/country-specific factors are used, inventory compilers should review the level of QC associated with the underlying data. It is *good practice* that the inventory compiler cross-check national level default factors against plant-level factors to determine if these are representative.

**Peer review**

Inventory compilers should involve magnesium industry experts in a thorough review of the inventory estimate, giving consideration to potential confidentiality issues. Historical production data may be less sensitive to public disclosure than current data and could be utilised for an external peer review of plant level emissions.

### Verification of $SF_6$ emissions data

Inventory compilers should sum the amount of $SF_6$ used by different industrial sectors (e.g., magnesium, electrical equipment) and compare this value with the total usage of $SF_6$ in the country, obtained from import/export and production data. This provides an upper bound on the potential emissions.[16]

## 4.5.4.2 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, Section 6.11. 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 estimates from the magnesium source category separately by industry segments such as primary production, secondary production and casting.

The following additional information can provide a reasonable degree of transparency in reporting:

### Direct reporting

- Number of magnesium plants reporting;
- The types of processes and manufacture employed;
- Magnesium and magnesium products produced;
- $SF_6$ emissions associated with the magnesium segment;
- Use of other protective cover gases with global warming potential; and
- Emission factor data (and reference) for each protective cover gas with global warming potential.

### National cover gas sales-based estimate of potential emissions

- National $SF_6$ consumption (and reference);
- National use of HFC-134a assigned to the magnesium sector;
- National use of FK 5-1-12 assigned to the magnesium sector;
- Assumptions for allocating $SF_6$ , HFC-134a, FK 5-1-12, used to magnesium;
- Estimate of percentage of national $SF_6$, HFC-134a, FK 5-1-12, used in magnesium (and reference); and
- Any other assumptions made.

In most countries, the magnesium industry will be represented by a small number of plants. In this industry, the activity level data and cover gas emissions (that are directly related to activity levels) may be considered confidential business information and public reporting may be subject to confidentiality considerations.

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[16] It may not always be the case that such aggregated consumption data will provide an upper limit on emissions. It is possible, depending on the national characteristics of the $SF_6$ consuming industry that in some years actual emissions of $SF_6$ may be greater than consumption of $SF_6$. For instance, consumption in die casting of magnesium may be very low, there may not be much semiconductor manufacturing, but a considerable bank of $SF_6$ in electrical equipment may have evolved through the years. In this case, leakage from bank combined with emissions resulting from decommissioning of equipment may lead to actual emissions that exceed consumption of $SF_6$ (potential emissions). See also Section 8.2 on $SF_6$ emissions from electrical equipment.

# 4.6 LEAD PRODUCTION

## 4.6.1 Introduction

### PRIMARY PRODUCTION PROCESSES

There are two primary processes for the production of rough lead bullion from lead concentrates. The first type is sintering/smelting, which consists of sequential sintering and smelting steps and constitutes roughly 78 percent of the primary lead production. The second type is direct smelting, which eliminates the sintering step and constitutes the remaining 22 percent of primary lead production in the developed world. (Sjardin, 2003)

In the sintering/smelting process, the initial sintering blends lead concentrates with recycled sinter, lime rock and silica, oxygen, and high-lead-content sludge to remove sulphur and volatile metals via combustion (Metallurgical Industry, 1995). The process, which produces a sinter roast that consists of lead oxide and other metallic oxides, results in the emission of sulphur dioxide ($SO_2$) and energy-related carbon dioxide ($CO_2$) from the natural gas used to ignite the lead oxides (DOE, 2002). The sinter roast is then put in a blast furnace along with ores containing other metals, air, smelter by-products, and metallurgical coke (Metallurgical Industry, 1995). The coke burns as it reacts with air and produces carbon monoxide (CO) that actually performs the reduction of the lead oxide by chemical reaction (DOE, 2002). The smelting process occurs in either a traditional blast furnace or an Imperial Smelting Furnace, and it is the reduction of the lead oxide during this process that produces $CO_2$ emissions (Sjardin, 2003). The sintering process produces molten lead bullion (Metallurgical Industry, 1995).

In the direct smelting process, the sintering step is skipped, and the lead concentrates and other materials are entered directly into a furnace in which they are melted and oxidized (Sjardin, 2003). A variety of furnaces are used for the direct smelting process, with the Isasmelt-Ausmelt, Queneau-Schumann-Lurgi, and Kaldo furnaces used for bath smelting and the Kivcet furnace used for flash smelting. A number of reducing agents, which include coal, metallurgical coke, and natural gas, are used in the process in different quantities for each furnace, which results in different levels of $CO_2$ emissions for each type of furnace (Sjardin, 2003; LDA, 2002). The direct smelting process offers significant environmental and potential cost saving benefits through the avoidance of the sintering process and is therefore expected to constitute a growing portion of primary refinery lead production in the future (LDA, 2002).

### SECONDARY PRODUCTION PROCESS

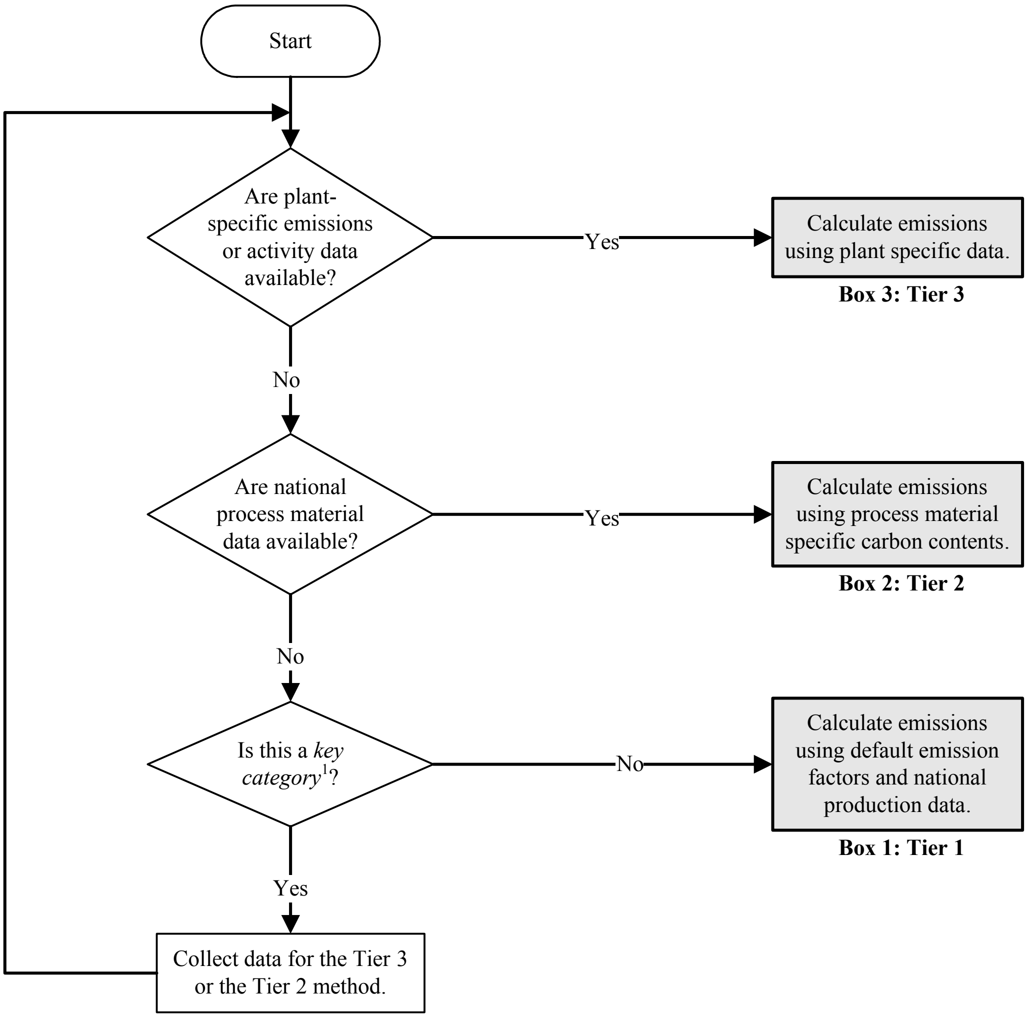
The secondary production of refined lead amounts to the processing of recycled lead to prepare it for reuse. The vast majority of this recycled lead comes from scrapped lead acid batteries. The lead acid batteries are either crushed using a hammer mill and entered into the smelting process with or without desulphurization or they are smelted whole (Sjardin, 2003). Traditional blast furnaces, Imperial Smelting Furnaces, electric arc furnaces, electric resistance furnaces, reverbatory furnaces, Isasmelt furnaces, Queneau-Schumann-Lurgi furnaces, and Kivcet furnaces can all be used for the smelting of these batteries and other recycled scrap lead (Sjardin, 2003). As with the furnaces used for primary lead bullion production, these furnaces generate different levels of $CO_2$ emissions from their use of differing types and quantities of reductants. The primary reductants are coal, natural gas, and metallurgical coke, although the electric resistance furnace uses petroleum coke (Sjardin, 2003).

## 4.6.2 Methodological Issues

### 4.6.2.1 CHOICE OF METHOD

The *IPCC Guidelines* outline three methods for calculating $CO_2$ emissions from lead production. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 4.15. The Tier 1 method calculates emissions from general emission factors applied to a country's total lead production and is the least accurate. This method is appropriate only when lead production is not a *key category*. The Tier 2 method uses country specific process material data for both primary and secondary production processes multiplied by the appropriate carbon contents of process materials. The Tier 3 method requires facility-specific measured activity or emissions data.

**Figure 4.15 Decision tree for estimation of $CO_2$ emissions from lead 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 1 METHOD

The simplest estimation method is to multiply default emission factors by lead production. When the only data available are national lead production statistics, it is *good practice* to use default emission factors. Equation 4.32 calculates total carbon dioxide emissions from lead production by summing emissions by source and accounting for emissions from secondary feedstock pre-treatment. If it is not possible to differentiate the type of production process, the default emission factor should be used. The default emission factor assumes a that 80 percent of production (including both primary and secondary) is smelted using an Imperial Smelting Furnaces or blast furnaces, while the remaining 20 percent is smelted using the direct smelting method in the Kivcet, Ausmelt, and Queneau-Schumann-Lurgi furnaces. This assumption is consistent with global lead production data (Sjardin, 2003).

**EQUATION 4.32**

**$CO_2$ EMISSIONS FROM LEAD PRODUCTION**

$$E_{CO2} = DS \bullet EF_{DS} + ISF \bullet EF_{ISF} + S \bullet EF_S$$

Where:

$E_{CO2}$ = $CO_2$ emissions from lead production, tonnes

DS = quantity of lead produced by Direct Smelting, tonnes

$EF_{DS}$ = emission factor for Direct Smelting, tonne $CO_2$/tonne lead product

ISF = quantity of lead produced from the Imperial Smelting Furnace, tonnes

$EF_{ISF}$ = emission factor for Imperial Smelting Furnace, tonne $CO_2$/tonne lead product

S = quantity of lead produced from secondary materials, tonnes

$EF_S$ = emission factor for secondary materials, tonne $CO_2$/tonne lead product

The $CO_2$ emission factors used in Equation 4.32 are shown in Table 4.21.

### TIER 2 METHOD

The Tier 2 method recognizes that there are substantial differences in carbon dioxide emissions for lead production depending on the production methodology and the source of the raw materials, either from secondary sources such as recycled batteries, or, from primary production from ores. Secondary lead sources may be pre-treated to remove impurities resulting in carbon dioxide emissions. Emissions can be calculated using country specific emission factors based on the use of reducing agents, furnace types and other process materials of interest. Factors can be developed based on carbon contents applicable to those materials. Table 4.22 provides carbon contents that can be used to derive country-specific factors. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual lead companies. Tier 2 is more accurate than Tier 1 because it takes into account the materials and the variety of furnace types used in the lead sector that contribute to $CO_2$ emissions for a particular country rather than assuming worldwide industry-wide practices.

### TIER 3 METHOD

If actual directly measured $CO_2$ emissions data are available from lead facilities, these data can be aggregated and used directly to account for national emissions using the Tier 3 method. Total national emissions will equal the sum of emissions reported from each facility. If facility emissions are not available, emissions should be calculated from plant-specific data for individual reducing agents and other process materials. To achieve a higher level of accuracy than Tier 2, it is *good practice* to develop emissions estimates at the plant-level because plants can differ substantially in their technology, specifically furnace technology. These data may be available from governmental agencies responsible for manufacturing or energy statistics, or from business or industry trade associations, but is preferably aggregated from data furnished by individual lead facilities.

## 4.6.2.2 CHOICE OF EMISSION FACTORS

### TIER 1 METHOD

When the only data available are national lead production statistics, it is *good practice* to use default emission factor of 0.52 tonne of $CO_2$/ tonne of lead (Sjardin 2003). This default should only be used when no information is available on the relative amounts of lead produced from primary and from secondary materials. If information is available, emissions should be calculated using the appropriate factors in Table 4.21. (Sjardin, 2003). The uncertainty in the default factor is high and varies depending on the mix of production methods and the percentage of secondary processing. In addition, the factor assumes that 80 percent of the world's lead production (including both primary and secondary) is smelted using an Imperial Smelting Furnaces, while the remaining 20 percent is smelted using the direct smelting method in the Kivcet, Ausmelt, and Queneau-Schumann-Lurgi furnaces (Sjardin, 2003).

**TABLE 4.21**
**GENERIC $CO_2$ EMISSION FACTORS FOR LEAD PRODUCTION BY SOURCE AND FURNACE TYPE**
**(tonnes $CO_2$/tonne product)**

| From Imperial Smelt Furnace (ISF) Production | From Direct Smelting (DS) Production | From Treatment of Secondary Raw Materials | Default Emission Factor (80% ISF, 20% DS) |
|---|---|---|---|
| 0.59 | 0.25 | 0.2 | 0.52 |

Source: Sjardin (2003)

### TIER 2 METHOD

This method offers the opportunity to adjust emission factors to reflect variations from the presumed norms based on plant-specific data for the carbon content of these materials and based on furnace type. The default carbon contents in Table 4.22 should be used if an inventory compiler does not have information on conditions in lead facilities, but has detailed activity data for the process materials. The default values in Table 4.22 are derived from the default values in Tables 1.2 and 1.3 in Volume 2, Chapter 1 and should be referenced for further information.

**TABLE 4.22**
**MATERIAL-SPECIFIC CARBON CONTENT FOR LEAD PRODUCTION (kg carbon/kg )**

| Process Materials | Carbon Content |
|---|---|
| Blast Furnace Gas | 0.17 |
| Charcoal* | 0.91 |
| Coal[1] | 0.67 |
| Coal Tar | 0.62 |
| Coke | 0.83 |
| Coke Oven Gas | 0.47 |
| Coking Coal | 0.73 |
| EAF Carbon Electrodes[2] | 0.82 |
| EAF Charge Carbon[3] | 0.83 |
| Fuel Oil[4] | 0.86 |
| Gas Coke | 0.83 |
| Natural Gas | 0.73 |
| Petroleum Coke | 0.87 |

Source: References for carbon content data are included in Table 1.2 and 1.3 in Volume 2, Chapter 1.

Notes:

[1] Assumed other bituminous coal

[2] Assumed 80 percent petroleum coke and 20 percent coal tar

[3] Assumed coke oven coke

[4] Assumed gas/diesel fuel

* 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.)

### TIER 3 METHOD

The Tier 3 method is based on aggregated emission estimates or the application of the Tier 2 at a 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 rates for all of the process materials and off-site transfers such as those listed in Table 4.22. While Table 4.22 provides default carbon contents, it is *good practice* under Tier 3 to adjust these values to reflect variations at the plant level from default values represented in the table. The default factors listed in Table 4.22 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 4.22 would not be applied to the Tier 3 method in most instances.

## 4.6.2.3 CHOICE OF ACTIVITY DATA

### TIER 1 METHOD

The Tier 1 method requires only the amount of lead produced in the country and if available, the amount produced by furnace type. These data may be available from governmental agencies responsible for manufacturing statistics, business or industry trade associations, or individual lead companies. These tonnages can then be multiplied by the corresponding emission factor in Table 4.21 to estimate $CO_2$ emissions from the sector or the default factor if furnace type is unavailable.

### TIER 2 METHOD

The Tier 2 method requires only the total amounts of reducing agents and other process materials used for lead production in the country. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual lead companies. These amounts can then be multiplied by the appropriate carbon contents in Table 4.22 and summed to determine total $CO_2$ 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 or activity data. If emissions data are not available, the Tier 3 method requires activity data to be collected at the plant level and aggregated for the sector. The amounts of reducing agents and the type of furnace used are more accurately determined in this manner. These data may be available from governmental agencies responsible for manufacturing or energy statistics, or from business or industry trade associations, but are preferably aggregated from data furnished by individual lead facilities. This approach also allows for additional accuracy by allowing individual companies to provide more accurate plant-specific data and/or to use more relevant emission factors to reflect carbon contents and furnace types that may differ from the default factors used in the Tier 2 method.

### 4.6.2.4 COMPLETENESS

In estimating emissions from this source category, there is a risk of double counting or omission in either the IPPU or the Energy Sector. As a general guide, all process emissions from lead production should be reported in the IPPU Sector.

### 4.6.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from lead production should be calculated using the same method for every year in the time series. Where data are unavailable to support a Tier 3 method for all years in the time series, these gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5, Time Series Consistency and Recalculation.

## 4.6.3 Uncertainty assessment

Uncertainty estimates for lead production result predominantly from uncertainties associated with activity data, and from uncertainty related to the emission factor. Table 4.23 provides an overview of the uncertainties for emission factors and activity data.

### 4.6.3.1 EMISSION FACTOR UNCERTAINTIES

The default emission factors used in Tier 1 may have an uncertainty of ± 50 percent. Tier 2 carbon contents are expected to have an uncertainty of ± 15 percent. Tier 3 unit specific emission factors would be expected to be within 5 percent if plant-specific carbon content data are available.

### 4.6.3.2 ACTIVITY DATA UNCERTAINTIES

National production statistics should be available and likely have an uncertainty of ± 10 percent. For Tier 2, the total amount of reducing agents and process materials used for lead production would likely be within 10 percent. Tier 3 requires plant-specific information on production data (about 5 percent uncertainty). In addition, actual emissions data for tier 3 would be expected to have ± 5 percent uncertainty.

TABLE 4.23
UNCERTAINTY RANGES

| Method | Data Source | Uncertainty Range |
|---|---|---|
| Tier 1 | National Production Data | ± 10% |
| | Default Emission Factor | ± 50% |
| | Emission Factors by Process Type | ± 20% |
| Tier 2 | Amounts and Types of Reducing Agents Used | ± 10% |
| | Process Material Carbon Contents | ± 15% |
| Tier 3 | Facility-Derived = Process Materials Data | ± 5% |
| | Facility-Specific Measured $CO_2$ Data | ± 5% |
| | Facility-Specific Emission Factors | ± 5% |

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

### 4.6.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventories agencies are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, Chapter 6, specific procedures of relevance to this source category are outlined below.

**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.

**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 conditions or technology. For lead production, inventory compilers should compare plant data with other plants.

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

**Expert review**

Inventory compilers should include key industrial trade organisations associated with lead production in a review process. This process should begin early in the inventory development process to provide input to the development and review of methods and data acquisition

Third party reviews are also useful for this source category, particularly related to initial data collection, measurement work, transcription, calculation and documentation.

**Activity data check**

For all tier levels, inventory compilers should check with Volume 2: Energy to ensure that emissions from reducing agents and process materials (coal, coke, natural gas, etc.) are not double-counted or omitted.

Inventory compilers should examine any inconsistency between data from different plants to establish whether these reflect errors, different measurement techniques or result from real differences in emissions, operational conditions or technology. This is particularly relevant to the plant-specific estimates of amounts of reducing agents or reported carbon content of process materials.

Inventory compilers should compare aggregated plant-level estimates to industry totals for process materials consumption where such trade data are available.

### 4.6.4.2 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, Section 6.11. 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.

#### TIER 1 METHOD

Besides reporting of estimated emissions, it is *good practice* to report the total lead production by process and corresponding emission factors used.

#### TIER 2 METHOD

*Good practice* is to document the estimated or calculated emissions, all activity data, and corresponding carbon contents any assumptions or data justifying alternative values. There should be a clear explanation of the linkage with the Volume 2, Energy, to demonstrate that double counting or missing emissions have not occurred.

#### TIER 3 METHOD

*Good practice* is to document the calculated emissions and source of all data, taking into account the need to protect the confidentiality of data for specific facilities if the data are business-sensitive or of a proprietary nature. In addition, inventory compilers should for all tiers, document all information needed to reproduce the estimate, as well as the QA/QC procedures.

# 4.7 ZINC PRODUCTION

## 4.7.1 Introduction

### PRIMARY PRODUCTION PROCESSES

There are three different types of primary zinc production.  The first method is a metallurgical process called electro-thermic distillation. The process is used to combine roasted concentrate and secondary zinc products into a sinter feed that is burned to remove zinc, halides, cadmium, and other impurities. The resulting zinc oxide-rich sinter is combined with metallurgical coke in an electric retort furnace that reduces the zinc oxides and produces vaporized zinc which is captured in a vacuum condenser. The reduction results in the release of non-energy carbon dioxide ($CO_2$) emissions. The electro-thermic distillation process is used in the United State and in Japan. (Sjardin, 2003; European IPPC Bureau, 2001)

The second method of zinc production is a pyrometallurgical process involving the use of an Imperial Smelting Furnace, which allows for the simultaneous treatment of lead and zinc concentrates. The process results in the simultaneous production of lead and zinc and the release of non-energy $CO_2$ emissions. The metallurgical coke/coal reductant used in this process must be allocated to lead and zinc production in order to perform an emission calculation without double counting. A mass based allocation results in a factor of 0.74 tonnes coke/tonne zinc. (Sjardin, 2003; European IPPC Bureau, 2001)

The third zinc production method is the electrolytic process, which is a hydrometallurgical technique. In this process, zinc sulphide is calcined, resulting in the production of zinc oxide. The zinc oxide is then leached in sulphuric acid and purified to remove iron impurities, copper, and cadmium. The zinc is then drawn out of the solution using electrolysis. The electrolytic process does not result in non-energy $CO_2$ emissions. (Sjardin 2003; European IPPC Bureau 2001)

### SECONDARY PRODUCTION PROCESSES

There are more than 40 hydrometallurgical and pyrometallurgical technologies that can be used to recover zinc metal from various materials. The preferred method for a given situation depends on the zinc source (contamination level and zinc concentration) and the desired end use for the recovered zinc. The process frequently consists of zinc concentration (through physical and/or chemical separation), sintering, smelting, and refining. In some cases, high grade zinc is removed from this process after physical concentration and consumed by other industries, including iron and steel manufacture, brass manufacture, and zinc die-casting, without going through the rest of the process steps. (Sjardin, 2003)

The sintering, smelting, and refining steps are identical to the steps used in the primary zinc production process, so certain smelting processes are considered emissive, while the sintering and refining steps are considered non emissive from the perspective of non-energy $CO_2$ emissions. When the concentration step involves the use of a carbon-containing reductant and high temperatures to volatilize or fume zinc from the source materials, the process could result in non-energy $CO_2$ emissions. The Waelz Kiln and slag reduction or fuming processes are two such concentration methods. The Waelz Kiln process, which is used to concentrate zinc in flue dusts, sludges, slags, and other zinc-containing materials, involves the use of metallurgical coke as a reductant. However, the reduced zinc is re-oxided during the processes and the metallurgical coke also serves as a heat source during the process. The slag reduction or fuming process, which is used strictly to concentrate zinc in molten slags from copper and zinc smelting, involves the use of coal or another carbon source as a reductant. (Sjardin, 2003; European IPPC Bureau, 2001)

## 4.7.2 Methodological issues

### 4.7.2.1 CHOICE OF METHOD

The *IPCC Guidelines* outline several approaches for calculating $CO_2$ emissions from zinc production. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 4.16. The Tier 3 method may be used if facility-specific measured emissions data are available. Tier 2 method uses country specific emissions factors for both primary and secondary production processes. The Tier 1 method is very simple and it may lead to errors due to its reliance on assumptions rather than actual data. The Tier 1 method calculates emissions from general emission factors applied to a country's total zinc production and is the least rigorous method. This method should only be used when zinc production is not a *key category*.

## TIER 1 METHOD

The simplest estimation method is to multiply default emission factors by zinc product type (Equation 4.33). When the only data available are national zinc production statistics, it is *good practice* to use default emission factors. If material specific data are not available to calculate emissions using the Tier 2 methodology, but the process type is known, inventory compilers can calculate emissions using Equation 4.34.

**EQUATION 4.33**
**$CO_2$ EMISSIONS FROM ZINC PRODUCTION (TIER 1)**

$$E_{CO2} = Zn \bullet EF_{default}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from zinc production, tonnes

Zn = quantity of zinc produced, tonnes

$EF_{default}$ = default emission factor, tonnes $CO_2$/tonne zinc produced

**EQUATION 4.34**
**$CO_2$ EMISSIONS FROM ZINC PRODUCTION (TIER 1)**

$$E_{CO2} = ET \bullet EF_{ET} + PM \bullet EF_{PM} + WK \bullet EF_{WK}$$

Where:

$E_{CO2}$ = $CO_2$ emissions from zinc production, tonnes

ET= quantity of zinc produced by electro-thermic distillation, tonnes

$EF_{ET}$ = emission factor for electro-thermic distillation, tonnes $CO_2$/tonne zinc produced

PM = quantity of zinc produced by pyrometallurgical process (Imperial Smelting Furnace Process) , tonnes

$EF_{PM}$ = emission factor for pyrometallurgical process, tonnes $CO_2$/tonne zinc produced

WK = quantity of zinc produced by Waelz Kiln process, tonnes

$EF_{WK}$ = emission factor for Waelz Kiln process, tonnes $CO_2$/tonne zinc produced

## TIER 2 METHOD

Emission can be calculated using country specific emission factor based on aggregated plant statistics on the use of reducing agents, furnace types and other process materials of interest is developed based on default emission factors applicable to those materials. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual zinc companies. Tier 2 is more accurate than Tier 1 because it takes into account the materials and the variety of furnace types used in the zinc sector that contribute to $CO_2$ emissions for a particular country rather than assuming industry-wide practices.

## TIER 3 METHOD

If actual measured $CO_2$ emissions data are available from zinc facilities, these data can be aggregated and used directly to account for national emissions using the Tier 3 method.

### 4.7.2.2 CHOICE OF EMISSION FACTORS

#### TIER 1 METHOD

The emission factor for the pyrometallurgaical process (Imperial Smelting Furnace) is an aggregate, weighted emission factor encompassing both primary and secondary zinc production in Europe (Sjardin, 2003), No data was available to determine an emission factor for the electro-thermic process. An emission factor based on the amount of coke consumed per tonne of EAF dust consumed in a Waelz Kiln furnace was developed based on the materials balance provided by Viklund-White (2000), wherein Viklund-White finds that 400 kg of coke are consumed for every metric tonne of EAF dust consumed.

TABLE 4.24
TIER 1 $CO_2$ EMISSION FACTORS FOR ZINC PRODUCTION

| Process | Emission Factor | Source |
|---|---|---|
| Waelz Kiln<br>(tonne of $CO_2$/ tonne zinc) | 3.66 | Derived from Viklund-White C. (2000) The Use of LCA for the Environmental Evaluation of the Recycling of Galvanized Steel. ISIJ International. Volume 40 No. 3: 292-299. |
| Pyrometeallurgical (Imperial Smelting Furnace)<br>(tonne of $CO_2$/ tonne zinc) | 0.43 | Sjardin 2003. $CO_2$ Emission Factors for Non-Energy Use in the Non-Ferrous Metal, Ferroalloys and Inorganics Industry. Copernicus Institute, Utrecht, The Netherlands. June 2003. |
| Electro-thermic | Unknown | |
| Default Factor<br>(tonne of $CO_2$/ tonne zinc) | 1.72 | default factor is based on weighting of known emission factors (60% Imperial Smelting, 40% Waelz Kiln) |

#### TIER 2 METHOD

The Tier 2 method requires the calculation of a country specific emission factor based on the total amount of reducing agents and other carbon containing process materials used for zinc production in the country. These country specific emission factors should be based on aggregated plant statistics on the use of reducing agents, furnace types and other process materials of interest. An emission factor was developed based on the amount of metallurgical coke consumed per tonne of EAF dust consumed: 0.4 tonnes coke/ tonne EAF dust consumed (Viklund-White, 2000). If activity data are available, an emission factor of 1.23 tonnes of EAF dust per tonne of zinc could be used to calculate emissions. When producing zinc from EAF dust in a Waelz Kiln furnace, the complexities of the process suggest that emission factors are more accurate if they are based on the amount of EAF dust consumed rather than the total zinc produced . This is because the amount of reduction materials (metallurgical coke) consumed is directly dependent upon the amount, and zinc content, of the EAF dust consumed. Weighing equipment is used in the Waelz Kiln process to control the amount of metallurgical coke entered into the kiln (Sjardin 2003; European IPPC Bureau 2001).

### 4.7.2.3 CHOICE OF ACTIVITY DATA

#### TIER 1 METHOD

The Tier 1 method requires only the amount of zinc produced in the country, and if available, the process type. These data may be available from governmental agencies responsible for manufacturing statistics, business or industry trade associations, or individual zinc companies. These tonnages can then be multiplied by the default emission factors to estimate $CO_2$ emissions.

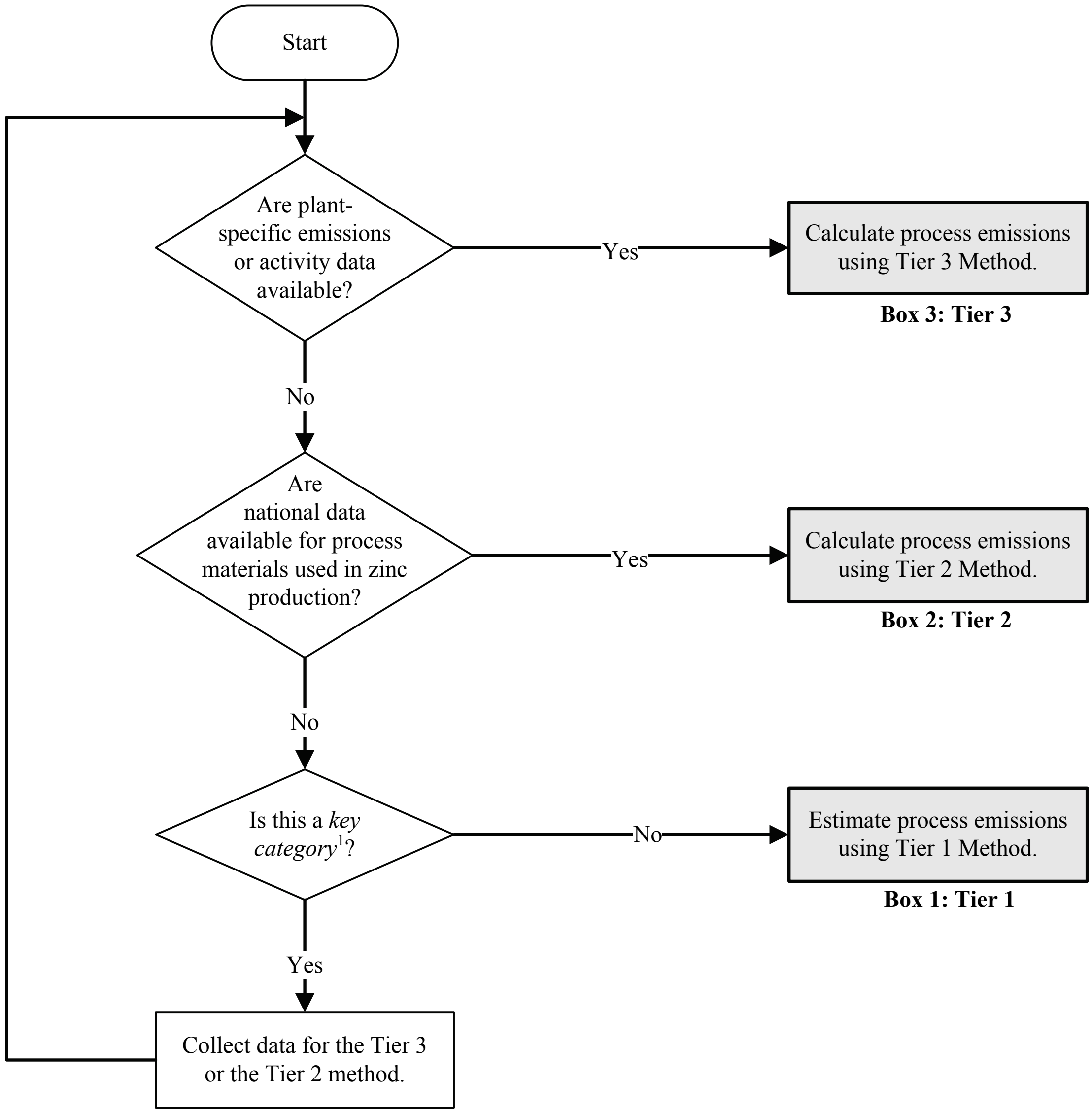
#### TIER 2 METHOD

The Tier 2 method requires the calculation of a country specific emission factor based on the total amount of reducing agents and other carbon containing process materials used for zinc production in the country. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual zinc companies. These country specific emission factors can then be multiplied by the production amount to determine total $CO_2$ emission from the sector. 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.

### TIER 3 METHOD

The Tier 3 method requires collection, compilation, and aggregation of facility-specific measured emissions data, if any. However, activity data collected at the plant-level can also be used, with separate emission factors for each plant multiplied by plant specific production. 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.

**Figure 4.16 Decision tree for estimation of $CO_2$ emissions from zinc 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.

## 4.7.2.4 COMPLETENESS

In estimating emissions from this source category, there is a risk of double-counting or omission in either the Industrial Processes or the Energy Sector. It is important to note that the Tier 1 emission factor assumes that the $CO_2$ emissions from the combustion of various fuels used for production of heat in the calcining, sintering, leaching, purification smelting, and refining processes are captured within the $CO_2$ from fossil fuel combustion emission category. In using the tier 2 or 3 methodologies, double-counting can be avoided. The largest source of potential double-counting, emissions from coke production, are calculated in Section 4.2 and reported in the Energy Sector.

#### 4.7.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from zinc production should be calculated using the same method for every year in the time series. Where data are unavailable to support a Tier 3 method for all years in the time series, these gaps should be recalculated according to the guidance provided in Volume 1, General Guidance and Reporting.

### 4.7.3 Uncertainty assessment

Uncertainty estimates for zinc production result predominantly from uncertainties associated with activity data, and from uncertainty related to the emission factors. Table 4.25 provides an overview of the uncertainties for emission factors and activity data.

#### 4.7.3.1 EMISSION FACTOR UNCERTAINTIES

The default emission factors used in Tier 1 may have an uncertainty of ± 50 percent. Tier 2 country specific emission factors are expected to have an uncertainty of ± 15 percent. Tier 3 unit specific emission factors would be expected to be within 5 percent if plant-specific carbon content data are available.

#### 4.7.3.2 ACTIVITY DATA UNCERTAINTIES

National production statistics should be available and likely have an uncertainty of ± 10 percent. For Tier 2, the total amount of reducing agents and process materials used for lead production would likely be within 10 percent. Tier 3 actual emissions data would be expected to have ± 5 percent uncertainty.

TABLE 4.25
UNCERTAINTY RANGES

| Method | Data Source | Uncertainty Range |
|---|---|---|
| Tier 1 | National Production Data<br>Default Emission Factors<br>Process Specific Emission Factors | ± 10%<br>± 50%<br>± 20% |
| Tier 2 | National Reducing Agent & Process Materials Data<br>Country Specific Emission Factors | ± 10%<br>± 15% |
| Tier 3 | Facility-Derived = Process Materials Data<br>Facility-Specific Measured $CO_2$ Data<br>Facility-Specific Emission Factors | ± 5%<br>± 5%<br>± 5% |

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

#### 4.7.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. In addition to the guidance in Volume 1, specific procedures of relevance to this source category are outlined below.

**Review of emission factors**

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

#### 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 conditions or technology. For zinc production, inventory compilers should compare plant data with other plants.

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

#### Expert review

Inventory compilers should include key industrial trade organisations associated with zinc production in a review process. This process should begin early in the inventory development process to provide input to the development and review of methods and data acquisition.

Third party reviews are also useful for this source category, particularly related to initial data collection, measurement work, transcription, calculation and documentation.

#### Activity data check

For all tier levels, inventory compilers should check to ensure that emissions from reducing agents and process materials (coal, coke, natural gas, etc.) are not double-counted as energy related emissions or omitted.

Inventory compilers should examine any inconsistency between data from different plants to establish whether these reflect errors, different measurement techniques or result from real differences in emissions, operational conditions or technology. This is particularly relevant to the plant-specific estimates of amounts of reducing agents or reported carbon content of process materials.

Inventory compilers should compare aggregated plant-level estimates to industry totals for process materials consumption where such trade data are available.

## 4.7.4.2 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, Section 6.11. 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.

### TIER 1 METHOD

Besides reporting of estimated emissions, it is *good practice* to report the total zinc production by process and corresponding emission factors used.

### TIER 2 METHOD

*Good practice* is to document the estimated or calculated emissions, all activity data, and corresponding emission factors and any assumptions or data justifying alternative emission factors.

### TIER 3 METHOD

*Good practice* is to document the calculated emissions and source of all data, taking into account the need to protect the confidentiality of data for specific facilities if the data are business-sensitive or of a proprietary nature. In addition, inventory compilers should for all tiers, document all information needed to reproduce the estimate, as well as the QA/QC procedures

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# CHAPTER 5

# NON-ENERGY PRODUCTS FROM FUELS AND SOLVENT USE

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# 5 NON-ENERGY PRODUCTS FROM FUELS AND SOLVENT USE

## 5.1 INTRODUCTION

This section provides methods for estimating emissions from the first use of fossil fuels as a product for primary purposes other than i) combustion for energy purposes and ii) use as feedstock or reducing agent. Emissions from the latter two uses are accounted for by methods described in the chemical industry (Chapter 3) and in metal industry (Chapter 4).

The products covered here comprise lubricants, paraffin waxes, bitumen/asphalt, and solvents. Emissions from further uses or disposal of the products after first use (i.e., the combustion of waste oils such as used lubricants) are to be estimated and reported in the Waste Sector when incinerated or in the Energy Sector when energy recovery takes place.

Generally, the methods for calculating carbon dioxide ($CO_2$) emissions from non-energy product uses follow a basic formula, in which the emission factor is composed of a carbon content factor and a factor that represents the fraction of fossil fuel carbon that is *Oxidised During Use* (ODU), e.g., actual co-combustion of the fraction of lubricants that slips into the combustion chamber of an engine). This concept is applied to oxidation during first use only of lubricants and paraffin waxes and not to subsequent uses (e.g., energy recovery):

**EQUATION 5.1**
**BASIC FORMULA FOR CALCULATING $CO_2$ EMISSIONS FROM NON-ENERGY PRODUCT USES**

$$CO_2\ Emissions = \sum_i \left( NEU_i \bullet CC_i \bullet ODU_i \right) \bullet 44/12$$

Where:

$CO_2$ Emissions = $CO_2$ emissions from non-energy product uses, tonne $CO_2$

$NEU_i$ = non-energy use of fuel *i*, TJ

$CC_i$ = specific carbon content of fuel *i*, tonne C/TJ (=kg C/GJ)

$ODU_i$ = ODU factor for fuel *i*, fraction

44/12 = mass ratio of $CO_2$/C

The production and use of asphalt for road paving and roofing and the use of solvents derived from petroleum and coal are either not sources or are negligible sources of direct greenhouse gas emissions. They are, however, included in this chapter since they are sometimes substantial sources of non-methane volatile organic compounds (NMVOC) and carbon monoxide (CO) emissions which eventually oxidise to $CO_2$ in the atmosphere. The resulting $CO_2$ input can be estimated from the emissions of these non-$CO_2$ gases (see Section 7.2.1.5 of Volume 1). While almost negligible for asphalt, for solvent use this may have some significance. Emissions from any other non-energy product of fossil fuels not described here should be reported under the subcategory 2D4 ‘Other’.

There may be a risk that some of the $CO_2$ emissions calculated for this source category could be partly accounted for elsewhere. Cases where this may occur are clearly indicated in the subsequent sections and should be cross-checked to avoid double counting.

Methane ($CH_4$) emissions from the activities covered in this chapter are expected to be minor or not to occur at all. Although some $CH_4$ emissions occur from asphalt production and use for road paving, no method to estimate $CH_4$ emissions is provided since these emissions are expected to be very negligible.

Section 1.4 of Chapter 1 of this volume provides guidance for assessing consistency and completeness of carbon emissions from non-energy and feedstock use of fuels by (a) checking that non-energy use/feedstock requirements of processes included in the inventory are in balance with the non-energy use/feedstock supply as recorded in national energy statistics, (b) checking that total reported bottom-up calculated $CO_2$ emissions from non-energy use/feedstock sources at different subcategory levels are complete and consistent, (c) documenting and reporting how these emissions are allocated in the inventory. The sources described in this chapter are part of the verification of completeness of fossil $CO_2$ from non-energy sources and reporting of their allocation.

TABLE 5.1
NON-ENERGY PRODUCT USES OF FUELS AND OTHER CHEMICAL PRODUCTS

| **Types of fuels used** | **Examples of non-energy uses** | **Gases covered in this chapter** | |
|---|---|---|---|
| | | **$CO_2$** | **NMVOC, CO** |
| Lubricants | Lubricants used in transportation and industry; Section 5.2 | X | |
| Paraffin waxes | Candles, corrugated boxes, paper coating, board sizing, adhesives, food production, packaging; Section 5.3 | X | |
| Bitumen; road oil and other petroleum diluents | Used in asphalt production for road paving and e.g., in roofing; Section 5.4 | | X |
| White spirit[1], kerosene[2], some aromatics | As solvent e.g. for surface coating (paint), dry cleaning; Section 5.5 | | X |

## 5.2 LUBRICANT USE

### 5.2.1 Introduction

Lubricants are mostly used in industrial and transportation applications. Lubricants are produced either at refineries through separation from crude oil or at petrochemical facilities. They can be subdivided into (a) motor oils and industrial oils, and (b) greases, which differ in terms of physical characteristics (e.g., viscosity), commercial applications, and environmental fate.

### 5.2.2 Methodological issues

The use of lubricants in engines is primarily for their lubricating properties and associated emissions are therefore considered as non-combustion emissions to be reported in the IPPU Sector. However, in the case of 2-stroke engines, where the lubricant is mixed with another fuel and thus on purpose co-combusted in the engine, the emissions should be estimated and reported as part of the combustion emissions in the Energy Sector (see Volume 2).

It is difficult to determine which fraction of the lubricant consumed in machinery and in vehicles is actually combusted and thus directly results in $CO_2$ emissions, and the fraction not fully oxidised that results firstly in NMVOC and CO emissions (except for the use in 2-stroke engines, which is excluded here). For this reason, these NMVOC and CO emissions are very seldom reported by countries in the emission inventories. Therefore, for calculating $CO_2$ emissions the total amount of lubricants lost during their use is assumed to be fully combusted and these emissions are directly reported as $CO_2$ emissions.

Regulations and policies for the disposal of used oil in most OECD countries often restrict landfilling and dumping, and encourage the separate collection of used oil. A small proportion of lubricants oxidises during use, but the main contribution to emissions is when the waste lubricants are collected at the end of their use, in accordance with country-specific regulations, and subsequently combusted. These waste oil handling emissions, however, are to be reported in the Waste Sector (or in the Energy Sector when energy recovery takes place). Figure 5.1 illustrates this.

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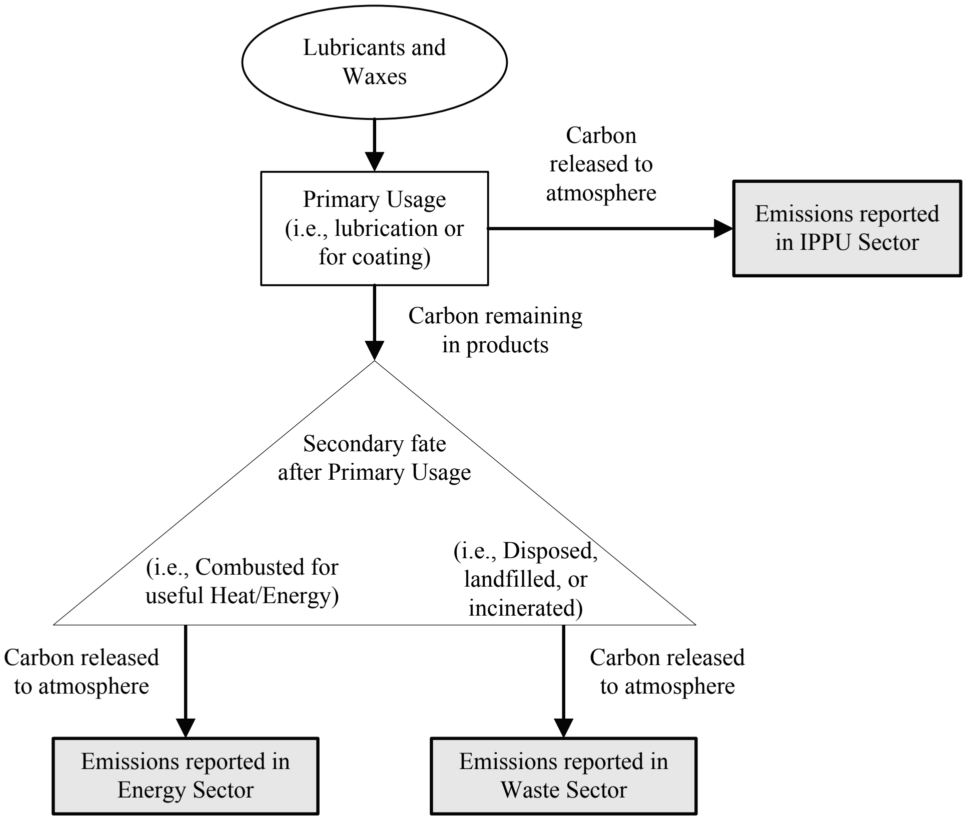
[1] Also known as mineral turpentine, petroleum spirits, industrial spirit ('SBP').

[2] Also known as paraffin or paraffin oils (UK, South Africa).

**Figure 5.1 Sectoral allocation of emissions from lubricants and waxes**



Since $CH_4$ and $N_2O$ emissions are very small in comparison to $CO_2$, these can be neglected for the greenhouse gas calculation.

## 5.2.2.1 CHOICE OF METHOD

There are two methodological tiers for determining emissions from the use of lubricants. Both Tier 1 and Tier 2 rely on essentially the same analytical approach, which is to apply emission factors to activity data on the amount of lubricant consumption in a country (in energy units, e.g., TJ). The Tier 2 method requires data on the quantities of different types of lubricants, excluding the amount used in 2-stroke engines, in combination with type-specific *Oxidised During Use* (ODU) factors to activity data, preferably country-specific, while the Tier 1 method relies on applying one default ODU factor to total lubricant activity data (see decision tree, Figure 5.2). Since the default ODU factor is four times smaller for greases than for lubricating oils, using a higher tier method will primarily capture the impact of using actual fractions of oils and greases in the emission calculation. It is considered *good practice* to use the Tier 2 method when this is a *key category*.

**Tier 1:** $CO_2$ emissions are calculated according to Equation 5.2 with aggregated default data for the limited parameters available and the ODU factor based on a default composition of oil and greases in total lubricant figures (in TJ units):

**EQUATION 5.2**
**LUBRICANTS – TIER 1 METHOD**

$$CO_2\ Emissions = LC \bullet CC_{Lubricant} \bullet ODU_{Lubricant} \bullet 44/12$$

Where:

$CO_2$ Emissions = $CO_2$ emissions from lubricants, tonne $CO_2$

LC = total lubricant consumption, TJ

$CC_{Lubricant}$ = carbon content of lubricants (default), tonne C/TJ (= kg C/GJ)

$ODU_{Lubricant}$ = ODU factor (based on default composition of oil and grease), fraction

44/12 = mass ratio of $CO_2$/C

**Tier 2:** The Tier 2 method for lubricants relies on a similar equation, however detailed data on the quantities consumed per type of lubricants use (in energy units, e.g., TJ) and, preferably, country-specific emission factors should be used. The emission factors are composed of fuel type specific carbon content and the ODU factor:

**EQUATION 5.3**

**LUBRICANTS – TIER 2 METHOD**

$$CO_2\ Emissions = \sum_i \left( LC_i \bullet CC_i \bullet ODU_i \right) \bullet 44/12$$

Where:

$CO_2$ Emissions = $CO_2$ emissions from lubricants, tonne $CO_2$

$LC_i$ = consumption of lubricant type *i*, TJ

$CC_i$ = carbon content of lubricant type *i*, tonne C/TJ (= kg C/GJ)

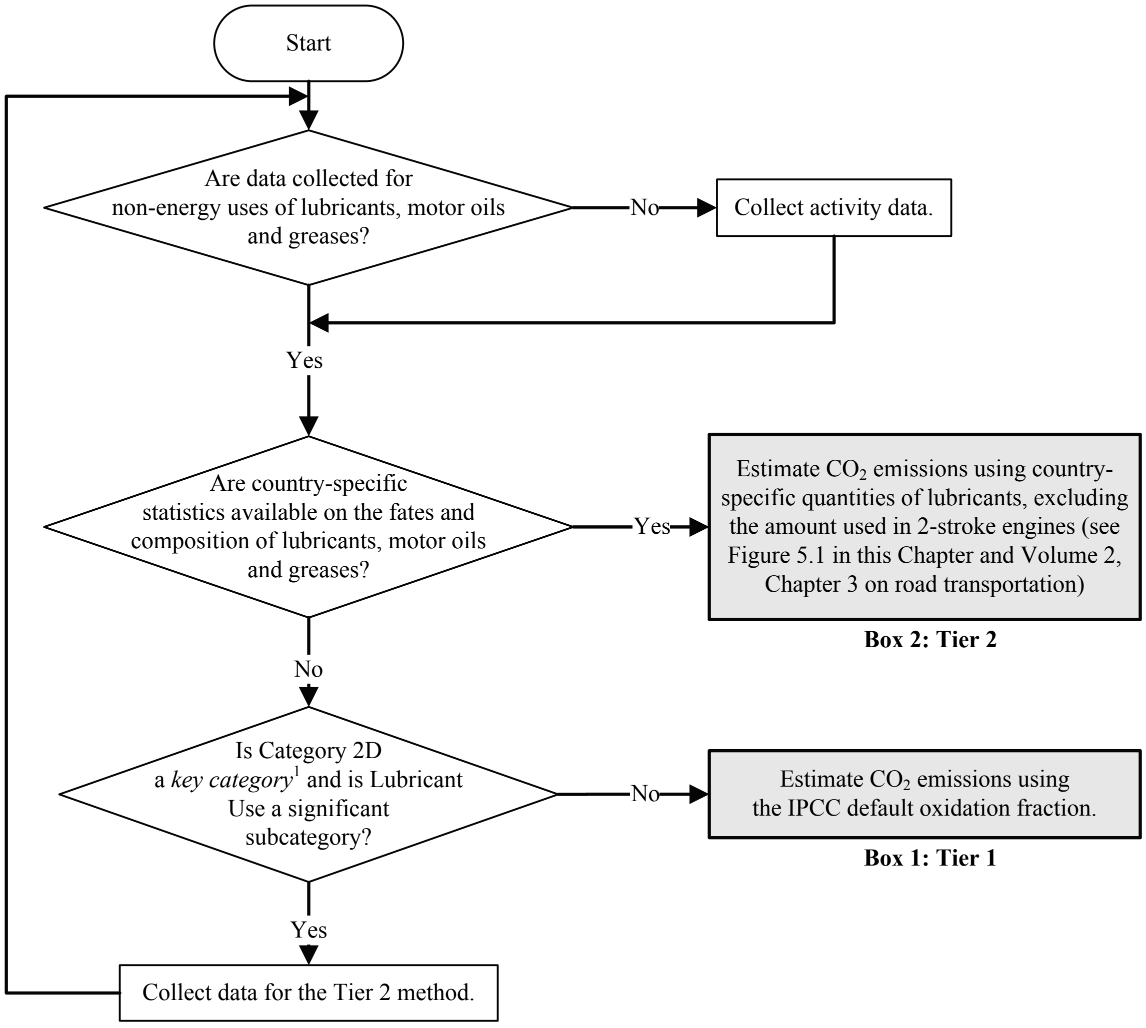
$ODU_i$ = ODU factor for lubricant type *i*, fraction

44/12 = mass ratio of $CO_2$/C

Lubricant *i* refers to motor oils/industrial oils and greases separately, excluding the amount used in 2-stroke engines.

In both tiers the carbon contents may be the default value for lubricants described in Volume 2 (Chapter 1, Table 1.3), or a country-specific value, if available.

**Figure 5.2 Decision tree for $CO_2$ from non-energy uses of lubricants**



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.

### 5.2.2.2 CHOICE OF EMISSION FACTORS

The emission factor is composed of a specific carbon content factor (tonne C/TJ) multiplied by the ODU factor. A further multiplication by 44/12 (the mass ratio of $CO_2$/C) yields the emission factor (expressed as tonne $CO_2$/TJ). For lubricants the default carbon contents factor is 20.0 kg C/GJ on a Lower Heating Value basis. (See Table 1.3 in Chapter 1 of Volume 2. Note that kg C/GJ is identical to tonne C/TJ.) It is assumed that use is combustion resulting in 100 percent oxidation to $CO_2$, with no long-term storage of carbon in the form of ash or post-combustion residue. A small fraction of lubricating oils is oxidised during use (see Table 5.2). An even smaller fraction of greases are oxidised during use. Default ODU factors for oils (20 percent) and greases (5 percent) are based on limited available data (Table 5.2).

**Tier 1:** Having only total consumption data for all lubricants (i.e., no separate data for oil and grease), the weighted average ODU factor for lubricants as a whole is used as default value in the Tier 1 method. Assuming that 90 percent of the mass of lubricants is oil and 10 percent is grease, applying these weights to the ODU factors for oils and greases yields an overall (rounded) ODU factor of 0.2 (Table 5.2). This ODU factor can then be applied to an overall carbon content factor, which may be country-specific or the default value for lubricants to determine national emission levels from this source when activity data on the consumption of lubricants is known (Equation 5.2).

**Tier 2:** Those countries with specific details on the specific quantities of lubricants used as motor oils/industrial oils and as greases can apply different ODU factors, either the default values of 0.2 and 0.05, respectively, or their own ODU factors for lubricants and greases based on national knowledge. These default or country-specific ODU factors can then be multiplied with the country-specific carbon content factors or the single default IPCC carbon content factor for lubricants to determine national emission levels (Equation 5.3).

TABLE 5.2
DEFAULT OXIDATION FRACTIONS FOR LUBRICATING OILS, GREASE AND LUBRICANTS IN GENERAL

| Lubricant / type of use | Default fraction in total lubricant [a] (%) | ODU factor |
|---|---|---|
| Lubricating oil (motor oil /industrial oils) | 90 | 0.2 |
| Grease | 10 | 0.05 |
| **IPCC Default for total lubricants [b]** | | **0.2** |

[a] Excluding the use in 2-stroke engines.

[b] Assuming 90 percent lubricating oil consumption and 10 percent grease consumption and rounded to one significant digit.

Source: Rinehart (2000).

### 5.2.2.3 CHOICE OF ACTIVITY DATA

Data on the non-energy use of lubricants are required to estimate emissions, with activity data expressed in energy units (TJ). To convert consumption data in physical units, e.g., in tonnes, into common energy units, e.g., in TJ (on a Lower Heating Value basis), calorific values are required (for specific guidance see Section 1.4.1.2 of Chapter 1 of Volume 2 on Energy). Basic data on non-energy products used in a country may be available from production, import and export data and on the energy/non-energy use split in national energy statistics. Additional information may need to be collected to determine the amount of lubricants being used in 2-stroke engines, which should be excluded from the Tier 2 calculation in this source category. For the Tier 2 method, the individual quantities applied as motor oil/industrial oils and as greases need to be separately known. For specific guidance on the data collection for lubricants used for 2-stroke engines, see Chapter 3 on Road Transport of Volume 2: Energy.

### 5.2.2.4 COMPLETENESS

Emissions from the use of lubricants in 2-stroke engines should be accounted for in the Energy Sector. Any emissions that occur due to oxidation from post-use combustion or degradation after disposal should be accounted for separately in the Waste Sector (or Energy Sector, if combustion is used for energy recovery). To avoid double counting and to ensure completeness, the proper allocation of those emissions not related to the non-combustion usage of lubricants in the Energy and Waste Sectors should be cross-checked.

#### 5.2.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from lubricants should be calculated using the same method and data sets for every year in the time series.

### 5.2.3 Uncertainty assessment

#### 5.2.3.1 EMISSION FACTOR UNCERTAINTIES

The default ODU factors developed are very uncertain, as they are based on limited knowledge of typical *lubricant* oxidation rates. Expert judgment suggests using a default uncertainty of 50 percent.

The carbon content coefficients are based on two studies of the carbon content and heating value of lubricants, from which an uncertainty range of about ±3 percent is estimated (U.S.EPA, 2004).

#### 5.2.3.2 ACTIVITY DATA UNCERTAINTIES

Much of the uncertainty in emission estimates is related to the difficulty in determining the quantity of non-energy products used in individual countries, for which a default of 5 percent may be used in countries with well developed energy statistics and 10-20 percent in other countries, based on expert judgement of the accuracy of energy statistics. If the amount of lubricants used in 2-stroke engines, which is to be subtracted from the total consumption used here, is not known, the uncertainty in the activity data will be higher and biased (too high). In countries where a large fraction of the use is in 2-stroke engines, the uncertainty range in the activity data in this section is much higher at the lower end, and can be estimated from the estimated share of 2-stroke engines in the national consumption total.

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

#### 5.2.4.1 QUALITY ASSURANCE AND QUALITY CONTROL

It is *good practice* to check the consistency of the total annual consumption figure with the production, import and export data. In addition, it is recommended to compare the amounts discarded, recovered and combusted and the amount used in 2-stroke engines, if available, with total consumption figures in the calculation to check the internal consistency of activity data and ODU factors used in the calculation of different source categories across sectors.

#### 5.2.4.2 REPORTING AND DOCUMENTATION

It is *good practice* to report and document:

- The total amount of lubricants produced, imported, exported, consumed, and discarded are to be reported when available. In addition, the amount used for 2-stroke engines and subtracted should be reported. If the latter information is not available or not used in the emission calculation this should be reported.
- When using the Tier 2 method, the consumption data should be reported per type of lubricant used in the calculation.
- If the default ODU factor is used, this should be noted in the reporting documentation.
- If a country-specific emission factor for lubricants was developed, in other words, if a country-specific ODU factor and/or country-specific carbon contents fraction is used, the corresponding data should be provided with an explanation of how this was measured.
- The allocation of $CO_2$ emissions from lubricants in Table 1.6 on the allocation of $CO_2$ from non-energy use of fossil fuels (see Chapter 1 of this volume).

# 5.3 PARAFFIN WAX USE

## 5.3.1 Introduction

The category, as defined here, includes such products as petroleum jelly, paraffin waxes and other waxes, including ozokerite (mixtures of saturated hydrocarbons, solid at ambient temperature). Paraffin waxes are separated from crude oil during the production of light (distillate) lubricating oils. Paraffin waxes are categorised by oil content and the amount of refinement.

## 5.3.2 Methodological issues

Waxes are used in a number of different applications. Paraffin waxes are used in applications such as: candles, corrugated boxes, paper coating, board sizing, food production, wax polishes, surfactants (as used in detergents) and many others. Emissions from the use of waxes derive primarily when the waxes or derivatives of paraffins are combusted during use (e.g., candles), and when they are incinerated with or without heat recovery or in wastewater treatment (for surfactants). In the cases of incineration and wastewater treatment the emissions should be reported in the Energy or Waste Sectors, respectively (see Figure 5.1).

### 5.3.2.1 CHOICE OF METHOD

There are two methodological tiers for determining emissions and storage from paraffin waxes. Both Tier 1 and Tier 2 rely on essentially the same analytical approach, which is to apply emission factors to activity data on the amount of paraffin waxes consumed in a country (in energy units, e.g., TJ). The Tier 2 method relies on determining the actual use of paraffin waxes and applying a country-specific ODU factor to activity data, while the Tier 1 method relies on applying default emission factors to activity data (see decision tree, Figure 5.3).

**Tier1:** $CO_2$ emissions are calculated according to Equation 5.4 with aggregated default data for the limited parameters available:

**EQUATION 5.4**
**WAXES – TIER 1 METHOD**

$$CO_2\ Emissions = PW \bullet CC_{Wax} \bullet ODU_{Wax} \bullet 44/12$$

Where:

$CO_2$ Emissions = $CO_2$ emissions from waxes, tonne $CO_2$

PW = total wax consumption, TJ

$CC_{Wax}$ = carbon content of paraffin wax (default), tonne C/TJ (= kg C/GJ)

$ODU_{Wax}$ = ODU factor for paraffin wax, fraction

44/12 = mass ratio of $CO_2$/C

**Tier 2:** The Tier 2 method for paraffin waxes relies on a similar equation, however detailed data on the quantities (possibly also on the types) of paraffin waxes produced (in energy units) and their respective use as well as country-specific emission factors should be used:

**EQUATION 5.5**
**WAXES – TIER 2 METHOD**

$$CO_2\ Emissions = \sum_i \left(PW_i \bullet CC_i \bullet ODU_i\right) \bullet 44/12$$

Where:

$CO_2$ Emissions = $CO_2$ emissions from waxes, tonne $CO_2$

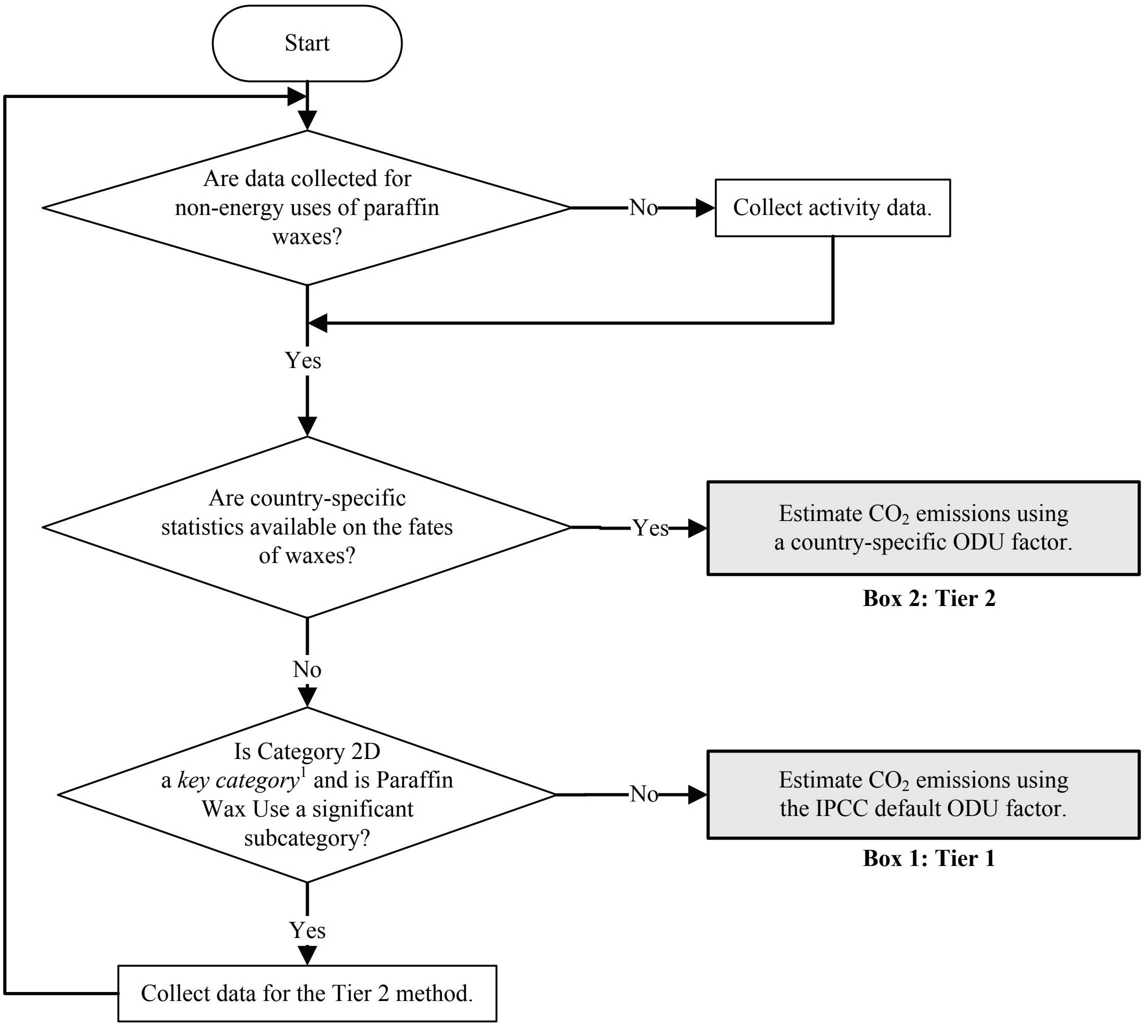
$PW_i$ = consumption of was type *i*, TJ

$CC_i$ = carbon content of wax type *i*, tonne C/TJ (= kg C/GJ)

$ODU_i$ = ODU factor for wax type *i*, fraction

44/12 = mass ratio of $CO_2$/C

**Figure 5.3 Decision tree for $CO_2$ from non-energy uses of paraffin waxes**



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.

### 5.3.2.2 CHOICE OF EMISSION FACTORS

A country-specific carbon content or default carbon content of 20.0 kg C/GJ (on a Lower Heating Value basis) should be applied. (See Table 1.3 in Chapter 1 of Volume 2. Note that kg C/GJ is identical to tonne C/TJ.) This default value is based on a combustion emission factor of 73.3 kg $CO_2$/GJ (API, 2004).

**Tier 1**: It can be assumed that 20 percent of paraffin waxes are used in a manner leading to emissions, mainly through the burning of candles, leading to a default ODU factor of 0.2 (Equation 5.4).

**Tier 2:** Those countries with specific details on the uses of paraffin waxes in the country can determine their own country-specific ODU factors for waxes based on national knowledge of the combustion (Equation 5.5). These factors can be combined with either the default carbon contents listed above or a country-specific carbon contents if any are available.

### 5.3.2.3 CHOICE OF ACTIVITY DATA

Data on the use of paraffin waxes are required to estimate emissions, with activity data expressed in energy units (TJ). To convert consumption data in physical units, e.g., in tonnes, into common energy units, e.g., in TJ (on a Lower Heating Value basis), calorific values are required (for specific guidance see Section 1.4.1.2 of Chapter 1 of Volume 2 on Energy). Basic data on non-energy products used in a country may be available from production, import and export data and on the energy/non-energy use split in national energy statistics. If the reported national statistics do not contain this as a separate fuel category but instead only show this as part of an aggregated ‘other oil products’ category, the national statistical agency should be contacted, since the oil product statistics are often collected at a more detailed level.

#### 5.3.2.4 COMPLETENESS

Emissions from incineration (without heat recovery) of wax coated boxes fall under the Waste Sector. Any emissions from paraffin waxes that are produced due to energy recovery should be reported in the Energy Sector.

#### 5.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from paraffin waxes should be calculated using the same method and data sets for every year in the time series. If a country-specific ODU factor is used, inventory compilers are encouraged to check whether the mix of applications with emissive and storage fates changes significantly over time. If that is the case, the ODU factors used per year should preferably reflect this change.

### 5.3.3 Uncertainty assessment

#### 5.3.3.1 EMISSION FACTOR UNCERTAINTIES

The default emission factors are highly uncertain, because knowledge of national circumstances of paraffin wax fates is limited. Ideally, a Tier 2 method would be employed in which national data on the use and fates of waxes can be used as a surrogate to determine the quantities destined for an emissive fate versus storage fate. The default carbon content coefficient is subject to an uncertainty range of ±5 percent (U.S.EPA, 2004). However, the ODU factor is highly dependent on specific-country conditions and policies and the default value of 0.2 exhibits an uncertainty of about 100 percent.

#### 5.3.3.2 ACTIVITY DATA UNCERTAINTIES

Much of the uncertainty in emission estimates is related to the difficulty in determining the quantity of non-energy products used and discarded in individual countries, for which a default of 5 percent may be used in countries with well developed energy statistics and 10-20 percent in other countries, based on expert judgement of the accuracy of energy statistics.

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

#### 5.3.4.1 QUALITY ASSURANCE AND QUALITY CONTROL

It is *good practice* to check the consistency of the total annual consumption figure with the production, import and export data. In addition, the amounts discarded, recovered and combusted, if available, may be compared with total consumption figures in the calculation to check the internal consistency of activity data and ODU factors used in the calculation of different source categories across sectors.

#### 5.3.4.2 REPORTING AND DOCUMENTATION

It is *good practice* to report and document country-specific emission factors, if these are used.

- If a country-specific emission factor for waxes was developed, in other words, if a country-specific ODU factor and/or country-specific carbon content fraction is used, the local value(s) with an explanation of their derivation should be provided .
- If the default ODU factor is used, this should be noted in the reporting documentation.

# 5.4 ASPHALT PRODUCTION AND USE

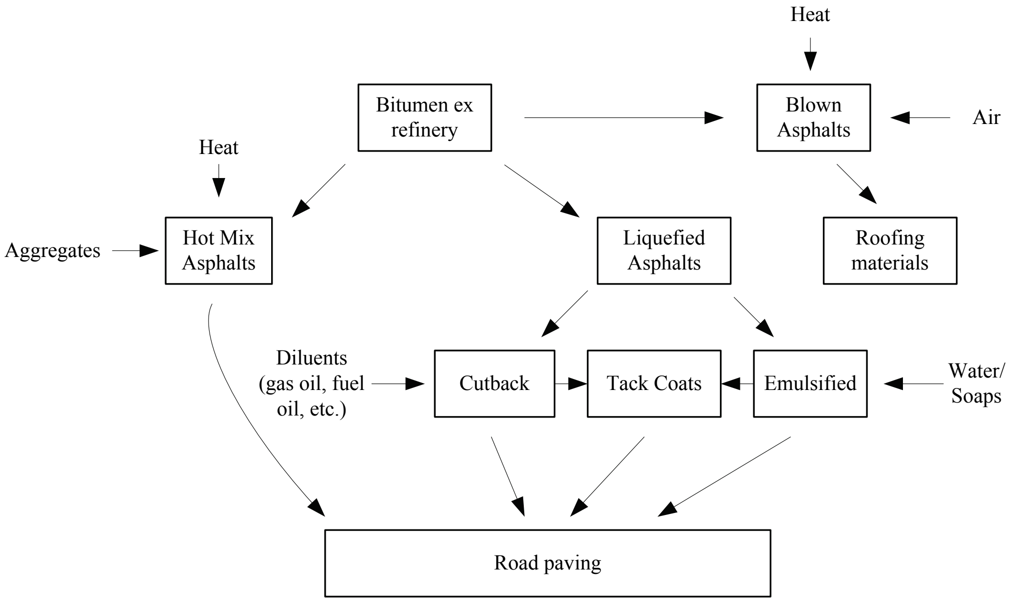
## 5.4.1 Introduction

This source category comprises the non-combustion emissions from the production of asphalt in asphalt plants other than refineries and its application (such as paving and roofing operations as well as subsequent releases from the surfaces). It includes asphalt blowing for roofing. The production and use of asphalt results mainly in emissions of NMVOC, CO, $SO_2$ and particulate matter, while the fate of the remaining hydrocarbons are stored in the product (much less than one per cent of the carbon is emitted). Emissions from the installation of roofing materials are assumed negligible. Emissions from the combustion of fuels needed to supply heat to the asphalt processes (production or heating of the asphalt mix) are covered under the Energy Sector.

Asphalt is commonly referred to as bitumen, asphalt cement, or asphalt concrete or road oil and is mainly produced in petroleum refineries. In some countries the laid mixed product is also referred to as 'asphalt' but it also known as 'macadam'. In view of the ambiguities created by differing nomenclatures, a single set of terms will be adopted here and applied uniformly in the text without implying any preferences for the terms used (see Box 5.1).

**BOX 5.1**
**ASPHALT PRODUCTION AND USE**

The heavy black and very viscous organic liquid mainly produced from refineries and used as a feedstock for the road paving and roofing materials will be termed bitumen, to distinguish it from the products made from it. This also conforms to the terminology used in international energy statistics, which may provide some of the data required for emissions estimation. At normal temperatures bitumen is in a semi-solid state. It is processed and used as illustrated in the figure below.



The diagram shows that bitumen may be heated and mixed with aggregate of various sizes, diluted with petroleum oils or water/soap emulsions, or heated and blown with air to polymerise/stabilise it and make it suitable for e.g., the treatment of roofing materials. These will be termed 'asphalt processes' and their products will be referred to as 'asphalt products'

Bitumen and aggregates are mixed in either a fixed or mobile plant, usually within 30 to 50 km of the road surface paving site (EAPA, 2003). In industrialised countries typically 80 to 90 percent of bitumen is used for the manufacture of road surface paving (U.S.EPA, 2004). However, in developing countries with rapid infrastructural growth, the amount of bitumen used for roofing products may be of the same order of magnitude as those used for road paving (UNFCCC, 2004). Other uses of asphalt products are as binder or sealant in the production of roofing material, as a foundation sealant, and other industrial uses such as pipe coating.

Direct greenhouse gas emissions, e.g., $CO_2$ or $CH_4$, associated with the production and use of asphalt are negligible since the majority of the light hydrocarbon compounds were extracted during the refining process to produce commercial fuels. From the EMEP/CORINAIR guidebook it can be concluded that $CH_4$ emissions from hot mix asphalt and cutback asphalt and from the asphalt roofing industry are negligible (EEA, 2005). Greenhouse gas emissions from the use of recycled asphalt pavements as aggregate for new road paving are also negligible.

## 5.4.2 Methodological issues

Emission methodologies and default emission factors for NMVOC and CO are presented in the Road Paving (SNAP code 040610), Roofing Materials (SNAP code 040611) and Asphalt Blowing (SNAP code 060310) sections of the EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005). It is recommended that users refer to the guidebook when developing detailed NMVOC and CO estimates. (See also Volume 1, Chapter 7 of these *Guidelines*.) Note that in EMEP/CORINAIR the emissions from asphalt blowing for roofing are separately accounted for (under miscellaneous chemical product manufacture with SNAP code 060310).

Limestone may be used as part of the aggregate in the asphalt. However, no $CO_2$ is assumed to be released in the heating process (see Section 2.5, Other Process Uses of Carbonates, under Chapter 2 of this volume).

### PRODUCTION AND USE OF ASPHALT FOR ROAD PAVING

Asphalt paving consist of a mix of aggregate, sand, filler, bitumen and occasionally a number of additives. Asphalt road surfaces are, thus, composed of compacted aggregate and bitumen binder. Hot Mix Asphalt (HMA) is by far the most widely used, generally over 80 percent, and produces very few emissions (EAPA, 2003). Other types of road paving include cutback asphalt and emulsified asphalt, which are both liquefied asphalts (EEA, 2005). Cutback asphalts are liquefied by blending with petroleum solvents (diluents such as heavy residual oils, kerosene or naphtha solvents) and therefore show a relatively high level of emissions of CO and NMVOC due to the evaporation of the diluent. Therefore most emissions from road paving will arise from the use of cutback asphalts. Depending on the evaporation rate, three types are distinguished: Rapid-Cure (RC), using a naphtha or gasoline-type diluent of high volatility, Medium-Cure (MC) using a diluent of medium volatility and Slow-Cure (SC) cutback asphalt which use oils of low volatility. This is in contrast to so-called emulsified asphalt that contains mostly water and little or no solvent. The amount of diluent used is usually lower in warm countries than in the cooler climates, and hence lower emission factors may be expected in warm countries.

Activity data for hot mix asphalt and production of cold mixes or ‘modified asphalt’ can be obtained for most European and several other industrialised countries from the European Asphalt Pavement Association (EAPA) or national paving and roofing associations such as the Asphalt Institute (EAPA, 2003; Asphalt Institute, 2004). Hot mix asphalt typically contains about 8 percent asphalt cement (bitumen) (EEA, 2005), but this may differ between countries (a figure of 5 percent has also been reported). For most industrialised countries the fraction of cutback asphalt is a few per cent, however several show shares of 5 percent to 12 percent, and exceptional shares up to 20 percent, or have none (EAPA, 2002; EAPA 2003; U.S. EPA, 2004). If the quantity of asphalt paved is not known but rather the area paved, a conversion factor of 100 kg asphalt/$m^2$ road surface may be used to calculate the mass of asphalt produced.

Gases are emitted from the asphalt plant (hot mix, cutback or emulsified), the road surfacing operations and subsequently by the road surface. The EMEP/CORINAIR Emission Inventory Guidebook provided process-specific uncontrolled emission factors for the different asphalt plants.

### ASPHALT ROOFING

The asphalt roofing industry produces saturated felt, roofing and siding shingles, roll roofing and sidings: asphalt shingles, smooth surfaced organic and asbestos felt roll roofing, mineral surfaced organic and asbestos felt roll roofing and sidings, asphalt saturated organic and asbestos felts, asphalt saturated and/or coated sheeting and asphalt compound. Most of these products are used in roofing and other building applications. Asphalt felt, roofing and shingle manufacture involves the saturation or coating of felt. Key steps in the total process include asphalt storage, asphalt blowing, felt saturation, coating and mineral surfacing, of which asphalt blowing is included here. Direct greenhouse gas emissions from asphalt roofing products are negligible compared to emissions such as NMVOC, CO and particulate matter.

Asphalt blowing is the process of polymerising and stabilising asphalt to improve its weathering characteristics. Air blown asphalts are used in the production of asphalt roofing products. Blowing may take place in an asphalt processing plant or an asphalt roofing plant (or in a refinery)[3]. Asphalt blowing leads to the highest emissions of NMVOC and CO, more than the other process steps. All asphalt used for non-paving applications has been blown (EEA, 2005).

## 5.4.3 Completeness

If no emissions are (explicitly) available for this source category, it should be checked whether they are already included elsewhere (e.g., in refinery emissions).

## 5.4.4 Uncertainty assessment

Although results from the use of more sophisticated methods are considered as the most accurate, the uncertainty for NMVOC and CO emissions from road paving and asphalt roofing may be in the range of ±25 percent and larger if the calculation was not based on detailed activity and control technology data (from –100 percent to +25 percent).

The emission factors for NMVOC and CO for batch mix and drum mix HMA production have an uncertainty range of about ±50 percent, while the default factors for total HMA production and for cutback asphalt production and use will be about ±100 percent uncertain (i.e., between -50 percent and +100 percent). When country-specific emission factors are used for cutback asphalt production and paving, the uncertainty in the emission factors may be considerably smaller, e.g. in the range of ±50 percent.

Production data for HMA and cutback asphalt may be as accurate as ±10 percent, when based on data compiled by the asphalt production or construction industry. However, when activity data on cutback asphalt needs to be extrapolated, the uncertainties are very large, since it has been observed for a number of countries that the amount of cutback asphalt used can vary substantially from year to year; factors of two or more are not rare (EAPA, 2002; EAPA 2003; U.S. EPA, 2004). Also data on the mix of HMA production plant types and control technology applied as well as on the mix of cutback asphalt types (RC, MC, SC) will generally be less accurate than total production data. The uncertainty in production statistics of asphalt roofing material may be as accurate as ±10 percent if accounting is complete. If that is not the case, the uncertainty at the high end of the range could be as high as 100 percent or more.

The default fossil carbon content fraction of NMVOC from asphalt production and use for road paving varies between 40 to 50 percent by mass and is about 80 percent for NMVOC from asphalt roofing (calculated from the NMVOC speciation provided in the EMEP/CORINAIR Emission Inventory Guidebook).

## 5.4.5 Reporting and Documentation

The relatively small emissions from production and use of asphalt, including asphalt blowing, should be reported under the subcategory 2D4 ‘Other’ of this source category 2D ‘Non-Energy Products from Fuels and Solvent Use’.

# 5.5 SOLVENT USE

## 5.5.1 Introduction

The use of solvents manufactured using fossil fuels as feedstocks can lead to evaporative emissions of various non-methane volatile organic compounds (NMVOC), which are subsequently further oxidised in the atmosphere. Fossil fuels used as solvent are notably white spirit and kerosene (paraffin oil). White spirit is used as an extraction solvent, as a cleaning solvent, as a degreasing solvent and as a solvent in aerosols, paints, wood preservatives, lacquers, varnishes and asphalt products. In Western Europe about 60 percent of the total white spirit consumption is used in paints, lacquers and varnishes. White spirit is the most widely used solvent in the paint industry.

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[3] In UNECE inventories related emissions are accounted for under miscellaneous chemical product manufacture (separately for asphalt roofing manufacture/application and for asphalt blowing, SNAP codes 040610 and 060310) or under fugitive emissions from refineries (see EMEP/CORINAIR Emission Inventory Guidebook), but in the greenhouse gas inventory all emissions, including the precursor emissions, should be reported under the subcategory 2D4 ‘Other’.

Methodologies for estimating these NMVOC emissions can be found in the EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005). This source category 'solvent use' is treated as a separate category because the nature of this source requires a somewhat different approach to emissions estimation than that used for calculating other emission categories. For this reason the *2006 IPCC Guidelines* treats this also as a separate subcategory. In the EMEP/CORINAIR guidebook the subcategory 'solvent and other product use' group 6 of the Selected Nomenclature for sources of Air Pollution (SNAP) and is subdivided into five subcategories. Excluding the fifth: 'other product use' that refers to F-gases, $N_2O$ and ammonia, which are covered elsewhere in the IPPU Volume these are:

- SNAP 0601: Paint application;
- SNAP 0602: Degreasing, dry cleaning and electronics;
- SNAP 0603: Chemical products manufacturing or processing. Including the processing of polyester, PVC, foams and rubber, manufacture of paints, inks, glues and adhesives and the finishing of textile
- SNAP 0604: Other use of solvents and related activities. Including such activities as 'enduction' (i.e., coating) of glass wool and mineral wool, printing industry, fat and oil extraction, uses of glues and adhesives, wood preservation, domestic solvent use (other than paint application) and vehicle underseal treatment and vehicle dewaxing.

Apart from emissions from road transport and, when occurring, production and handling of oil and biofuel combustion, this source category is often the largest source of national NMVOC emissions and its share may vary between 5 percent and 30 percent, with a global average of about 15 percent (Olivier and Berdowski, 2001).

## 5.5.2 Completeness

Emissions from this source category can be estimated using either a production-based or consumption-based approach. If total domestic sales figures of paints etc. are not available, apparent national consumption can be inferred from production, imports and exports. However, if trade statistics are not complete, this may introduce a significant uncertainty in the activity data. Thus, it is recommended that inventory compilers try to ensure that all significant evaporative uses of solvent and other product use are addressed by NMVOC emission estimates.

## 5.5.3 Developing a consistent time series

Usually for this source category only small annual changes are expected. However, when environmental policies are implemented to replace more toxic volatile compounds in solvents (e.g., with water,) both NMVOC emissions and the fossil carbon content of the NMVOC emissions may change over time.

## 5.5.4 Uncertainty assessment

The uncertainty of the NMVOC emissions will generally be quite large, e.g., about ±50 percent, except for countries that have developed a detailed inventory for these sources, in which case the uncertainty may be of the order of 25 percent. The default fossil carbon content fraction of NMVOC is 60 percent by mass, based on limited published national analyses of the speciation profile (U.S. EPA, 2002; Austria, 2004; Hungary, 2004; Klein Goldewijk *et al.*, 2005). It may vary between 50 and 70 percent carbon by mass, so having an uncertainty of about ±10 percent. Country-specific fractions should have a lower uncertainty, e.g., ±5 percent.

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# CHAPTER 6

# ELECTRONICS INDUSTRY EMISSIONS

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# 6 ELECTRONICS INDUSTRY EMISSIONS

## 6.1 INTRODUCTION

Several advanced electronics manufacturing processes utilise fluorinated compounds (FCs) for plasma etching intricate patterns, cleaning reactor chambers, and temperature control. The specific electronic industry sectors discussed in this chapter include semiconductor, thin-film-transistor flat panel display (TFT-FPD), and photovoltaic (PV) manufacturing (collectively termed 'electronics industry').[1]

The electronics industry currently emits both FCs that are gases at room temperature and FCs that are liquids at room temperature. The gases include $CF_4$, $C_2F_6$, $C_3F_8$, c-$C_4F_8$, c-$C_4F_8O$, $C_4F_6$, $C_5F_8$, $CHF_3$, $CH_2F_2$, nitrogen trifluoride ($NF_3$), and sulfur hexafluoride ($SF_6$), and are used in two important steps of electronics manufacturing: (i) plasma etching silicon containing materials and (ii) cleaning chemical vapour deposition (CVD) tool chamber-walls where silicon has deposited.[2] The majority of FC emissions results from limited utilisation efficiency (i.e., consumption) of the FC precursors during the etching or the cleaning process. In addition, a fraction of the fluorinated compounds used in the production process can be converted into by-product $CF_4$ and in some instances into $C_2F_6$, $CHF_3$ and $C_3F_8$.[3] Also, formation of $CF_4$ as a by-product of etching or cleaning carbon-containing low dielectric constant (low k) materials (or carbide) must be taken into account.[4] In addition, $F_2$, $COF_2$, and $ClF_3$ use may increase. These gases, although not in themselves contributors to global warming may lead to $CF_4$ formation under some conditions.

Electronics manufacturers use FCs for temperature control during certain processes. Also known as heat transfer fluids, these FCs are liquids at room temperature and have appreciable vapour pressures. Evaporative losses contribute to the total FC emissions. These evaporative losses occur during cooling of certain process equipment, during testing of packaged semiconductor devices and during vapour phase reflow soldering of electronic components to circuit boards. Evaporative losses do not appear to occur when liquid FCs are used to cool electronic components or systems during operation. In this application, the liquid FCs are contained in closed systems throughout the life of the product or system. More than 20 different liquid FCs are marketed, often as mixtures of fully fluorinated compounds, to the electronic sector.[5] Because the $CO_2$ equivalents of each liquid differ, each should be tracked and reported separately. The precise value of this conversion will be determined by the specific applicable reporting requirements.[6,7] In addition, liquid FCs are occasionally used to clean TFT-FPD panels during manufacture.

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[1] Recent comprehensive surveys of European and US PV manufacturers indicate that 40 to 50 percent of PV-manufacturers use relatively small quantities of FCs (predominantly $CF_4$ during etching of crystalline silicon wafers and $C_2F_6$ during chamber cleaning after deposition of SiNx films). Global usage, according to these surveys for 2004, was approximately 30 Mtonnes $CF_4$. While global FC use appears low in 2004, credible growth-forecasts of the PV industry are approximately 30 percent per year (and higher) for the foreseeable future. Morevoer, several reports extol the virtues of FC use as a means to increase manufacturing productivity and lower costs for silicon-based technologies (Shah *et al*., 2004; Maycock, 2005; Agostinelli *et al*., 2004 and Rentsch *et al*., 2005), Such expected growth rates and prospects for increase FC use motivate inclusion of FC emissions from PV manufacture in this chapter.

[2] Although $C_5F_8$ does not currently have a global warming potential (GWP) recognized by the IPCC, $C_5F_8$ emissions are discussed in this chapter. $C_5F_8$ is a direct greenhouse gas and emissions can be estimated using methods and data described in this chapter. $C_5F_8$'s atmospheric lifetime is approximately 1 year, resulting in a relatively low GWP (Sekiya, 2003).

[3] Emissions of $C_2F_6$ by-products have been observed from the decomposition of $C_4F_6$ molecules and may occur for other FC molecules with greater than two carbon atoms. Note that for most FC precursors, $C_2F_6$ formation as a by-product has not been observed. $CHF_3$ formation has been reported when c-$C_4F_8$ is used as an etchant in TFT-FPD manufacture and $C_3F_8$ by-product emissions have been reported when $C_4F_8O$ is used in chamber cleaning.

[4] Low dielectric constant (low k) materials were first used as insulators for the interconnect structure of semiconductor chips at the 0.25μm node and below. Many low k materials contain carbon that may be removed as $CF_4$ during etching of thin films or the cleaning of the CVD reactors used for low k deposition. $CF_4$ may also be formed during cleaning of CVD reactors used for carbide deposition.

[5] A relatively recent review summarises the uses of liquid FCs (heat transfer fluids), their chemical composition, GWPs, among other things. See Burton (2004a).

[6] These materials are marketed under the trade names Fluorinert™ and Galden®. The Fluorinert™ materials are selected from fully fluorinated alkanes, ethers, tertiary amines and aminoethers and mixtures thereof to obtain the desired properties. The Galden® fluids span a range of fully fluorinated polyethers, called perfluoropolyethers (PFPEs), also selected for the desired properties.

# 6.2 METHODOLOGICAL ISSUES

## 6.2.1 Choice of method

### 6.2.1.1 ETCHING AND CVD CLEANING FOR SEMICONDUCTORS, LIQUID CRYSTAL DISPLAYS, AND PHOTOVOLTAICS

Emissions vary according to the gases used in manufacturing different types of electronic devices, the process used (or more roughly, process type (e.g., CVD or etch)), the brand of process tool used, and the implementation of emission reduction technology.

The choice of methods will depend on data availability and is outlined in the decision tree, see Figure 6.1, Decision Tree for Estimation of FC Emissions from Electronics Manufacturing. Emissions from liquid FCs are estimated using Tier 1, 2 and 3 approaches and are described separately in this section.[8]

Continuous (in-situ) emissions monitoring is currently considered a technically and economically unviable means to estimate emissions from this industry. FC emissions are periodically measured, however, during the development of new processes and tools, and after the establishment of commercial-ready process conditions (also known as centreline process conditions).[9] The industry seeks, prior to the introduction of high-volume manufacturing, centreline process designs that minimize FC emissions. However, it must be noted that FC emissions can be affected by changes in process variables (e.g., pressure, temperature, plasma power, FC gas flow, processing time). Thus, the accuracy of the methods used for estimating emissions will be affected by eventual differences between the process used in production and the reference centreline process. In addition, the efficacy of FC emission control equipment depends on operating and maintaining the equipment according to the manufacturer's specifications: Increased gas flows, improper temperature settings, and failure to perform required maintenance will individually and collectively negatively impact performance.

The accuracy of estimated emissions depends on the method used. The Tier 1 method uses default values for all parameters and does not account for the use of emission control technology. The Tier 2a method uses company-specific data on the proportion of gas used in processes with and without emission control technology, but does not distinguish between etching and cleaning, and uses default values for the other parameters. The Tier 2b method uses company-specific data on the proportion of gas used in *etching* versus *cleaning* and the proportion of gas used in processes with emission control technology, but relies on default values for some or all of the other parameters. The most rigorous method, Tier 3 method, requires a complete set of process-specific values rather than defaults.

Table 6.1 summarises the data requirements for the tiered emissions estimating methods for electronics manufacturing.

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[7] Where a commercial mixture is used inventory compilers will need to ensure that the conversion of the mass of the mixture to $CO_2$ equivalents uses the appropriate conversion factors.

[8] The logic depicted in Figure 6.1 does not show the possibility of combining tiers to improve estimates of emissions. For example, improved estimates of emissions might be achieved by using Tier 3 for a specific gas and process and Tier 2b for other gases and processes instead of using only the Tier 2b method. Similarly, the Tier 2a and 2b methods might be combined to produce an improved estimate compared to using only Tier 2a. However, the Tier 1 method should not be combined with any other method.

[9] Centreline conditions refer to the conditions under which equipment manufacturers standardise their equipment for sale. These are nominal specifications for gas flows, chamber pressure, processing time, plasma power, etc. It is common for semiconductor manufacturers to modify these conditions to optimise for particular needs.

**TABLE 6.1**
**INFORMATION SOURCES NECESSARY FOR COMPLETING THE TIERED EMISSION ESTIMATING METHODS FOR ELECTRONICS MANUFACTURING**

| | **Data** | **Tier 1** | **Tier 2a** | **Tier 2b** | **Tier 3** |
|---|---|---|---|---|---|
| Process Gas Entering Tool | $FC_{i,p}$ = kg of gas *i* fed into specific process *p* or small set of common process tools (e.g., silicon nitride etch). | | | | M |
| | $FC_{i,p}$ = kg of gas *i* fed into broad process category (e.g., etching or CVD chamber cleaning). | | M | M(etch) & M(CVD) | |
| | h = Fraction of gas remaining in shipping container after use (heel). | | D | D | M |
| Process Gas Reactions and Destruction in Tool | $U_{i,p}$ = Use rate (fraction destroyed or transformed) for each gas *i* and process *p*. | | D | D(etch) & D(CVD) [a] | M |
| | $B_{CF4,i,p}$, $B_{C2F6,i,p}$, $B_{CHF3,i,p}$ and $B_{C3F8,i,p}$ = Emission factor for by-product emissions of $CF_4$, $C_2F_6$, $CHF_3$ and $C_3F_8$ respectively for gas *i* for each process. | | D | D(etch) & D(CVD) [a] | M |
| Downstream FC Emission Control | $a_{i,p}$ = Fraction of gas *i* volume fed into processes with certified FC emission control technologies. | | M | M | M |
| | $d_{i,p}$ = Fraction of gas *i* destroyed by the emission control technology. | | D | D [a] | M |
| | $d_{CF4,p}$, $d_{C2F6,p}$, $d_{CHF3,p}$ and $d_{C3F8,p}$ = Fraction of $CF_4$, $C_2F_6$, $CHF_3$ and $C_3F_8$ by-products respectively destroyed by the emission control technology.[b] | | | | M |
| Annual Production Capacity | $C_d$ = Annual manufacturing design capacity in surface area of substrate processed (e.g., silicon, glass). | M | | | |
| | $C_u$ = Fraction of annual capacity utilisation | D/M | | | |

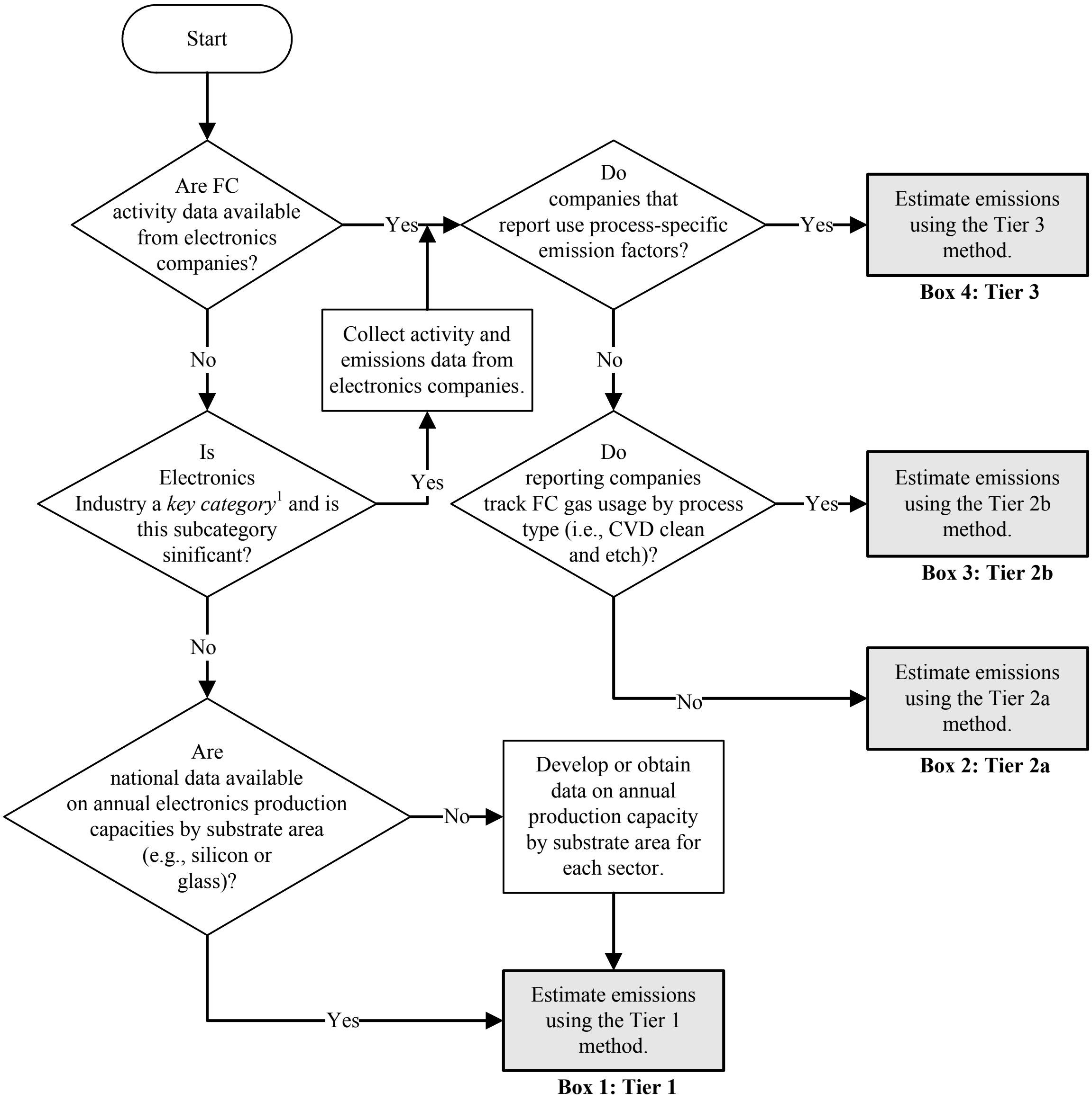
M = measure or acquire these values.

D = Use default factors from guidance.

[a] When available and supportable, M values may be substituted for D values for Tier 2a and 2b. See conditions in Table 6.6.

[b] There are no default values for Tier 2a and Tier 2b because the effect of by-products has been incorporated into the D-values for $d_{i,p}$ for gas *i*.

**Figure 6.1 Decision tree for estimation of FC emissions from electronics manufacturing**



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 1 METHOD – DEFAULT

The Tier 1 method is the least accurate estimation method and should be used only in cases where company-specific data are not available. The Tier 1 method, unlike the Tier 2 or 3 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce gas-specific emissions. Estimates are made simultaneously for all gases as listed in Table 6.2 and can only be used if reported as a complete set.

The calculation of emissions relies on a fixed set of generic emissions factors. The members of the set differ depending on the sector (or class) of electronic products being manufactured (semiconductors, TFT-FPDs or PV-cells). Each member of a set, which is a gas-specific emission factor, expresses an average emissions per unit of substrate area (e.g., silicon, TFT-FPD panel or PV-cell) consumed during manufacture. For any class of electronic products, the factors (members of the set) are multiplied by the annual capacity utilisation ($C_u$, a fraction) and the annual manufacturing design capacity ($C_d$, in units of giga square meters ($Gm^2$)) of substrate processes. The product ($C_u \bullet C_d$) is an estimate of the quantity of substrate consumed during electronics manufacture. The result is a set of annual emissions expressed in kg of the gases that comprise the set for each class of electronic products. Because the use of FCs varies widely during PV manufacture, a third factor to account for the proportion of PV manufacture that employs FC is needed to estimate FC emissions from the PV cells manufacturing. The Tier 1 formula is shown in Equation 6.1.

**EQUATION 6.1**
**TIER 1 METHOD FOR ESTIMATION OF THE SET OF FC EMISSIONS**

$$\{FC_i\}_{\mathbf{n}} = \{EF_i \bullet C_u \bullet C_d \bullet [C_{PV} \bullet \delta + (1-\delta)]\}_{\mathbf{n}} \qquad (i = 1, \ldots, n)$$

Where:

$\{FC_i\}_n$ = emissions of FC gas *i*, mass of gas *i*

**Note: $\{\ \}_n$** denotes the set for each class of products (semiconductors, TFT-FPD or PV-cells) and *n* denotes the number of gases included in each set (six for semiconductors, three for TFT-FPD manufacture and two for PV-cells. See Table 6.2.). The estimates are only valid if made and reported for all members of the set using this Tier 1 methodology.

$EF_i$ = FC emission factor for gas *i* expressed as annual mass of emissions per square meters of substrate surface area for the product class, (mass of gas i)/$m^2$

$C_u$ = fraction of annual plant production capacity utilisation, fraction

$C_d$ = annual manufacturing design capacity, $Gm^2$of substrate processed, except for PV manufacturing which is $Mm^2$

$C_{PV}$ = fraction of PV manufacture that uses FCs, fraction

$\delta$ = 1 when Equation 6.1 is applied to PV industry and zero when Equation 6.1 is applied to either semiconductor or TFT-FPD industries, dimensionless

This method does not account for differences among process types (etching versus cleaning), individual processes, or tools. It also does not account for the possible use of atmospheric emission-control devices.

In using Tier 1, inventory compilers should not modify, in any way, the set of the FCs assumed in Table 6.2. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods. Neither may inventory compilers use, for example, the Tier 1 factor for $CF_4$ to estimate the emissions of $CF_4$ from semiconductors and combine it with the results of other FC gases from a Tier 2 or Tier 3 method. (See also Section 6.2.2.1.)

### TIER 2a METHOD – PROCESS GAS-SPECIFIC PARAMETERS

This method calculates emissions for each FC used on the basis of company-specific data on gas consumption and on emission control technologies. It uses industry-wide default values for the 'heel' or fraction of the purchased gas remaining in the shipping container after use (h), the fraction of the gas 'used' (destroyed or transformed) in the semiconductor or TFT-FPD manufacturing process, and the fraction of the gas converted into $CF_4$ or $C_2F_6$ during the process. To use the Tier 2a method inventory compilers must have direct communication with industry (e.g., annual emissions reporting) to gather data and ensure that emission control technologies are installed and in use.

Total emissions are equal to the sum of emissions from the gas $FC_i$ used in the production process plus the emissions of by-product $CF_4$, $C_2F_6$, $CHF_3$ and $C_3F_8$ resulting from use of the gas $FC_{i.}$, as shown in Equations 6.2, 6.3, 6.4, 6.5 and 6.6. Unlike the Tier 3 and 2b methods that are explained later in this section, the Tier 2a method does not distinguish between processes or process types (etching versus cleaning), individual processes or tools. The default emission factors represent weighted averages (based on expert judgments of weights), formed separately for each gas, over *all* etch *and* CVD processes.

As discussed below in the section on emission factors, the Tier 2a method uses the emission factor for the process type (CVD or etch) in which the individual FC is most frequently used in the particular electronics sector. This method reflects a current trend where individual FCs tend to be used predominantly in particular process types (CVD or etch) throughout each industry. However, in countries with companies or plants that depart significantly from the industry-wide pattern of usage (e.g., by using a gas primarily in etch while others primarily use it in CVD), inventory compilers should evaluate the potential to introduce error by using the Tier 2a method rather than the Tier 2b method.

**EQUATION 6.2**
**TIER 2a METHOD FOR ESTIMATION OF FC EMISSIONS**

$$E_i = (1-h) \bullet FC_i \bullet (1-U_i) \bullet (1-a_i \bullet d_i)$$

Where:

$E_i$ = emissions of gas *i*, kg

$FC_i$ = consumption of gas *i*,(e.g., $CF_4$, $C_2F_6$, $C_3F_8$, c-$C_4F_8$, c-$C_4F_8O$, $C_4F_6$, $C_5F_8$, $CHF_3$, $CH_2F_2$, $NF_3$, $SF_6$), kg

h = fraction of gas remaining in shipping container (heel) after use, fraction

$U_i$ = use rate of gas *i* (fraction destroyed or transformed in process), fraction

$a_i$ = fraction of gas *i* volume used in processes with emission control technologies (company- or plant-specific), fraction

$d_i$ = fraction of gas *i* destroyed by the emission control technology, fraction

**EQUATION 6.3**
**BY-PRODUCT EMISSIONS OF $CF_4$**

$$BPE_{CF4,i} = (1-h) \bullet B_{CF4,i} \bullet FC_i \bullet (1-a_i \bullet d_{CF4})$$

Where:

$BPE_{CF4,i}$ = by-product emissions of $CF_4$ from the gas *i* used, kg

$B_{CF4,i}$ = emission factor, kg $CF_4$ created/kg gas *i* used

$d_{CF4}$ = fraction of $CF_4$ by-product destroyed by the emission control technology, fraction

**EQUATION 6.4**
**BY-PRODUCT EMISSIONS OF $C_2F_6$**

$$BPE_{C2F6,i} = (1-h) \bullet B_{C2F6,i} \bullet FC_i \bullet (1-a_i \bullet d_{C2F6})$$

Where:

$BPE_{C2F6,i}$ = by-product emissions of $C_2F_6$ from the gas *i* used, kg

$B_{C2F6,i}$ = emission factor, kg $C_2F_6$ created/kg gas *i* used

$d_{C2F6}$ = fraction of $C_2F_6$ by-product destroyed by the emission control technology, fraction

**EQUATION 6.5**
**BY-PRODUCT EMISSIONS OF $CHF_3$**

$$BPE_{CHF3,i} = (1-h) \bullet B_{CHF3,i} \bullet FC_i \bullet (1-a_i \bullet d_{CHF3})$$

Where:

$BPE_{CHF3,i}$ = by-product emissions of $CHF_3$ from the gas *i* used, kg

$B_{CHF3,i}$ = emission factor, kg $CHF_3$ created/kg gas *i* used

$d_{CHF3}$ = fraction of $CHF_3$ by-product destroyed by the emission control technology, fraction

**EQUATION 6.6**
**BY-PRODUCT EMISSIONS OF $C_3F_8$**

$$BPE_{C3F8,i} = (1-h) \bullet B_{C3F8,i} \bullet FC_i \bullet (1-a_i \bullet d_{C3F8})$$

Where:

$BPE_{C3F8,i}$ = by-product emissions of $C_3F_8$ from the gas *i* used, kg

$B_{C3F8,i}$ = emission factor, kg $C_3F_8$ created/kg gas *i* used

$d_{C3F8}$ = fraction of $C_3F_8$ by-product destroyed by the emission control technology, fraction

After estimating the emission of gas *i* ($E_i$) and the $CF_4$, $C_2F_6$, $CHF_3$ and $C_3F_8$ by-product emissions for each gas ($BPE_{CF4,i}$, $BPE_{C2F6,i}$, $BPE_{CHF3,i}$ and $BPE_{C3F8,i}$), inventory compilers or companies should sum these emissions across all gases to estimate the total aggregate FC emissions.

## TIER 2b METHOD – PROCESS TYPE-SPECIFIC PARAMETERS

The Tier 2b method requires data on the aggregate quantities of each gas fed into all etching processes and all cleaning processes ($FC_{i,p}$). Thus, it distinguishes only between broad process types (etching vs. CVD chamber cleaning), but it does not distinguish among the many possible individual processes or small sets of processes. Industry-wide default values can be used for any or all of the following:

- the fraction of the gas remaining in the shipping container after use termed the 'heel' (h);
- the fraction of the gas 'used' (destroyed or transformed) per process type ($U_{i,p}$);
- the emission factor for $CF_4$ by-product emissions in the process type ($B_{CF4,i,p}$);
- the emission factor for $C_2F_6$ by-product emissions in the process type ($B_{C2F6,i,p}$);
- the emission factor for $CHF_3$ by-product emissions in the process type ($B_{CHF3,i,p)}$); and
- the emission factor for $C_3F_8$ by-product emissions in the process type ($B_{C3F8,i,p}$).

Defaults are also presented (see Table 6.6) for the fraction of the gas destroyed by the emissions control technology by process type ($d_{i,p}$, $d_{CF4,p}$, $d_{C2F6,p}$, $d_{CHF3,p}$ and $d_{C3F8,p}$). Unless emission control technologies are installed, the default value for $a_{i,p}$, the fraction of gas volume fed into processes with emission control technologies, is zero. The default values for $U_{i,p}$, $B_{CF4,i,p}$, $B_{C2F6,i,p}$, $B_{CHF3,i,p}$ and $B_{C3F8,i,p}$ represent simple unweighted averages, formed separately for each gas, over *all* etch processes and over *all* CVD processes. Company or plant-specific emission factors may be substituted for default values when available. The equations account for the plant-specific use of emission-control devices, but do not account for differences among individual processes or tools or among manufacturing plants in their mix of processes and tools. Thus, Tier 2b estimates will be less accurate than Tier 3 estimates. Also, note that the Tier 2b method is applicable to semiconductor and TFT-FPD manufacture.

Emissions resulting from the use of a specific FC ($FC_i$) consist of emissions of $FC_i$ itself *plus* emissions of $CF_4$, $C_2F_6$, $CHF_3$ and $C_3F_8$ created as by-products during use of $FC_i$. The following calculation should be repeated for each gas for each process type:

**EQUATION 6.7**
**TIER 2b METHOD FOR ESTIMATION OF FC EMISSIONS**

$$E_i = (1-h) \bullet \sum_p \left[FC_{i,p} \bullet (1-U_{i,p}) \bullet (1-a_{i,p} \bullet d_{i,p})\right]$$

Where:

$E_i$ = emissions of gas *i*, kg

p = process type (etching vs. CVD chamber cleaning)

$FC_{i,p}$ = mass of gas *i* fed into process type *p* (e.g., $CF_4$, $C_2F_6$, $C_3F_8$, c-$C_4F_8$, c-$C_4F_8O$, $C_4F_6$, $C_5F_8$, $CHF_3$, $CH_2F_2$, $NF_3$, $SF_6$), kg

h = fraction of gas remaining in shipping container (heel) after use, fraction

$U_{i,p}$= use rate for each gas *i* and process type *p* (fraction destroyed or transformed), fraction

$a_{i,p}$ = fraction of gas *i* volume fed into process type *p* with emission control technologies (company-or plant-specific), fraction

$d_{i,p}$ = fraction of gas *i* destroyed by the emission control technology used in process type *p* (If more than one emission control technology is used in process type *p*, this is the average of the fraction destroyed by those emission control technologies, where each fraction is weighted by the quantity of gas fed into tools using that technology), fraction

**EQUATION 6.8**
**BY-PRODUCT EMISSIONS OF $CF_4$**

$$BPE_{CF4,i} = (1-h) \bullet \sum_{p} \left[ B_{CF4,i,p} \bullet FC_{i,p} \bullet \left(1 - a_{i,p} \bullet d_{CF4,p}\right) \right]$$

Where:

$BPE_{CF4,i}$ = by-product emissions of $CF_4$ converted from the gas *i* used, kg

$B_{CF4,i,p}$ = emission factor for by-product emissions of $CF_4$ converted from gas *i* in process type *p*, kg $CF_4$ created/kg gas *i* used

$d_{CF4,p}$ = fraction of $CF_4$ by-product destroyed by the emission control technology used in process type *p* (e.g., control technology type listed in Table 6.6), fraction

**EQUATION 6.9**
**BY-PRODUCT EMISSIONS OF $C_2F_6$**

$$BPE_{C2F6,i} = (1-h) \bullet \sum_{p} \left[ B_{C2F6,i,p} \bullet FC_{i,p} \bullet \left(1 - a_{i,p} \bullet d_{C2F6,p}\right) \right]$$

Where:

$BPE_{C2F6,i}$ = by-product emissions of $C_2F_6$ converted from the gas *i* used, kg

$B_{C2F6,i,p}$ = emission factor for by-product emissions of $C_2F_6$ converted from gas *i* in process type *p*, kg $C_2F_6$ created/kg gas *i* used

$d_{C2F6,p}$ = fraction of $C_2F_6$ by-product destroyed by the emission control technology used in process type *p* (e.g., control technology type listed in Table 6.6), fraction

**EQUATION 6.10**
**BY-PRODUCT EMISSIONS OF $CHF_3$**

$$BPE_{CHF3,i} = (1-h) \bullet \sum_{p} \left[ B_{CHF3,i,p} \bullet FC_{i,p} \bullet \left(1 - a_{i,p} \bullet d_{CHF3,p}\right) \right]$$

Where:

$BPE_{CHF3,i}$ = by-product emissions of $CHF_3$ converted from the gas *i* used, kg

$B_{CHF3,i,p}$ = emission factor for by-product emissions of $CHF_3$ converted from gas *i* in process type *p*, kg $CHF_3$ created/kg gas *i* used

$d_{CHF3,p}$ = fraction of $CHF_3$ by-product destroyed by the emission control technology used in process type *p* (e.g., control technology type listed in Table 6.6), fraction

**EQUATION 6.11**
**BY-PRODUCT EMISSIONS OF $C_3F_8$**

$$BPE_{C3F8,i} = (1-h) \bullet \sum_{p} \left[ B_{C3F8,i,p} \bullet FC_{i,p} \bullet \left(1 - a_{i,p} \bullet d_{C3F8,p}\right) \right]$$

Where:

$BPE_{C3F8,i}$ = by-product emissions of $C_3F_8$ from the gas *i* used, kg

$B_{C3F8,i,p}$ = emission factor for by-product emissions of $C_3F_8$ converted from gas *i* in process type *p*, kg $C_3F_8$ created/kg gas *i* used

$d_{C3F8,p}$ = fraction of $C_3F_8$ by-product destroyed by the emission control technology used in process type *p* (e.g., control technology type listed in Table 6.6), fraction

Note that in certain etching or cleaning recipes, multiple FC precursors can be used concurrently and emissions of $CF_4$, $C_2F_6$, $CHF_3$ or $C_3F_8$ as by-products may originate from each of the individual FC precursor decomposition. In such cases, emissions of $CF_4$, $C_2F_6$, $CHF_3$ or $C_3F_8$ by-products should be reported as originating from the FC gas with the largest mass flow.

### TIER 3 METHOD – PROCESS-SPECIFIC PARAMETERS

The Tier 3 method also uses Equations 6.7, 6.8, 6.9, 6.10 and 6.11. However, this method requires company-specific or plant-specific values for all the parameters used in these equations for each individual process or for each of small sets of processes (e.g., silicon nitride etching or plasma enhanced chemical vapour deposition (PECVD) tool chamber cleaning). Therefore, when using Equations 6.7, 6.8, 6.9, 6.10 and 6.11, inventory compilers need to interpret 'p' in these equations as a specific 'Process' (e.g., silicon nitride etching or plasma enhanced chemical vapour deposition (PECVD) tool chamber cleaning), not as 'Process type'.

For purposes of transparency and comparability, the values used for these emission parameters should be well documented (see Section 6.2.2).

#### $CF_4$ formation from C-containing films during semiconductor manufacturing

The Tier 2a, Tier 2b and Tier 3 methods account for $CF_4$ emissions formed during removal via etching of carbon-containing low dielectric constant (k) materials or cleaning CVD reactors containing low k or carbide films during semiconductor manufacture. $CF_4$ may be formed even if the FC precursor does not contain carbon or if the FC precursor is not a greenhouse gas.

For example, cleaning low k CVD reactors with $NF_3$ will produce $CF_4$ as a by-product. In these cases, Equation 6.7 should be used to report $NF_3$ emissions and the result of Equation 6.8 should be used to reflect emissions of $CF_4$ from the process. In those situations where $F_2$, $COF_2$, or $ClF_3$ is used in chamber cleaning, $CF_4$ may also be formed. In this case, $CF_4$ emissions are estimated using Equation 6.8 and the results added to the total $CF_4$ emissions obtained from Equation 6.7. In both cases, $B_{CF4,i,p}$ should be measured as the fraction of the mass of $CF_4$ produced over the mass of clean or etch gas introduced in the reactor.

After estimating emissions of each FC gas and emissions of $CF_4$, $C_2F_6$, $CHF_3$ and $C_3F_8$ as by-products, inventory compilers or companies should sum these emissions across all gases to arrive at an estimate of aggregate FC emissions from a particular process.

**BOX 6.1**

**EXAMPLE FOR SEMICONDUCTOR MANUFACTURE**

For example, if a source used $NF_3$ (for chamber cleaning and etch), $CHF_3$ (etch) and $CF_4$ (etch), the total emissions, if low k films were used, are estimated using Equation 6.7 for $NF_3$, $CHF_3$ and $CF_4$ and Equation 6.8 for the formation of $CF_4$ formed when removing low k films with $NF_3$. In equation form, the total is:

$$\text{Total FC emissions} = E_{NF3} + E_{CHF3} + E_{CF4} + BPE_{CF4,NF3}$$

## 6.2.1.2 HEAT TRANSFER FLUIDS

There are two methods for estimating emissions from the use of heat transfer fluids. The choice of methods will depend on the availability of activity data on the use of heat transfer fluids, and is outlined in the decision tree (see Figure 6.2, Decision Tree for Estimation of FC Emissions from Heat Transfer Fluids, and see Section 1.5 of Chapter 1, Choosing between the Mass-Balance and Emission-Factor Approach).

### TIER 1 – HEAT TRANSFER FLUIDS

Tier 1 is appropriate when company-specific data are not available on heat transfer fluids. It is the less accurate of the two methods for estimating emissions from losses of heat transfer fluids. The method, unlike the Tier 2 method, gives an estimate of aggregate emissions - a weighted average emission across all liquid FCs that is expressed as the mass of $C_6F_{14}$[10]. The calculation relies on a generic emission factor that expresses the average

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[10] In the absence of GWP estimates, the appropriate GWP for $C_6F_{14}$ has been used as a proxy (to derive the default emission factor). (See the Inventory of U.S. Greenhouse Gas and Sinks: 1990-2003, the footnote to Table 4-58, page 166. (U.S. EPA, 2005))

aggregate emissions per unit of silicon consumed during semiconductor manufacturing. The formula is shown in Equation 6.12.

**EQUATION 6.12**
**TIER 1 METHOD FOR ESTIMATION OF TOTAL FC EMISSIONS FROM HEAT TRANSFER FLUIDS**

$$FC_{liquid,total} = EF_l \bullet C_u \bullet C_d$$

Where:

$FC_{liquid,\ total}$ = total FC emissions as expressed as the mass of $C_6F_{14}$, Mt $C_6F_{14}$

$EF_l$ = emission factor (aggregate FC emissions per $Gm^2$ of silicon consumed during the period expressed as the mass of $C_6F_{14}$ (See Table 6.2.)), Mt $C_6F_{14}/Gm^2$

$C_u$ = average capacity utilisation for all semiconductor manufacturing facilities in the country during the period, fraction

$C_d$ = design capacity of semiconductor manufacturing facilities in the country, $Gm^2$

## TIER 2 METHOD – HEAT TRANSFER FLUIDS

There is one Tier 2 method for estimating actual emissions from the use of each FC fluid. This method is a mass-balance approach that accounts for liquid FC usage over an annual period. It is appropriate when company-specific data are available. Over the course of a year, liquid FCs are used to fill newly purchased equipment and to replace FC fluid loss from equipment operation through evaporation. The Tier 2 method neglects fluid losses during filling new or existing equipment or when decommissioning old equipment (which is reasonable for these costly fluids).[11] Inventory compilers should obtain from companies the chemical composition of the fluid(s) for which emissions are estimated. The method is expressed in Equation 6.13.

**EQUATION 6.13**
**TIER 2 METHOD FOR ESTIMATION OF FC EMISSIONS FROM HEAT TRANSFER FLUIDS**

$$FC_i = \rho_i \bullet \left[ I_{i,t-1}(l) + P_{i,t}(l) - N_{i,t}(l) + R_{i,t}(l) - I_{i,t}(l) - D_{i,t}(l) \right]$$

Where:

$FC_i$ = emissions of $FC_i$, kg

$\rho_i$ = density of liquid $FC_i$, kg/litre

$I_{i,t-1}(l)$ = the inventory of liquid $FC_i$ at the end of the previous period, litres

$P_{i,t}(l)$ = net purchases of liquid $FC_i$ during the period (net of purchases and any returns), litres

$N_{i,t}(l)$ = total charge (or nameplate capacity) of new installed, litres

$R_{i,t}(l)$ = total charge (or nameplate capacity) of retired or sold equipment, litres

$I_{i,t}(l)$ = inventory of liquid $FC_i$ at end of the period, litres

$D_{i,t}(l)$ = amount of $FC_i$ recovered and sent offsite from retired equipment during the period, litres

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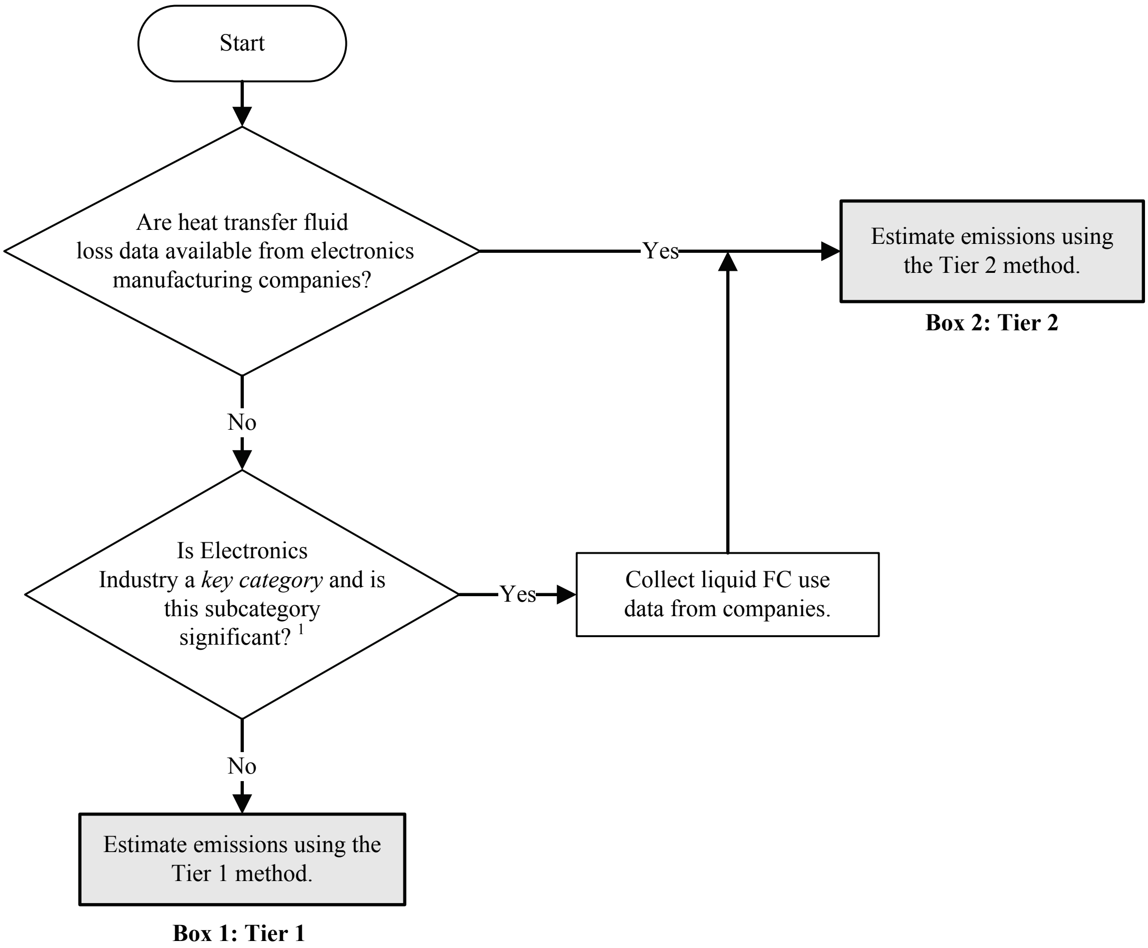
[11] Prices for heat transfer fluids vary from $55 – 130/litre. 3M, a manufacturer of a popular heat transfer fluid estimates that a vintage 2 000 manufacturing plant may loose 1 900 litres/year via evaporation. Manufactures of testing equipment that use heat transfer fluids report loss rates of approximately 30 litres/year/system for newer designs that reduce evaporative losses and 50 litres/year/system for older designs.

**Figure 6.2 Decision tree for estimation of FC emissions from HT fluid loss from electronics manufacturing**



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

## 6.2.2 Choice of emission factors[12]

### 6.2.2.1 ETCHING AND CVD CLEANING FOR SEMICONDUCTORS, LIQUID CRYSTAL DISPLAYS, AND PHOTOVOLTAICS

### TIER 1

The default emission factors for the Tier 1 method is presented in Table 6.2 below.

In using Tier 1, it is not *good practice* to modify, in any way, the set of the FCs or the values of the emission factors assumed in Table 6.2. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods. For example, inventory compilers may not use the Tier 1 factor for $CF_4$ to estimate the emissions of $CF_4$ from semiconductors and combine it with the results of other FC gases from a Tier 2 or Tier 3 method. It should be also noted that the Tier 1 FC emission factors presented in Table 6.2 should not be used for any purpose other than estimating annual FC-aggregate emissions from semiconductor, TFT-FPD or PV manufacturing for compilation of the national greenhouse gas inventory.

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[12] Sources and methods for developing emissions factors, if not explicitly provided in Chapter 6, can be found in Burton (2006).

**TABLE 6.2**
**TIER 1 GAS-SPECIFIC EMISSION FACTORS FOR FC EMISSIONS FROM ELECTRONICS MANUFACTURING**

| Electronics Industry Sector | Emission Factor (EF) (Mass per Unit Area of Substrate Processed) | | | | | | |
|---|---|---|---|---|---|---|---|
| | **$CF_4$** | **$C_2F_6$** | **$CHF_3$** | **$C_3F_8$** | **$NF_3$** | **$SF_6$** | **$C_6F_{14}$** |
| Semiconductors, $kg/m^2$ | 0.9 | 1. | 0.04 | 0.05 | 0.04 | 0.2 | NA |
| TFT-FPDs, $g/m^2$ | 0.5 | NA | NA | NA | 0.9 | 4. | NA |
| PV-cells[a], $g/m^2$ | 5 | 0.2 | NA | NA | NA | NA | NA |
| Heat Transfer Fluids[b], $kg/m^2$ | NA | NA | NA | NA | NA | NA | 0.3 |

[a] EFs adapted from unpublished work of Fthenakis, Alsema and Agostinelli. (Fthenakis ,2005) Note that factor is applicable only to silicon-specific technologies and is applied for abatement.

[b] EF assumes HTFs have the same GWP and $C_6F_{14}$ represents a suitable proxy. The origin of this factor is described in Burton, 2004, and is based in part on the work of Tuma and Tousignant (2001).

### TIER 2

As discussed above, emissions factors based on simple electronics production variables are not adequate to account for all of the factors that influence emissions. Data for each of the following parameters are necessary to prepare a reliable estimate:

- The gases used;
- The process type (CVD or etch) used;
- The brand of process tool used;
- Emission reduction technology.

Default values have been developed for the parameters used in Tier 2a and 2b methods (See Figure 6.1) on the basis of direct measurements, literature, and expert judgement (see Tables 6.3, 6.4, and 6.5 Tier 2 Default Emission Factors for FCs Emissions from Semiconductor[12], TFT-FPD[13], and PV[12] Manufacturing respectively). Given the difficulty in representing the diverse production conditions within the electronics industry, default emission parameters are inherently uncertain. While accuracy can be improved with larger sets of measured data and where factors are applied to similar processes using similar or identical chemical recipes, developing default factors necessarily involves some form of averaging across all of the data.

Electronics industry specialists expect that rapid technical innovation by chemical and equipment suppliers and electronics manufacturers will result in major emission reductions in the future (i.e., 2006 onwards). As a result, emission factors for these categories should evolve to reflect these changes. The semiconductor and TFT-FPD industries have established mechanisms through the World Semiconductor Council and the World LCD Industry Cooperation Committee, respectively, to evaluate global emission factors. The PV industry may be considering establishing a mechanism for tracking its PFC emissions during PV manufacture. (Fthenakis, 2006)

FC-use during PV manufacture may or may not increase. Existing evidence suggests that, should FC-use in this industry grow, efforts will be made to control their emissions (Agostinelli *et al*., 2004; Rentsch *et al*., 2005). Inventory compilers may wish to periodically consult with the industry to better understand global and national circumstances.

Tables 6.3 and 6.4 include two entries for $NF_3$: Remote-$NF_3$ and $NF_3$. The first refers to a cleaning method in which the film cleaning-agents formed from $NF_3$ (F-atoms) are produced in a plasma upstream (remote) from the chamber being cleaned. The last, denoted as simply $NF_3$, refers to an in-situ $NF_3$ cleaning process that is analogous to the process for other cleaning gases like $C_2F_6$ and $C_3F_8$.

The default value for the fraction of gas remaining in the shipping container (heel) is 0.10.

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[13] The emissions factors (EFs) for TFT-FPD manufacturing are simple (unweighted) averages developed from gas- and process-specific values published by Nishida *et al*. (2005).

### TABLE 6.3
### TIER 2 DEFAULT EMISSION FACTORS FOR FC EMISSIONS FROM SEMICONDUCTOR MANUFACTURING

| | Greenhouse Gases with TAR GWP | | | | | | | | | Greenhouse Gases without TAR GWP | | | Non-GHGs Producing FC By-products[‡] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Process Gas (i)** | **$CF_4$** | **$C_2F_6$** | **$CHF_3$** | **$CH_2F_2$** | **$C_3F_8$** | **$c\text{-}C_4F_8$** | **$NF_3$ Remote** | **$NF_3$** | **$SF_6$** | **$C_4F_6$** | **$C_5F_8$** | **$C_4F_8O$** | **$F_2$** | **$COF_2$** |
| **Tier 2a** | | | | | | | | | | | | | | |
| **1-Ui** | 0.9 | 0.6 | 0.4 | 0.1 | 0.4 | 0.1 | 0.02 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | NA | NA |
| **$B_{CF4}$** | NA | 0.2 | 0.07 | 0.08 | 0.1 | 0.1 | 0.02[†] | 0.09 | NA | 0.3 | 0.1 | 0.1 | 0.02[†] | 0.02[†] |
| **$B_{C2F6}$** | NA | NA | NA | NA | NA | 0.1 | NA | NA | NA | 0.2 | 0.04 | NA | NA | NA |
| **$B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 0.04 | NA | NA |
| **Tier 2b** | | | | | | | | | | | | | | |
| **Etch 1-Ui** | 0.7* | 0.4* | 0.4* | 0.06* | NA | 0.2* | NA | 0.2 | 0.2 | 0.1 | 0.2 | NA | NA | NA |
| **CVD 1-Ui** | 0.9 | 0.6 | NA | NA | 0.4 | 0.1 | 0.02 | 0.2 | NA | NA | 0.1 | 0.1 | NA | NA |
| **Etch $B_{CF4}$** | NA | 0.4* | 0.07* | 0.08* | NA | 0.2 | NA | NA | NA | 0.3* | 0.2 | NA | NA | NA |
| **Etch $B_{C2F6}$** | NA | NA | NA | NA | NA | 0.2 | NA | NA | NA | 0.2* | 0.2 | NA | NA | NA |
| **CVD $B_{CF4}$** | NA | 0.1 | NA | NA | 0.1 | 0.1 | 0.02[†] | 0.1[†] | NA | NA | 0.1 | 0.1 | 0.02[†] | 0.02[†] |
| **CVD $B_{C2F6}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 0.04 | NA | NA |

Notes: NA denotes not applicable based on currently available information

[‡] The default emission factors for $F_2$ and $COF_2$ may be applied to cleaning low-k CVD reactors with $ClF_3$.

* Estimate includes multi-gas etch processes

[†] Estimate reflects presence of low-k, carbide and multi-gas etch processes that may contain a C-containing FC additive

**TABLE 6.4**
**TIER 2 DEFAULT EMISSION FACTORS FOR FC EMISSIONS FROM LCD MANUFACTURING**

| | Greenhouse Gases with TAR GWP | | | | | | | | | Greenhouse Gases without TAR GWP | | | Non-GHGs Producing FC By-products | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Process Gas (i)** | **$CF_4$** | **$C_2F_6$** | **$CHF_3$** | **$CH_2F_2$** | **$C_3F_8$** | **$c\text{-}C_4F_8$** | **$NF_3$ Remote** | **$NF_3$** | **$SF_6$** | **$C_4F_6$** | **$C_5F_8$** | **$C_4F_8O$** | **$F_2$** | **$COF_2$** |
| **Tier 2a** | | | | | | | | | | | | | | |
| **1-Ui** | 0.6 | NA | 0.2 | NA | NA | 0.1 | 0.03 | 0.3 | 0.6 | NA | NA | NA | NA | NA |
| **$B_{CF4}$** | NA | NA | 0.07 | NA | NA | 0.009 | NA | NA | NA | NA | NA | NA | NA | NA |
| **$B_{CHF3}$** | NA | NA | NA | NA | NA | 0.02 | NA | NA | NA | NA | NA | NA | NA | NA |
| **$B_{C2F6}$** | NA | NA | 0.05 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **$B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **Tier 2b** | | | | | | | | | | | | | | |
| **Etch 1-Ui** | 0.6 | NA | 0.2 | NA | NA | 0.1 | NA | NA | 0.3 | NA | NA | NA | NA | NA |
| **CVD 1-Ui** | NA | NA | NA | NA | NA | NA | 0.03 | 0.3 | 0.9 | NA | NA | NA | NA | NA |
| **Etch $B_{CF4}$** | NA | NA | 0.07 | NA | NA | 0.009 | NA | NA | NA | NA | NA | NA | NA | NA |
| **Etch $B_{CHF3}$** | NA | NA | NA | NA | NA | 0.02 | NA | NA | NA | NA | NA | NA | NA | NA |
| **Etch $B_{C2F6}$** | NA | NA | 0.05 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{CF4}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C2F6}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |

Notes: NA denotes not applicable based on currently available information

## TABLE 6.5
## TIER 2 DEFAULT EMISSION FACTORS FOR FC EMISSIONS FROM PV MANUFACTURING

| | Greenhouse Gases with TAR GWP | | | | | | | | | Greenhouse Gases without TAR GWP | | | Non-GHGs Producing FC By-products | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Process Gas (i)** | **$CF_4$** | **$C_2F_6$** | **$CHF_3$** | **$CH_2F_2$** | **$C_3F_8$** | **$c\text{-}C_4F_8$** | **$NF_3$ Remote** | **$NF_3$** | **$SF_6$** | **$C_4F_6$** | **$C_5F_8$** | **$C_4F_8O$** | **$F_2$** | **$COF_2$** |
| **Tier 2a** | | | | | | | | | | | | | | |
| **1-Ui** | 0.7 | 0.6 | 0.4 | NA | 0.4 | 0.2 | NA | 0.2 | 0.4 | NA | NA | NA | NA | NA |
| **$B_{CF4}$** | NA | 0.2 | NA | NA | 0.2 | 0.1 | NA | 0.05 | NA | NA | NA | NA | NA | NA |
| **$B_{C2F6}$** | NA | NA | NA | NA | NA | 0.1 | NA | NA | NA | NA | NA | NA | NA | NA |
| **$B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **Tier 2b** | | | | | | | | | | | | | | |
| **Etch 1-Ui** | 0.7 | 0.4 | 0.4 | NA | NA | 0.2 | NA | NA | 0.4 | NA | NA | NA | NA | NA |
| **CVD 1-Ui** | NA | 0.6 | NA | NA | 0.1 | 0.1 | NA | 0.3 | 0.4 | NA | NA | NA | NA | NA |
| **Etch $B_{CF4}$** | NA | 0.2 | NA | NA | NA | 0.1 | NA | NA | NA | NA | NA | NA | NA | NA |
| **Etch $B_{C2F6}$** | NA | NA | NA | NA | NA | 0.1 | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{CF4}$** | NA | 0.2 | NA | NA | 0.2 | 0.1 | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C2F6}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |

Notes: NA denotes not applicable based on currently available information

### TABLE 6.6
### TIER 2a & 2b DEFAULT EFFICIENCY PARAMETERS FOR ELECTRONICS INDUSTRY FC EMISSION REDUCTION TECHNOLOGIES[a,b,e]

| Emission Control Technology | $CF_4$ | $C_2F_6$ | $CHF_3$ | $C_3F_8$ | c-$C_4F_8$ | $NF_3$[f] | $SF_6$ |
|---|---|---|---|---|---|---|---|
| **Destruction**[c] | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.95 | 0.9 |
| **Capture/Recovery**[d] | 0.75 | 0.9 | 0.9 | NT | NT | NT | 0.9 |

[a] Values are simple (unweighted) averages of destruction efficiencies for all abatement technologies. Emission factors do not apply to emission control technologies which cannot abate $CF_4$ at destruction or removal efficiency (DRE) $\geq$ 85 percent when $CF_4$ is present as an input gas or by-product and all other FC gases at DRE $\geq$ 90 percent. If manufacturers use any other type of emission control technology, its destruction efficiency is 0 percent when using the Tier 2 methods.

[b] Tier 2 emission control technology factors are applicable only to electrically heated, fuelled-combustion, plasma, and catalytic devices that

- are specifically designed to abate FCs,
- are used within the manufacturer's specified process window and in accordance with specified maintenance schedules and
- have been measured and has been confirmed under actual process conditions, using a technically sound protocol, which accounts for known measurement errors including, for example, $CF_4$ by-product formation during $C_2F_6$ as well as the effect of dilution, the use of oxygen or both in combustion abatement systems

[c] Average values for fuelled combustion, plasma, and catalytic abatement technologies.

[d] Average values for cryogenic and membrane capture and recovery technologies.

[e] Vendor data verified by semiconductor manufacturers. Factors should only be used when an emission control technology is being utilised and maintained in accordance with abatement manufacturer specifications.

[f] Use of $NF_3$ in the etch process is typically small compared to CVD. The aggregate emissions of $NF_3$ from etch and CVD under Tier 2b will usually not be greater than estimates made with Tier 2a or Tier 1 methods.

NT = not tested.

### Process tool emission factors

The procedures for calculating process tool emission factors for Tier 2a and Tier 2b methods are identical. Process tool emission factors are defined as the amount of greenhouse gas emitted divided by the amount of greenhouse gas used in the process. The emission factors correspond to the '$(1 – U_i)$' term in the Tier 2 formulas. For example, the emission factor of 0.9 for $CF_4$ (see Table 6.3 above, Tier 2a value) means that 90 percent of the $CF_4$ used in the process is emitted as $CF_4$.

By-product emission factors were also calculated. The major by-product emission of significance is $CF_4$. While it is generally held that the only gases that emit significant amounts of $CF_4$ as a by-product are $C_2F_6$ and $C_3F_8$, the data provided by tool manufacturers and chemical suppliers showed that $CF_4$ is also formed from mixtures of gases (e.g., that contain $CHF_3$ or $CH_2F_2$) and c-$C_4F_8$. As a result of this discussion, $CF_4$ by-product emission factors were calculated for $CHF_3$, $CH_2F_2$, $C_2F_6$, $C_3F_8$, c-$C_4F_8$ and $C_4F_8O$. For example, a value of 0.1for $C_3F_8$ (taken from Table 6.3 above, Tier 2a value) means that 10 percent of the $C_3F_8$ used is converted into $CF_4$. However, $C_2F_6$ may also be emitted from the decomposition of molecules such as $C_4F_6$. As described previously, $CF_4$ may also be formed when etching or cleaning chambers where carbon-containing films are present.

In order to calculate the Tier 2b process tool emission factors, data were collected from process equipment and gas manufacturers. The data were collected according to process type (either Chemical Vapour Deposition (CVD) or etch) and also by type of gas (e.g. $C_2F_6$, $CF_4$). The methods used to conduct the emissions testing were real time Quadrupole Mass Spectrometry (QMS) and Fourier Transform Infrared Spectroscopy (FTIR), the best known methods for measuring process tool emissions. Calibration standards (usually 1 percent mixtures with a balance of $N_2$) were used to quantify the results. The measurement protocol and quality control requirements that were followed are outlined in the 'Guidelines for Environmental Characterisation of Semiconductor Equipment.' (Meyers *et al.*, 2001)[14] The emission factors for Tier 2b (see Tables 6.3 and 6.4 above) are the simple (unweighted) average of the data collected for each gas for etch and CVD, rounded to one significant figure.[12, 16]

In order to determine the Tier 2a process tool emission factors, knowledge of the amounts of gas used in typical semiconductor manufacturing processes is required. The Tier 2a emission factors were obtained using weights provided by industry experts for the proportion of each gas used in etching and cleaning processes. For example, the Tier 2b emission factors for $C_2F_6$ (Table 6.3) are 0.5 (etch) and 0.6 (CVD). The distribution of $C_2F_6$ usage between etching and CVD chamber cleaning processes during semiconductor manufacture is 20:80. Applying these weights to each of the emission factors gives 0.6 for the Tier 2a factor for $C_2F_6$ to one significant figure.

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[14] These guidelines have also been adopted by flat panel display manufacturers for measuring FC-emissions during flat panel device manufacture.

The corresponding distribution of $SF_6$ usage in TFT-FPD manufacture is 50:50, which gives 0.6 for corresponding Tier 2a emission factor (Table 6.4).[15]

For Tier 3 emission factors, semiconductor manufacturers use company or plant-specific values rather than using default values as listed in Table 6.1 above. In order to assure the quality of emission factors, emission testing should be conducted in accordance with accredited methods.[16] If a third-party supplier conducts the emissions testing, the semiconductor manufacturer should make sure that the third-party supplier is capable of meeting all of the requirements outlined in Revision 3.0 of the Equipment Environmental Characterisation Guidelines (SIA, 2000). Semiconductor manufacturers who use emission factors provided by the process tool equipment supplier should make sure that the emission factors are applicable to their specific manufacturing process. Manufacturing methods with process parameters (e.g., pressure, flow rate) that deviate from centreline conditions may have different emission factors than those provided by the tool manufacturer.

### Emission control technology factors for Tier 2 methods

Emissions control technologies are developing at a rapid pace along with electronics manufacturing technology. Default control technology emission factors in Table 6.6 are based on tests of control devices that have been optimised for specific processes and tools. Results are expected to vary across tools and gas flow rates. Emission factors are not applicable to all tools or processes in semiconductor, liquid crystal display, or photovoltaic manufacturing facilities. The Tier 2 default destruction efficiency parameters presented in Table 6.6 are only applicable when the inventory compiler can demonstrate through communication with facility managers and subsequent documentation that emissions control technologies are operated and maintained in accordance with manufacturer specifications. If companies use any other type of abatement device, they should assume that its destruction efficiency is 0 percent under the Tier 2 a and b methods.

Assumptions for the emissions control technology emission factors for the Tier 2 (a & b) methods include:

(i) Specific emissions control technologies are not listed; emission factors for each chemical were established based on results achieved during testing of emissions control technologies in semiconductor manufacturing applications;

(ii) Emission factors should only be used when abatement is applied to emissions that fall within the operating range specified by the abatement manufacturer to meet or exceed the factors listed in Table 6.6;

(iii) Emission factors apply only to that portion of emissions that pass through a properly operating and maintained control device; emission factors should not be applied when control device is bypassed, not operating according to manufacturer specifications, or not maintained in accordance with specifications.

(iv) Emission factors do not apply to emission control technologies which cannot abate $CF_4$ at a destruction removal efficiency (DRE) $\geq 85$ percent when $CF_4$ is present as an input gas or by-product and all other FC gases at DRE $\geq 90$ percent. If manufacturers use any other type of emission control technology, its destruction efficiency is 0 percent when using the Tier 2 methods.

The default Tier 2 emission control factors in Table 6.6, Default Efficiency Parameters for Electronics Industry FC Emission Reduction Technologies were calculated from data received from equipment suppliers, abatement technology suppliers and electronic device manufacturers. It should be noted that only data from abatement devices that were specifically designed to abate FCs were used in the calculation. Data were received from combustion abatement devices (all of which used some type of fuel), plasma abatement devices, electrically heated abatement devices, and catalytic abatement devices.

The values presented in Table 6.6, Default Efficiency Parameters for Electronics Industry FC Emission Reduction Technologies, are the results of all of the data received for optimized technologies and for each input gas, rounded down to the next 5 percent (e.g., an average of 98 percent would be rounded down to 0.95). The averages were rounded down to reflect that (i) emissions control devices vary in their efficacy depending upon what gas they are optimised to destroy, and (ii) the efficacy of emission control devices depends on the type of tool they are installed on (150, 200 or 300mm wafers) and the amount of FC gas flown through that particular tool, and total exhaust flow through the emissions control device. An emission control device that can destroy 99 percent of a FC when it is optimised to destroy that FC on a certain tool may destroy less than 95 percent of that FC when it is optimised to destroy something else or when it is used on a tool for which it was not designed, or if the FC or total exhaust flow exceeds a certain limit. Electronics manufacturers and abatement tool manufacturers

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[15] The 50:50 $SF_6$ usage rates represent an average for the leading TFT-FPD manufacturing regions of Japan, Republic of Korea and Taiwan. That proportion was provided by Nishida (2006) and Kim (2006).

[16] One example of an internationally accredited testing method is Meyers *et al.* (2001).

should ensure that the abatement system installed is properly sized and maintained and that the emission control device can meet or exceed the default emission factor highlighted in Table 6.6.

#### 6.2.2.2 HEAT TRANSFER FLUIDS

The emission factor for the Tier 1 method is presented in Table 6.2. There is no emission factor for the Tier 2 method for estimating emissions from evaporation of heat transfer fluids.

### 6.2.3 Choice of activity data

Activity data for the electronics industry consists of data on gas sales and use or the annual amount of electronics substrate processed (e.g., $m^2$ of silicon processed for semiconductors). For the more data-intensive Tier 2 methods, gas purchase data at the company or plant-level are necessary. For the Tier 1 methods, inventory compilers will need to determine the total surface area of electronic substrates processed for a given year. Silicon consumption may be estimated using an appropriate edition of the World Fab Watch (WFW) database, published quarterly by Semiconductor Equipment & Materials International (SEMI)[17]. The database contains a list of plants (production as well as R&D, pilot plants, etc.) worldwide, with information about location, design capacity, wafer size and much more. Similarly, SEMI's 'Flat Panel Display Fabs on Disk' database provides an estimate of glass consumption for global TFT-FPD manufacturing.

The activity data in Table 6.7 reflect design capacity figures. Semiconductor and TFT-FPD manufacturing plants are not operated at design capacities for sustained periods, such as a full year. Instead, the capacity fluctuates depending on product demand. For semiconductor manufacturing, publicly available industry statistics show that the global annual average capacity utilisation during the period 1991 – 2000 varied between 76 and 91 percent, with an average value of 82 percent and most probable value of 80 percent. When country-specific capacity utilisation data are not available, the suggested capacity utilisation for semiconductor manufacturing is 80 percent. This should be used consistently for a time series of estimates. For TFT-FPD manufacturing, publicly available capacity utilisation data are not available. The TFT-FPD manufacturing industry, like the semiconductor manufacturing industry, lowers product prices to maintain the highest practical plant capacity utilisation. By analogy, therefore, it is suggested to use 80 percent to estimate substrate glass consumption using the design capacities provided in Table 6.7 for country TFT-FPD manufacturers. For PV manufacturing, published capacity utilisation data ranges between 77 – 92 percent, with the average for the years 2003 and 2004 of 86 percent. Therefore, 86 percent is the recommended default figure for $C_u$ (see Equation 6.1) to use.

When estimating emissions during PV manufacture, one should account for the fraction of the industry that actually employs FCs ($C_{PV}$ in Equation 6.1). Because recent surveys indicate that between 40 – 50 percent of PV manufacture actually uses FC, and the usage trend may be increasing, the recommended default value for $C_{PV}$ is 0.5.

Table 6.7 summarises the capacity for 2003, 2004 and 2005 for countries, which in total, account for more than 90 percent of world capacity in 2003.

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[17] The term 'fab' is synonymous with clean room/manufacturing facility. Semiconductor and flat panel display manufacturing plants are often called fabrication plants, from which the abbreviation 'fab' follows.

TABLE 6.7
COUNTRY TOTAL SILICON (Si) AND GLASS DESIGN CAPACITIES ($Mm^2$) FOR 2003, 2004 AND 2005

| | Annual Si design capacities, $Mm^2$ | | | Annual Glass design capacities, $Mm^2$ | | |
|---|---|---|---|---|---|---|
| **Country Totals** | **2003[1]** | **2004[2]** | **2005[2]** | **2003[1]** | **2004[2]** | **2005[2]** |
| Australia | 0.0008 | 0.0008 | 0.0008 | NA | NA | NA |
| Austria | 0.0201 | 0.0201 | 0.0201 | NA | NA | NA |
| Belgium | 0.0040 | 0.0040 | 0.0040 | NA | NA | NA |
| Canada | 0.0041 | 0.0041 | 0.0041 | NA | NA | NA |
| China | 0.1436 | 0.1982 | 0.3243 | 0.0432 | 0.0432 | 0.8154 |
| Czech Republic | 0.0057 | 0.0057 | 0.0057 | NA | NA | NA |
| France | 0.0653 | 0.0674 | 0.0674 | NA | NA | NA |
| Germany | 0.1622 | 0.1622 | 0.1622 | NA | NA | NA |
| China, Hong Kong | 0.0059 | 0.0059 | 0.0059 | NA | NA | NA |
| Hungary | 0.0006 | 0.0006 | 0.0006 | NA | NA | NA |
| India | 0.0128 | 0.0128 | 0.0128 | NA | NA | NA |
| Ireland | 0.0175 | 0.0430 | 0.0430 | NA | NA | NA |
| Israel | 0.0310 | 0.0310 | 0.0564 | NA | NA | NA |
| Italy | 0.0431 | 0.0431 | 0.0609 | NA | NA | NA |
| Japan | 0.9091 | 0.9235 | 0.9639 | 4.5746 | 5.3256 | 6.9201 |
| Latvia | 0.0019 | 0.0019 | 0.0019 | NA | NA | NA |
| Malaysia | 0.0284 | 0.0284 | 0.0284 | NA | NA | NA |
| Netherlands | 0.0301 | 0.0301 | 0.0301 | 0.0209 | 0.0209 | 0.0209 |
| Republic of Belarus | 0.0077 | 0.0077 | 0.0077 | NA | NA | NA |
| Russia | 0.0250 | 0.0250 | 0.0325 | NA | NA | NA |
| South Korea | 0.3589 | 0.3742 | 0.3937 | 5.8789 | 9.4679 | 12.4857 |
| Singapore | 0.1730 | 0.1730 | 0.1985 | 0.2821 | 0.2821 | 0.2821 |
| Slovakia | 0.0043 | 0.0043 | 0.0043 | NA | NA | NA |
| South Africa | 0.0021 | 0.0021 | 0.0021 | NA | NA | NA |
| Sweden | 0.0019 | 0.0019 | 0.0019 | NA | NA | NA |
| Switzerland | 0.0098 | 0.0098 | 0.0098 | NA | NA | NA |
| Thailand | 0.0000 | 0.0000 | 0.0094 | NA | NA | NA |
| Turkey | 0.0000 | 0.0000 | 0.0000 | NA | NA | NA |
| United Kingdom | 0.0597 | 0.0597 | 0.0936 | NA | NA | NA |
| United States of America | 0.6732 | 0.6921 | 0.7190 | 0.0000 | 0.0000 | 0.0000 |
| Vietnam | 0.0000 | 0.0000 | 0.0000 | NA | NA | NA |
| Global Total | 3.3206 | 3.4972 | 3.8849 | 15.0572 | 23.9959 | 33.7459 |

[1] Country totals include fab in production

[2] Country totals include fabs under construction and announced.

NA = not applicable.

Sources: Extractions from World Fab Watch Database, January 2004 Edition for Semiconductor Manufacturing and Flat Panel Display Fabs on Disk Database (Strategic Marketing Associates, 2004a), October 2004 Edition for TFT-FPD Manufacturing (Strategic Marketing Associates, 2004b).

TABLE 6.8
COUNTRY TOTAL PV PRODUCTION CAPACITY[a] FOR 2003, $Mm^2$

| | |
|---|---|
| Australia | 0.135 |
| Austria | 0.0307 |
| Canada | 0.0154 |
| Denmark | 0.00254 |
| France | 0.162 |
| Germany | 0.817 |
| Italy | 0.100 |
| Japan | 3.72 |
| Norway | 0.0138 |
| Portugal | 0.115 |
| S. Korea | 0.462 |
| Spain | 0.715 |
| Sweden | 0.377 |
| Switzerland | 0.00238 |
| United Kingdom | 0.0269 |
| United States | 1.02 |

[a]Capacities for all PV manufacturing technologies, includes those that may not use FCs during PV manufacture; World average capacity utilisation for 2003 = 86%.

Source: IEA, 2004. PV participating survey countries.

## 6.2.4 Completeness

Complete accounting of emissions from the semiconductor industry should be achievable in most countries because there are a limited number of companies and plants. There are four issues related to completeness that should be addressed:

- **Other by-products:** A number of transformation by-products are generated as a result of FC use for chamber cleaning and etching. As highlighted above, formation of $CF_4$ and $C_2F_6$ can result from the decomposition of other FC gases. Also, $CF_4$ formation has been observed in the cleaning of low k CVD chambers. In this case, the Tier 3 method should be used to accurately estimate emissions.
- **New chemicals:** Completeness will be an issue in the future as the industry evaluates and adopts new chemical processes to improve its products. Industry-wide efforts to reduce FC emissions are also accelerating the review of new chemicals. Consequently, *good practice* for this industry is to incorporate a mechanism that accounts for greenhouse gases not listed in the IPCC Third Assessment Report (e.g., $C_4F_6$, $C_5F_8$, Fluorinerts™, and Galdens®). These new FC materials have high GWPs or may produce high GWP by-product emissions.
- **Other sources:** A small amount of FCs may be released during gas handling (e.g. distribution) and by sources such as research and development (e.g. university) scale plants and tool suppliers. These emissions are not believed to be significant (e.g., less than 1 percent of this industry's total emissions).
- **Other products or processes:** FC use has been identified in the electronics industry in emissive applications including: micro-electro-mechanical systems (MEMS),[18] hard disk drive manufacturing, device testing (FC liquids), vapour phase reflow soldering,[19] and precision cleaning.[20]

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[18] Emissions from micro-electro-mechanical systems (MEMS) manufacturing may be estimated using methods similar to those used for the other electronic sub sectors. Company-specific emission and abatement factors are required. Very small amounts of FCs are also used in and research and development laboratories/facilities.

### 6.2.5 Developing a consistent time series

Use of FCs by the semiconductor industry began in the late 1970s and accelerated significantly beginning in the early 1990s. Determining a base year emissions level may present difficulties because few data are available for emissions occurring before 1995. If historical emissions estimates were based on simple assumptions (e.g., use equals emissions), then these estimates could be improved by applying the methods described above. If historical data are not available to permit use of a Tier 3 or 2 method, then the Tier 1 method using default emission parameters can be used retrospectively. Both Tier 1 and Tier 2 could then be applied simultaneously for the years in which more data become available to provide a comparison or benchmark. This should be done according to the guidance provided in Volume 1, Chapter 5.

In order to ensure a consistent emissions record over time, an inventory compiler should recalculate FC emissions for all years reported whenever emissions calculation procedures are changed (e.g., if an inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, the inventory compiler will need to consider how current plant data can be used to recalculate emissions for these years. It may be possible to apply current plant-specific emission parameters to sales data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emission trends are real and not an artefact of changes in procedure.

## 6.3 UNCERTAINTY ASSESSMENT

Use of the Tier 3 method will result in the least uncertain inventory. Given the limited number of plants and the close monitoring of production processes at the plant level, collection of data for use in Tier 2b or Tier 3 methods should be technically feasible. Inventory compilers should seek the advice of the industry on uncertainties, using the approaches to obtaining expert judgement outlined in Volume 1, Chapter 3.

Of all the methods, Tier 1 is the most uncertain. Using a single factor to account for the FC emissions from the diversity of semiconductor products is a glaring simplification. The factors presented in Table 6.2 are heavily weighted toward the manufacture of advanced vintage-late-1990s memory and logic products, having 3 to 5 layers, respectively, manufactured on the silicon wafer. The factors for countries that are currently manufacturing products at the leading-edge of technology (and are not using measures to reduce FC emissions) would be larger, while countries that manufacture products that use older technologies or manufacture simpler devices would use the same or an even smaller factor.

The Tier 1 emissions factors for TFT-FPD manufacturing represents a weighted average of the estimated aggregate PFC emissions per unit area of substrate glass consumed during TFT-FPD manufacture for the area where data were available (Burton, 2004b). The estimated emissions reported for Japan used Tier 2b factors for semiconductor manufacturing from *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC, 2000) in semiconductor manufacturing (Nishida *et al*., 2004). For emissions from Taiwan's TFT-FPD manufacturers, the method for estimating emissions was not reported (Leu *et al*., 2004). However, subsequently Leu (2004) reported an aggregate emission factor having a similar magnitude to that developed by Burton (2004b). The uncertainty in the Tier 1 emissions factor for TFT-FPD manufacture is probably large, but not known at this time.

When using Tier 3 method for semiconductor and TFT-FPD manufacturing, the resulting estimates of emissions will be more accurate than the Tier 2a, 2b or Tier 1 methods, on the order of ± 30 percent (95 percent confidence interval). Uncertainty in the efficacy of emission control technology appears to contribute most to this uncertainty, especially the variability in the uptime of emission control devices and in flow rates to emission control devices that may exceed device design limits.

Estimates of emissions from using heat transfer fluids using the Tier 2 method will be more accurate than Tier 1 method, of the order of ± 20 percent (95 percent confidence interval).

### 6.3.1 Emission factor uncertainties

The uncertainties in the emission factors suggested for the Tier 2b and 2a methods are shown in Table 6.9 for semiconductor manufacturing and Table 6.10 for TFT-FPD manufacturing. The factors were developed

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[19] Emissions from vapour phase reflow soldering may be estimated to equal annual net FC purchases for maintaining vapour phase reflow soldering equipment.

[20] Emissions from precision cleaning are to be accounted for in Section 7.2 (Solvents) of this Volume.

specifically for this guidance. For Tier 2b, relative errors for each entry (process and gas in the case of Tier 2b) were estimated as the standard deviation of the factors provided by an expert group, normalised to the simple (unweighted) average, rounded to one significant figure.[12] The estimate for each value was then doubled to estimate the 95 percent confidence interval. The same procedure was used to estimate the relative errors for product-formation factors (B). The corresponding estimates for the Tier 2a method were derived for the Tier 2b estimates, using the estimates of gas usage employed in development of the emission factors (see Section 6.2.2 Tier 2).

Tier 1 emission factors will have an uncertainty range that is skewed towards values close to zero extending up to 200 percent (95 percent confidence interval for semiconductor and TFT-FPD manufacture). Uncertainty estimates for PV manufacturing are not available.

## 6.3.2 Activity data uncertainties

Gas consumption constitutes the unit of activity to estimate emissions during semiconductor, TFT-FPD and PV manufacture for the Tier 2a and 2b methods. Gas consumption can be either measured or estimated from data on gas purchases, and requires knowledge of h, the unused gas returned to gas suppliers in the shipping containers. The uncertainties (95 percent confidence interval) in gas consumption and h, whether measured or estimated using expert judgment are shown in Table 6.10, Relative Errors (95 percent confidence interval) for Activity Data for Tier 2a and 2b Methods for Semiconductor and TFT-FPD Manufacture.

For Tier 1 method, the unit of activity is substrate consumption. Uncertainties in the Tier 1 activity data are attributed principally to missing data entries in the WFW and FPD databases. An estimate of the reliability of entries derived from the WFW in Table 6.7 is ± 10 percent (95 percent confidence interval), which reflects errors due to missing and incorrect entries in the database. The 95 percent confidence interval in capacity utilisation over the 1991-2000 period is ± 12 percentage points (i.e., from 70 percent utilisation to 94 percent utilisation). The corresponding entries for TFT-FPD and PV manufacture are assumed to be similar to those for semiconductor manufacturing.

**TABLE 6.9**
**TIER 2 DEFAULT ESTIMATES OF RELATIVE ERRORS (%) FOR EMISSION FACTOR FOR FC EMISSIONS FROM SEMICONDUCTOR MANUFACTURING, 95 PERCENT CONFIDENCE INTERVALS***

| | Greenhouse Gases with TAR GWP | | | | | | | | | Greenhouse Gases without TAR GWP | | | Non-GHGs Producing FC By-products | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Process Gas (i)** | **$CF_4$** | **$C_2F_6$** | **$CHF_3$** | **$CH_2F_2$** | **$C_3F_8$** | **c-$C_4F_8$** | **$NF_3$ Remote** | **$NF_3$** | **$SF_6$** | **$C_4F_6$** | **$C_5F_8$** | **$C_4F_8O$** | **$F_2$** | **$COF_2$** |
| **Tier 2a** | | | | | | | | | | | | | | |
| **1-Ui** | 15 | 30 | 100 | 400 | 20 | 80 | 400 | 70 | 300 | 300 | 80$^{\dagger}$ | 40 | NA | NA |
| **$B_{CF4}$** | NA | 90 | 300 | 200 | 60 | 100 | 200 | 200 | NA | 200 | 100$^{\dagger}$ | 80 | 200 | 200 |
| **$B_{C2F6}$** | NA | NA | NA | NA | NA | 200 | NA | NA | NA | 200 | 200 | NA | NA | NA |
| **$B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 40 | NA | NA |
| **Tier 2b** | | | | | | | | | | | | | | |
| **Etch 1-Ui** | 60 | 100 | 100 | 700 | NA | 200 | NA | 300 | 300 | 300 | 200$^{\dagger}$ | NA | NA | NA |
| **CVD 1-Ui** | 10 | 30 | NA | NA | 0.4 | 30 | 400 | 70 | NA | NA | 30$^{\dagger}$ | 40 | NA | NA |
| **Etch $B_{CF4}$** | NA | 200 | 300 | 200 | NA | 200 | NA | NA | NA | 200 | 200$^{\dagger}$ | NA | NA | NA |
| **Etch $B_{C2F6}$** | NA | NA | NA | NA | NA | 200 | NA | NA | NA | 200 | 200$^{\dagger}$ | NA | NA | NA |
| **CVD $B_{CF4}$** | NA | 80 | NA | NA | 60 | 60 | 200 | 200 | NA | NA | 60$^{\dagger}$ | 80 | 200 | 200 |
| **CVD $B_{C2F6}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 40 | NA | NA |

Notes: NA denotes not applicable based on currently available information

* Values that exceed 100% imply a distribution that is skewed towards values close to zero extending up to the value given.

† Estimate relies on an analogy to c-$C_4F_8$ as the data for $C_5F_8$ were insufficient to estimate a confidence interval.

### TABLE 6.10
### TIER 2 DEFAULT ESTIMATES OF RELATIVE ERRORS (%) FOR EMISSION FACTOR FOR FC EMISSIONS FROM LCD MANUFACTURING, 95 PERCENT CONFIDENCE INTERVALS

| | **Greenhouse Gases with TAR GWP** | | | | | | | | | **Greenhouse Gases without TAR GWP** | | | **Non-GHGs Producing FC By-products** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Process Gas (i)** | **$CF_4$** | **$C_2F_6$** | **$CHF_3$** | **$CH_2F_2$** | **$C_3F_8$** | **$c\text{-}C_4F_8$** | **$NF_3$ Remote** | **$NF_3$** | **$SF_6$** | **$C_4F_6$** | **$C_5F_8$** | **$C_4F_8O$** | **$F_2$** | **$COF_2$** |
| **Tier 2a** | | | | | | | | | | | | | | |
| **1-Ui** | 50 | NA | 8 | NA | NA | 5 | 70 | 20 | 20 | NA | NA | NA | NA | NA |
| **$B_{CF4}$** | NA | NA | 30 | NA | NA | 40 | NA | NA | NA | NA | NA | NA | NA | NA |
| **$B_{CHF3}$** | NA | NA | NA | NA | NA | 20 | NA | NA | NA | NA | NA | NA | NA | NA |
| **$B_{C2F6}$** | NA | NA | 40 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **Tier 2b** | | | | | | | | | | | | | | |
| **Etch 1-Ui** | 50 | 100 | 8 | NA | NA | 5 | NA | 60 | NA | NA | NA | NA | NA | NA |
| **CVD 1-Ui** | NA | NA | NA | NA | NA | NA | 70 | 20 | 6 | NA | NA | NA | NA | NA |
| **Etch $B_{CF4}$** | NA | NA | 30 | NA | NA | 40 | NA | NA | NA | NA | NA | NA | NA | NA |
| **Etch $B_{CHF3}$** | NA | NA | NA | NA | NA | 20 | NA | NA | NA | NA | NA | NA | NA | NA |
| **Etch $B_{C2F6}$** | NA | NA | 40 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{CF4}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C2F6}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **CVD $B_{C3F8}$** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |

Notes: NA denotes not applicable based on currently available information

# 6.4 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

## 6.4.1 Quality Assurance/Quality Control (QA/QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1 and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

Additional general guidance for higher tier QA/QC procedures is also included in Volume 1, Chapter 6. Due to the highly competitive nature of the semiconductor industry, provisions for handling confidential business information should be incorporated into the verification process. Methods used should be documented, and a periodic audit of the measurement and calculation of data should be considered. A QA audit of the processes and procedures should also be considered.

## 6.4.2 Reporting and Documentation

Care should be taken not to include emissions of HFCs used as ODS substitutes with those used in semiconductor manufacturing. It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. 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.

Explicit reporting on emissions in this industry would improve the transparency and comparability of emissions. As a number of FCs gases are emitted by this industry, reporting by individual gas species rather than by chemical type would also improve the transparency and usefulness of this data. Efforts to increase transparency should take into account the protection of confidential business information related to specific gas use. Country-level aggregation of gas-specific emissions data should protect this information in countries with three or more manufacturers. Table 6.11, Information Necessary for Full Transparency of Estimates of Emissions from Semiconductor Manufacturing, shows the supporting information necessary for full transparency in reported emissions estimates.

*Good practice* for Tier 3 is to document the development of company-specific emission factors, and to explain the deviation from the generic default values. Given confidentiality concerns, inventory compilers may wish to aggregate this information across manufacturers. In cases where manufacturers in a country have reported different emission or conversion factors for a given FC and process or process type, inventory compilers may provide the range of factors reported and used.

**TABLE 6.11**

**INFORMATION NECESSARY FOR FULL TRANSPARENCY OF ESTIMATES OF EMISSIONS FROM ELECTRONICS MANUFACTURING**

| Data | Tier 1 | Tier 2a | Tier 2b | Tier 3 |
|---|---|---|---|---|
| Total surface area of electronics substrate processed (e.g., $m^2$ silicon, $m^2$ glass) | X | | | |
| Capacity utilisation for semiconductor, TFT-FPD and PV manufacturing | X | | | |
| Fraction of PV manufacturing capacity that uses FC gases | X | | | |
| Emissions of each FC (rather than aggregated for all FCs) | | X | X | X |
| Sales/purchases of each FC | | X | | |
| Mass of each FC used in each process or process type | | | X | X |
| Fraction of each FC used in processes with emission control technologies | | X | X | X |
| Use rate for each FC for each process or process type (This and following information is necessary only if default value is not used) | | | | X |
| Fraction of each FC transformed into $CF_4$ for each process or process type | | | | X |
| Fraction of gas remaining in shipping container | | | | X |
| Fraction of each FC destroyed by emission control technology | | | | X |
| Fraction of $CF_4$ by-product destroyed by emission control technology | | | | X |

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# CHAPTER 7

# EMISSIONS OF FLUORINATED SUBSTITUTES FOR OZONE DEPLETING SUBSTANCES

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# 7 EMISSIONS OF FLUORINATED SUBSTITUTES FOR OZONE DEPLETING SUBSTANCES

## 7.1 INTRODUCTION

### 7.1.1 Chemicals and relevant application areas covered

Hydrofluorocarbons (HFCs) and, to a very limited extent, perfluorocarbons (PFCs), are serving as alternatives to ozone depleting substances (ODS) being phased out under the Montreal Protocol. Current and expected application areas of HFCs and PFCs include (IPCC/TEAP, 2005):

- refrigeration and air conditioning;
- fire suppression and explosion protection;
- aerosols;
- solvent cleaning;
- foam blowing; and
- other applications[1].

These major groupings of current and expected usage are referred to in this chapter as *applications* within the ODS substitutes category. This introduction (Section 7.1) provides a general framework for estimating emissions from ODS substitutes, and subsequent sections (Sections 7.2 through 7.7) provide more specialised guidance on the individual applications introduced above. Some of these applications themselves encompass products or uses with diverse emission characteristics, and countries will produce more rigorous estimates if they account for this diversity through the adoption of disaggregated assessments (higher tier). Additionally, the use of HFCs and PFCs in some applications, specifically rigid foam (typically closed-cell foam), refrigeration and fire suppression, can lead to the development of long-lived *banks* of material. The emission patterns from these uses can be particularly complex and methods employing disaggregated data sets are essential to generate accurate emissions estimates. Other applications, such as aerosols and solvent cleaning may have short-term inventories of stock but, in the context of emission estimation, can still be considered as sources of prompt emission. This statement also applies to flexible foams (typically open-cell foam).

HFCs and PFCs are not controlled by the Montreal Protocol because they do not contribute to depletion of the stratospheric ozone layer. HFCs are chemicals containing only hydrogen, carbon, and fluorine. Prior to the Montreal Protocol and the phase-out of various ODS, the only HFCs produced were HFC-152a, which is a component of the refrigerant blend R-500, and HFC-23, a low temperature refrigerant which is a by-product of HCFC-22[2] production. HFC-134a entered production in 1991 and a variety of other HFCs have since been introduced and are now being used as ODS substitutes (IPCC/TEAP, 2005) among other applications. When collecting data on HFC and PFC consumption for reporting purposes, care needs to be taken to include those HFCs in blends, but, at the same time, to avoid including those components of a blend which are not required to be reported (e.g., CFCs and HCFCs).

HFCs and PFCs have high global warming potentials (GWPs) and, in the case of PFCs, long atmospheric residence times. Table 7.1 gives an overview of the most important HFCs and PFCs (IPCC Second Assessment Report (IPCC, 1996); IPCC Third Assessment Report (IPCC, 2001); IPCC/TEAP, 2005), including their main application areas. The various HFCs and PFCs have very different potencies as greenhouse gases. PFCs have particularly high GWPs regardless of the integrated time horizon adopted because of their long atmospheric lifetimes. The consumption patterns relating to individual gases must be known, therefore, or estimated with reasonable accuracy, to achieve useful assessments for the contribution to global warming from emissions of these groups of chemicals.

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[1] HFCs and PFCs may also be used as ODS substitutes in sterilisation equipment, for tobacco expansion applications, and as solvents in the manufacture of adhesives, coating and inks.

[2] HCFCs - hydrochlorofluorocarbons.

As CFCs, halons, carbon tetrachloride, methyl chloroform, and, ultimately, HCFCs are being finally phased out[3], HFCs are being selectively used as replacements. PFCs are also being used, but only to a limited extent. Even though up to 75 percent of previous application of CFC may now be covered by non fluorocarbon technologies (IPCC/TEAP, 2005), HFC use is expected to continue to grow at least in the short term.

**TABLE 7.1**
**MAIN APPLICATION AREAS FOR HFCS AND PFCS AS ODS SUBSTITUTES [1]**

| Chemical | Refrigeration and Air Conditioning | Fire Suppression and Explosion Protection | Aerosols | | Solvent Cleaning | Foam Blowing | Other Applications[2] |
|---|---|---|---|---|---|---|---|
| | | | Propellants | Solvents | | | |
| HFC-23 | X | X | | | | | |
| HFC-32 | X | | | | | | |
| HFC-125 | X | X | | | | | |
| HFC-134a | X | X | X | | | X | X |
| HFC-143a | X | | | | | | |
| HFC-152a | X | | X | | | X | |
| HFC-227ea | X | X | X | | | X | X |
| HFC-236fa | X | X | | | | | |
| HFC-245fa | | | | X | | X | |
| HFC-365mfc | | | | X | X | X | |
| HFC-43-10mee | | | | X | X | | |
| PFC-14[3] ($CF_4$) | | X | | | | | |
| PFC-116 ($C_2F_6$) | | | | | | | X |
| PFC-218 ($C_3F_8$) | | | | | | | |
| PFC-31-10 ($C_4F_{10}$) | | X | | | | | |
| PFC-51-14[4] ($C_6F_{14}$) | | | | | X | | |

[1] Several applications use HFCs and PFCs as components of blends. The other components of these blends are sometimes ODSs and/or non-greenhouse gases. Several HFCs, PFCs and blends are sold under various trade names; only generic designations are used in this chapter.

[2] Other applications include sterilisation equipment, tobacco expansion applications, plasma etching of electronic chips (PFC-116) and as solvents in the manufacture of adhesive coatings and inks (Kroeze, 1995; U.S. EPA, 1992a).

[3] PFC-14 (chemically $CF_4$) is used as a minor component of a proprietary blend. Its main use is for semiconductor etching.

[4] PFC-51-14 is an inert material, which has little or nil ability to dissolve soils. It can be used as a carrier for other solvents or to dissolve and deposit disk drive lubricants. PFCs are also used to test that sealed components are hermetically sealed.

## 7.1.2 General methodological issues for all ODS substitute applications

### 7.1.2.1 OVERVIEW OF ODS SUBSTITUTE ISSUES

#### LEVELS OF DATA AGGREGATION

Each application discussed above can be divided into sub-applications. When selecting a method for estimating emissions, it is *good practice* to consider the number and relevance of sub-applications, the data availability, and the emission patterns. Applications with a high number of sub-applications (refrigeration has six major sub-applications; foam has even more) will generally benefit from a higher level of disaggregation in their data sets, owing to the differences between the sub-applications. Accordingly, for rigorous emissions estimates, inventory compilers are likely to favour estimating emissions for each sub-application separately. In this chapter, such an

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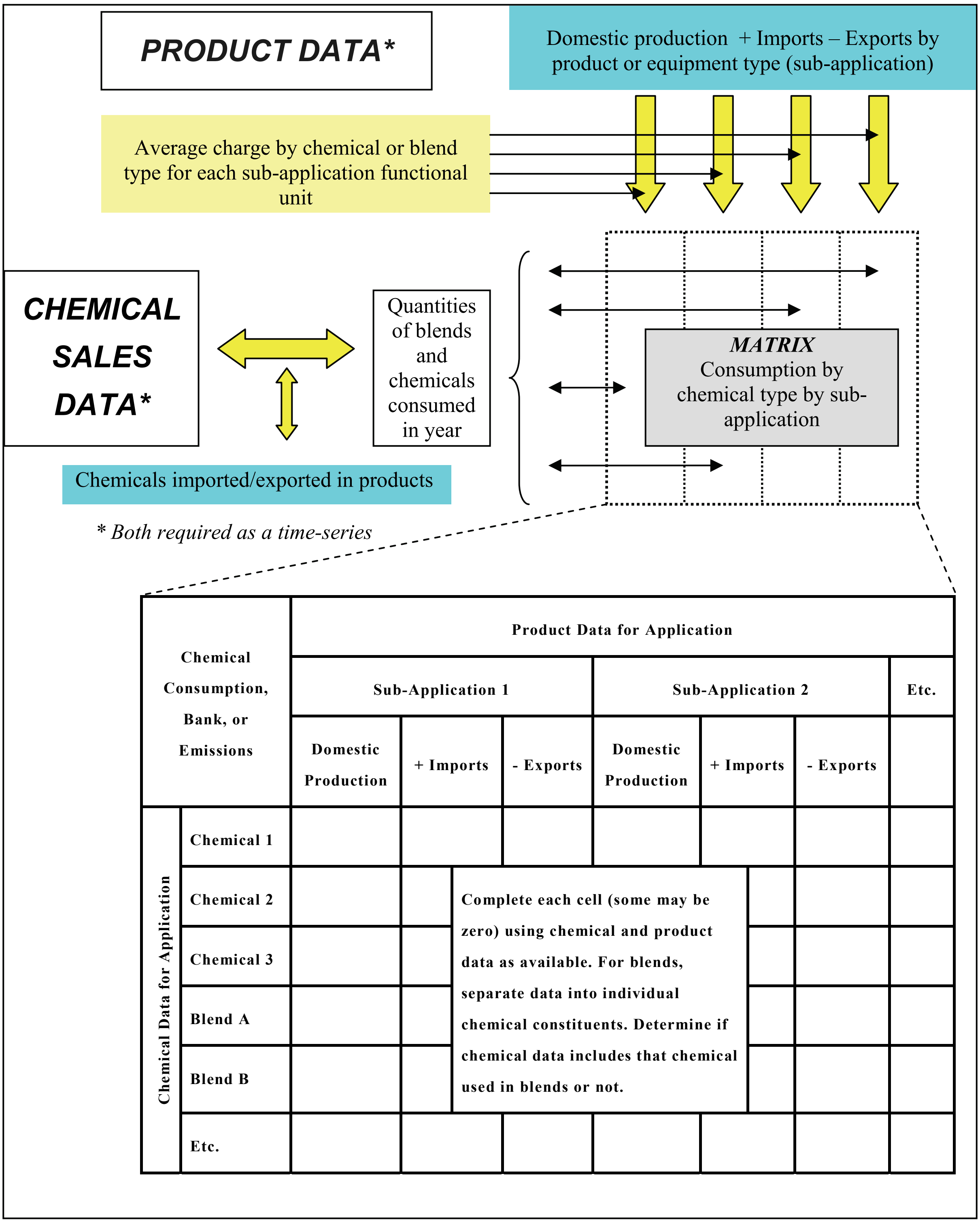
[3] Refer to http://hq.unep.org/ozone/ for the phaseout schedules dictated under the Montreal Protocol.

approach defines a Tier 2 method, whereas methods based on datasets aggregated at the application level are all classified as Tier 1. Even if few sub-applications exist, estimating emissions by sub-application may still be most appropriate owing to the differences in emission patterns, chemical use, data gathering methodologies, and/or data availability. Fire protection, for example, has only two major sub-applications, but each has unique emission characteristics and a disaggregated (Tier 2) method will produce better emission estimates. On the other hand, if emission patterns of sub-applications are similar and if data are difficult to collect in disaggregated form, estimating emissions at an aggregated application level (Tier 1) can be an appropriate approach to produce reliable emission estimates. For example, although several sub-applications exist within the aerosol propellants application, because the emission patterns and chemicals used are similar, estimating emissions at an application level may be sufficient to yield good results.

**Figure 7.1 Disaggregation of chemical data across an application**



* *Both required as a time-series*

| Chemical Consumption, Bank, or Emissions | | Product Data for Application | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Sub-Application 1 | | | Sub-Application 2 | | | Etc. |
| | | Domestic Production | + Imports | - Exports | Domestic Production | + Imports | - Exports | |
| Chemical Data for Application | Chemical 1 | | | | | | | |
| | Chemical 2 | | | Complete each cell (some may be zero) using chemical and product data as available. For blends, separate data into individual chemical constituents. Determine if chemical data includes that chemical used in blends or not. | | | | |
| | Chemical 3 | | | | | | | |
| | Blend A | | | | | | | |
| | Blend B | | | | | | | |
| | Etc. | | | | | | | |

## TYPES OF DATA

It is important early on in the estimation process to decide about how and from where data is to be collected. Data on chemical sales (sometimes referred to as *top-down* data) typically comes on a substance-by-substance basis, although even this can be complicated by the use of blends. Data on markets (sometimes referred to as *bottom-up* data) will tend to come in the form of equipment or product sales at the sub-application level, although this data will typically be influenced by the existence of imports and exports of such equipment or products. This data often need to be accompanied by an estimate of the share of the market that uses a particular technology. For example, different chemicals (including some not subject to reporting) may be used in the same sub-application. Additionally, the average amount of chemical used by each product type within the sub-application may vary. The two routes (chemicals and products) represent the two axes of a matrix and a disaggregated approach requires completion (or near completion) of that matrix (Figure 7.1). Completing this matrix is typically accomplished by using combinations of both types of data (i.e., both *top-down* and *bottom-up* data), comparing the results, and adjusting as appropriate.

## DATA AVAILABILITY

There are often difficulties in collecting data for both Tier 1 and Tier 2 methods if chemical suppliers at the national level believe that there are confidentiality implications arising from disclosure of information. In practice, this has been one of the major barriers to reliable emissions estimates at the national level.

In order to overcome some of these constraints, there has, in recent years, been an effort to develop global and regional databases which provide information on historic and current activity (chemical consumption) data at the country level for specific applications and sub-applications. The value of this approach is that these data can be validated against chemical sales at regional, or even global, level and thereby avoids breeching confidentiality restrictions required by the suppliers. As these databases have developed, (for example, those developed under the oversight of the relevant UNEP Technical Options Committees under the Montreal Protocol) they have become increasingly sophisticated in their analyses of use patterns which are often well-understood at the sub-application level (see Box 7.1). This means that the two axes of the matrix described earlier can be addressed from these datasets and Tier 2 methods can be facilitated at a country level without a massive investment of resource. This activity data can then be combined with default emission factors or with country-specific emission factor data, if this is available, to derive appropriate emissions estimates. Of course, it is important to exercise care in making use of such databases and it is important to choose reputable well-documented sources. Nonetheless, the use of globally or regionally derived data of this type can deliver reliable estimates. An alternative strategy could be to use information generated from such a database to benchmark information collected nationally.

In either case, it is important that data is generated in a form that will fit with relevant reporting requirements (e.g., the Common Reporting Format of the United Nations Framework Convention on Climate Change (UNFCCC)). These requirements may vary with time during the lifetime of these *Guidelines*. Accordingly, the structuring of activity datasets should be sufficiently flexible to deal with such changes.

In some instances the complexity of the chemical and equipment supply chain can create additional challenges regarding data availability. As highlighted in Section 7.5, there are a range of containers that can be used to supply the mobile air conditioning market, from semi-bulk containers for OEMs; to intermediate containers for the average vehicle servicing centre (10-15kg); to small 300-500g cans for the do-it-yourself market. Since wastage levels will vary substantially between these differing supply-chain approaches, inventory compilers need to consider how to assess these losses in practice. The use of containers is not only limited to mobile air conditioning, but is often prevalent in other sectors of the refrigerant market, aerosols and in fire suppression. Inventory compilers could consider treating the supply of ODS substitutes as a separate element of the inventory. However, even if this route is taken, it will require detailed knowledge of the sub-applications to understand the range of sizes used and proportion of each. Accordingly, it is viewed as most appropriate to evaluate container losses (often termed *heels*) within each application and sub-application, although it would be *good practice* to compare estimated losses within different applications and sub-applications using the similar sized containers to ensure some uniformity of approach.

### BOX 7.1
### GLOBAL AND REGIONAL DATABASES FOR ODS SUBSTITUTES

Global and regional databases are typically developed for specific applications by experts in the field. These experts often have good professional contacts with industry sources, and are familiar with access to relevant market studies and other reports that shed light onto the consumption patterns of regions and countries. From this knowledge base it is possible to cross-reference product data, either at regional level or even at global level, with chemical consumption data. It is common for such databases to predict future consumption as well as to assess current consumption. This makes them valuable also as a policy development tool. However, it is important that such databases are properly maintained and are regularly cross-checked with actual chemical consumption data whenever it becomes available in order to be assured that any new trends or other sources of discrepancy are accounted for and fully reconciled wherever possible.

For example, individual members of the UNEP Technical Options Committees (TOCs) under the Montreal Protocol have prepared a number of global activity datasets that can assist countries in preparing estimates of ODS substitute emissions. Particularly relevant are the databases used to support the development of the IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons (IPCC/TEAP, 2005), because information on the phase-out of ozone-depleting substances is directly relevant for estimating the phase-in of substitutes. The assumptions behind these datasets have been documented in a number of summary reports which can be found at http://epa.gov/ozone/snap/emissions/index.html (e.g., Clodic D., Palandre, L., McCulloch, A., Ashford, P. and Kuijpers, L.. 'Determination of comparative HCFC and HFC emission profiles for the Foam and Refrigeration sectors until 2015.' Report for ADEME and US EPA., 2004). These existing datasets have been regularly peer-reviewed by other experts from within the relevant TOCs and have been used by the Parties to the Montreal Protocol to assess transitions in chemical markets and chemical use patterns.

If national data are difficult to obtain, countries can search the IPCC Emissions Factor Database (EFDB) for datasets such as those discussed above. All such databases should be structured to facilitate their use in inventory reporting. The EFDB is likely to become the home for a number of such global/regional databases in due course, either as additional sources for applications already covered or as new sources for applications not previously covered. Although inclusion of databases in the EFDB provides general assurance of due process, it is *good practice* for countries to ensure that all data taken from the EFDB are appropriate for their national circumstances and that peer review is sufficient for this complex area of activity.

## TYPES OF EMISSION ESTIMATES

In contrast with the earlier *Guidelines*, both Tier 1 and Tier 2 methods proposed in this chapter result in estimates of *actual* emissions rather than *potential* emissions. This reflects the fact that they take into account the time lag between consumption of ODS substitutes and emission, which, as noted previously, may be considerable in application areas such as closed cell foams, refrigeration and fire extinguishing equipment. A time lag results from the fact that a chemical placed in a new product may only slowly leak out over time, often not being released until end-of-life. A household refrigerator, for example, emits little or no refrigerant through leakage during its lifetime and most of its charge is not released until its disposal, many years after production. Even then, disposal may not entail significant emissions if the refrigerant and the blowing agent in the refrigerator are both captured for recycling or destruction.

The *potential* emission method, in which emissions are assumed to equal the amount of virgin chemical consumed annually in the country minus the amount of chemical destroyed or exported in the year of consideration, is now presented only as a reference scenario in the QA/QC section. As noted above, the *potential* method does not take into account accumulation or possible delayed release[4] of chemicals in various products and equipment, which means that, over the short term (e.g., 10-15 years), estimates may become very inaccurate. Therefore, it is not considered *good practice* to use the *potential* method for national estimates.[5]

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[4] Sometimes from types of equipment and products which have since converted out of halocarbon technologies.

[5] The Conference of the Parties to the UNFCCC, at its third session, affirmed '… that the actual emissions of hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride should be estimated, where data are available, and used for

## TIMING OF EMISSIONS AND THE SIGNIFICANCE OF BANKS

In many applications ODS substitutes such as HFCs and PFCs serve their purpose only if they are contained (e.g., refrigeration and air conditioning), while in other applications, they are meant to be emitted (e.g., as an aerosol propellant). These differences are important to understand, so that the year in which emissions occur can be accurately assessed, and hence *actual* emissions can be accurately estimated.

Where emissions occur within the first two years, they are usually referred to as *prompt* emissions. Examples of applications and sub-applications exhibiting *prompt* emissions include aerosols, aerosol solvents, open-cell foams and in some cases non-aerosol solvents. In general, emissions from applications or sub-applications exhibiting *prompt* emissions can be estimated by determining annual chemical consumption and then assuming all emissions occur within the first year or two of consumption. Thus, if chemical consumption is unknown prior to a certain date, emission estimates a year or two after that date will nonetheless be accurate and relatively little accuracy will be gained by searching for or estimating chemical consumption from prior years.

Where delays in emission occur, the cumulative difference between the chemical that has been consumed in an application or sub-application and that which has already been released is known as a *bank*. Applications in which banks typically occur include refrigeration and air conditioning, fire protection, closed-cell foams, and often non-aerosol solvents. The definition of bank encompasses the presence of the chemical at all parts of the lifecycle and may even include waste streams. By way of example, blowing agent still present in foamed products which may have already been land-filled is still part of the bank, since it is chemical which has been consumed and still remains to be released. In practice, most equipment-related sub-applications (e.g. in refrigeration and fire protection) are unlikely to carry their charges into the waste stream and the total of the chemical contained in the equipment currently in use becomes a close approximation to the actual bank.

Estimating the size of a bank in an application or sub-application is typically carried out by evaluating the historic consumption of a chemical and applying appropriate emission factors. Where more than one sub-application exists, but a Tier 1 method is being followed, a composite emission factor needs to be applied. However, in view of the uncertainties surrounding such composite emission factors, Tier 2 methods will always be preferred for applications with multiple sub-applications, particularly where these are dissimilar in nature.

It is also sometimes possible to estimate the size of bank from a detailed knowledge of the current stock of equipment or products. A good example is in mobile air conditioning, where automobile statistics may be available providing information on car populations by type, age and even the presence of air conditioning. With knowledge of average charges, an estimate of the bank can be derived without a detailed knowledge of the historic chemical consumption, although this is still usually useful as a cross-check.

## APPROACHES FOR EMISSION ESTIMATES

Even among those applications which retain the chemicals over time, there are some significant distinctions. In some instances (e.g., refrigeration) the quantity of HFC or PFC is typically topped-up during routine servicing. If equipment were topped-up annually and the market was otherwise static (i.e., no growth in the equipment stock), the actual emissions would be consistent with consumption for that year. Under such circumstances, it is not necessary to know the precise equipment stock as long as the consumption of HFC or PFC is known by type at the sub-application level. This is the basis of the mass-balance approach which is referred to throughout this chapter as Approach B. More discussion on the mass-balance approach is found in Chapter 1, Section 1.5 of this volume. However, a mass-balance approach is not appropriate for other situations or for other products (e.g., foams) where consumption occurs only at the point of manufacture, while emissions may continue to a limited extent throughout the lifetime of the product. In such instances, it is usually better to revert to an emission-factor approach (i.e., methods based on activity (consumption) data and emission factors). Such methods can be operated at both aggregated (Tier 1) and disaggregated (Tier 2) levels and are referred to throughout this chapter as Approach A. Accordingly, a Tier 1a method will be an emission-factor approach with a low level of disaggregation, while a Tier 2b method will be a mass-balance approach with a relatively high degree of disaggregation (at least to the sub-application level). Further information on the choice between using a mass-balance approach and an emission-factor approach is found in Chapter 1, Section 1.5. In general, mass-balance approaches are only considered for ODS substitutes stored or used in pressurised containers and so many applications do not consider Approach B at all. Where Approach B is considered (e.g., refrigeration and fire protection) the choice of method is discussed under that part of Chapter 7 addressing the application in question.

Some methods described for these specific applications can have characteristics of both approaches, and the mass-balance approach can be used to cross-check and validate the results of an activity (consumption) data/emission factor approach. Accordingly, whilst the labelling conventions will remain unchanged throughout

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the reporting of emissions. Parties should make every effort to develop the necessary sources of data;'. (Decision 2/CP.3, Methodological issues related to the Kyoto Protocol) to avoid confusion, it may be that some methods are labelled Tier 1a/b or Tier 2a/b because they are seen to contain elements of both approaches. This is most common in the case of Tier 1 methods where data is limited and one approach can be usefully used to cross-check the other.

Table 7.2 below summarises what kind of data are required to implement different tiers and approaches.

TABLE 7.2
OVERVIEW OF DATA REQUIREMENTS FOR DIFFERENT TIERS AND APPROACHES

| | Approach A (emission-factor approach) | Approach B (mass-balance approach) |
|---|---|---|
| Tier 2 (emission estimation at a disaggregated level) | • Data on chemical sales and usage pattern by sub-application [country-specific or globally/regionally derived]<br>• Emission factors by sub-application [country-specific or default] | • Data on chemical sales by sub-application [country-specific or globally/regionally derived]<br>• Data on historic and current equipment sales adjusted for import/export by sub-application [country-specific or globally/regionally derived] |
| Tier 1 (emission estimation at an aggregated level) | • Data on chemical sales by application [country-specific or globally/regionally derived]<br>• Emission factors by application [country-specific or (composite) default] | • Data on chemical sales by application [country-specific or globally/regionally derived]<br>• Data on historic and current equipment sales adjusted for import/export by application [country-specific or globally/regionally derived] |

In the six sections that follow (Sections 7.2 to 7.7), decision trees are included for each application to assist in the identification of data needs and the selection of approach for individual sub-applications, where these exist.

### 7.1.2.2 CHOICE OF METHOD

As already described, emissions of ODS substitutes can be estimated in a variety of ways with varying degrees of complexity and data intensity. This chapter provides less data-intensive Tier 1 methods, typically based on low levels of disaggregation, and more data-intensive Tier 2 methods, which require higher levels of disaggregation. A third Tier (Tier 3), based on actual monitoring and measurement of emissions from point sources, is technically possible for specific sub-applications but this is rarely, if ever, employed for ODS substitutes, because the individual point sources are widely disparate. Accordingly, Tier 3 methods are not addressed further in this chapter.

#### TIER 1 METHODS

Tier 1 methods tend to be less data-intensive and less complex than Tier 2 because emission estimates are usually carried out at the application level rather than for individual products or equipment types. However, the approaches proposed vary considerably depending on the characteristics of the specific application. There can be Tier 1a approaches, Tier 1b approaches and, sometimes, combinations of the two (Tier 1 a/b). The latter is often the case where data are in short supply. Effectively, the output of a Tier 1a approach can be cross-checked using a Tier 1b method. In general, however, the simple methods tend to be based primarily on a Tier 1a approach (emission-factor approach) with the default emission factor being up to 100 percent for prompt release applications.

For simpler Tier 1 approaches, the chemical sales data at the application level is usually sufficient. However, separating out individual components of blends can still represent a considerable challenge. Irrespective of the Tier 1 methodology chosen, countries will need to report emissions of individual HFCs and PFCs. Information on the practical use of the various commercial types of HFC/PFC refrigerants, blowing agents, solvents, etc. will therefore be required. Many of these products are mixtures of two or more HFCs and/or PFCs, and the composition of fluids for similar purposes may vary according to individual formulas developed by different chemical companies.

#### Tier 1a – Emission-factor approach at the application level

Tier 1a relies on the availability of basic activity data at the application level, rather than at the level of equipment or product type (sub-application). This activity data may consist of annual chemical consumption data and, for applications exhibiting delayed emissions, banks derived therefrom. Once activity data have been established at the application level, composite emission factors (see Section 7.1.2.3) are then also applied at the application level. These more aggregated emission factors (e.g., all rigid foams) can be a composite or weighted average of the emission factors developed for Tier 2a covering individual equipment or product types, or can be a validated approximation approach (e.g., Gamlen *et al*. 1986).

The calculation formula for Net Consumption within the Tier 1a method is as follows:

**EQUATION 7.1**

**CALCULATION OF NET CONSUMPTION OF A CHEMICAL IN A SPECIFIC APPLICATION**

$$Net\ Consumption = Production + Imports - Exports - Destruction$$

Net Consumption values for each HFC or PFC are then used to calculate annual emissions for applications exhibiting prompt emissions as follows:

**EQUATION 7.2A**

**CALCULATION OF EMISSIONS OF A CHEMICAL FROM A SPECIFIC APPLICATION**

$$Annual\ Emissions = Net\ Consumption \bullet Composite\ EF$$

Where:

Net Consumption = net consumption for the application

Composite EF = composite emission factor for the application

Note that, as discussed in the Choice of Activity Data section, inventory compilers may have access to chemical consumption data at the aggregate level rather than by application. In this case, it will be necessary as an early step to determine the share of total consumption represented by each application.

In equation 7.1, *Production* refers to production of new chemical. Reprocessing of recovered fluid should not be included in consumption estimates. *Imports* and *Exports* include bulk chemicals but, for a Tier 1 method is unlikely to contain the quantity of chemical contained in products, such as refrigerators, air-conditioners, packaging materials, insulating foams, fire extinguishers etc. unless regional allocation system or other method of approximation has been used. The term *composite emission factor* refers to an emissions rate that summarises the emissions rates of different types of equipment, product or, more generally, sub-applications within an ODS application area. Composite emission factors should account for assembly, operation and, where relevant in the time-series, disposal emissions.

Although destruction of virgin HFCs and PFCs is not currently practised widely, and may be technically difficult in some cases (UNEP TEAP Task Force on Destruction Technologies (UNEP-TEAP, 2002)), it should be included as a potential option to reduce consumption. It should be noted that destruction of virgin chemicals, as considered here, is distinct from the destruction of HFCs and PFCs in the end-of-life phase, which is strictly an emission reduction measure. By-product emissions during HFC/PFC production and fugitive emissions related to production and distribution have to be calculated separately.

Even in simple Tier 1a methods, it is usually necessary to account for the potential development of banks, where these can occur. Banks are the amounts of chemical that have accumulated throughout the lifecycle, either in supply chains, products, equipment or even waste streams but which, as of the end of the most recent year, has not been emitted. At the application level, banks can be estimated using relatively straight-forward algorithms and assumptions provided that the historic Net Consumption is known for each year following the introduction of the substance or, where this period exceeds the average lifetime of the product or equipment, over that average lifetime. Relevant application level emission factors are then applied to the banks to deal with emissions during the lifetime of the products or equipment. This same process is carried out for Tier 2a methods but, in that case, at the sub-application level. More general information on banks is contained in Section 7.1.2.1.

In cases where banks occur, Equation 7.2A is then modified to the following:

**EQUATION 7.2B**

**CALCULATION OF EMISSIONS OF A CHEMICAL FROM AN APPLICATION WITH BANKS**

$$\begin{aligned} Annual\ Emissions = {} & Net\ Consumption \bullet Composite\ EF_{FY} \\ & + Total\ Banked\ Chemical \bullet Composite\ EF_{B} \end{aligned}$$

Where:

Net Consumption = net consumption for the application

Composite $EF_{FY}$ = composite emission factor for the application for first year

Total Banked Chemical = bank of the chemical for the application

Composite $EF_B$ = composite emission factor for the application for bank

Composite emission factors are determined by taking an average of the applicable sub-application emission factors, weighted according to the activity in each sub-application. Sub-application emission factors can be country-specific where known or default. In practice, if sub-application data are known, inventory compilers would opt for a Tier 2 (disaggregated approach). If only application level data are known, representative composite emission factors from other studies or default composite emission factors provided in this chapter can be used.

### Tier 1b – Mass-balance approach at the application level

The mass balance approach also estimates emissions from assembly, operation, and disposal, but does not rely on emission factors. Instead, the method uses measured consumption (i.e., sales) of each chemical in the country or facility being considered. It is generally limited to ODS Substitutes contained in pressurised systems. The general equation is as follows[6]:

**EQUATION 7.3**
**GENERAL MASS BALANCE EQUATION FOR TIER 1b**

$$Emissions = Annual\ Sales\ of\ New\ Chemical - (Total\ Charge\ of\ New\ Equipment$$
$$- Original\ Total\ Charge\ of\ Retiring\ Equipment)$$

Industry needs to purchase new chemical from manufacturers in order to replace leakage (i.e., emissions) from the current equipment stock, or the equipment will not function properly. If the equipment stock did not change from year to year, then annual chemical consumption alone would provide a reasonable estimate of actual leakage or emissions. The total equipment stock, and the chemical charge it contains, however, does change from year to year. Some amount of new equipment containing a chemical charge is introduced each year, and some amount of old equipment that was charged originally is retired each year. If the total chemical charge contained in all equipment is increasing as a result of this annual turnover, then total annual chemical consumption will overestimate emissions (i.e., the charge contained in new equipment is greater than the original charge of the retired equipment). Conversely, if the total chemical charge in all equipment is decreasing, then total annual chemical consumption will underestimate emissions.

In order to make good use of data on annual sales of new chemical, it is therefore also necessary to estimate the total charge contained in new equipment, and the original charge contained in retiring equipment. The total charge of new equipment minus the original total charge of retiring equipment represents the net change in the charge of the equipment stock. (Using the mass balance approach, it is *not* necessary to know the total amount of each chemical in equipment stock in order to calculate emissions.) Where the net change is positive, some of the new chemical is being used to satisfy the increase in the total charge, and therefore cannot be said to replace emissions from the previous year.

Industry also requires new chemical to replace destroyed gas and for stockpiles. Additionally, not all equipment will be serviced annually. Terms can be added to the general equation to account for these factors but are not typically adopted within simple Tier 1b methods.

This approach is most directly applicable to the pressure equipment used in refrigeration and air conditioning, and fire protection applications because these are where chemical sales are most typically used to offset operational emissions. However, since the basic method is relatively simple to apply, it is more typical to extend the approach to the sub-application level (i.e., a Tier 2b method). Further elaboration and modification of this approach is provided in the description of each application. In practice, Tier 1b methods are most commonly used as a further cross-check to Tier 1a methods. Where basic Net Consumption data is lacking, regional and international databases and models have been developed that allocate regional chemical sales for different end uses (sub-applications) at a country level. These can therefore be used to source relevant data.

## TIER 2 METHODS – APPLIED AT THE SUB-APPLICATION LEVEL

There are two versions of the Tier 2 method, both of which result in emission calculations for each individual chemical and distinct types of products or equipment at the sub-application level or within a sub-application. The

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[6] Boundary conditions: If there is no net change in the total equipment charge, then annual sales are equal to emissions. If the net change in the total equipment charge is equal to annual sales, then emissions are zero.

individual chemicals and products/equipment within the sub-application form the matrix referred to earlier in this section and their analysis is comparable with methods currently applied by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) for CFCs, HCFCs and HFCs (McCulloch, Midgley and Ashford, 2001 and 2003; Ashford, Clodic, Kuijpers and McCulloch, 2004).

Both versions of the Tier 2 methodology follow two general steps:

i. Calculation or estimation of the time series of net consumption of each individual HFC and PFC chemical at a relatively detailed product and equipment level to establish the consumption basis for emission calculations. (e.g., refrigerators, other stationary refrigeration/AC equipment, appliance foams, insulated panels, pipe insulation, etc.)

ii. Estimation of emissions using the activity data and resulting bank calculations derived from step (i), and either emission factors that reflect the unique emission characteristics related to various processes, products and equipment (Tier 2a) or, relevant new and retiring equipment information at the sub-application level to support a mass balance approach. (Tier 2b).

The difference between Tier 2a and Tier 2b is the same as that for Tier 1a and Tier 1b – namely Tier 2a methods use an emission-factor approach while Tier 2b methods follow a mass-balance approach. Both, however, need to be operated at a level of disaggregation appropriate to a Tier 2 method, typically at least at the sub-application level.

If the requisite data are available, a Tier 2 method is preferred for estimating emissions from ODS substitutes, particularly where the sub-applications within an overall application area are relatively heterogeneous. Some countries may already have the relevant information available to apply a Tier 2 methodology. Other countries might not have access to data for Tier 2 at present, but they are encouraged to establish routines to collect either country-specific or globally or regionally-derived activity data by chemical and sub-application within an application area (e.g., different types of refrigeration and air conditioning sub-applications). Tier 1, in contrast, requires data collection at a more aggregated application level (e.g., refrigeration and air conditioning in its totality).

As a first step in using the Tier 2 method, countries may wish to make first order approximation of the information needed for step (i). This will give direction to more focused data collection efforts in certain application areas or sub-categories. Table 7.3 gives examples of HFC/PFC consumption distribution at the application level in 2002 among various application areas in selected countries. Since HFCs and PFCs have only recently entered the market in some applications, the relative size of consumption in each application will continue to change over time and should be updated regularly at a country level.

TABLE 7.3

EXAMPLE DISTRIBUTION OF HFC/PFC USE BY APPLICATION AREA (2002)[a]

| Country | Refrigeration Air Conditioning | Foam Blowing | Solvent[b] | Fire Protection[b] | Aerosol Propellant[b] | Other Applications[b] |
|---|---|---|---|---|---|---|
| Austria | 18% | 81% | 0% | 1% | 0% | 0% |
| Denmark | 81% | 18% | 0% | 0% | 1% | 0% |
| Norway | 72% | 11% | 0% | 16% | 1% | 0% |
| Sweden | 48% | 42% | 0% | 4% | 6% | 0% |
| United Kingdom | 31% | 22% | 0% | 9% | 38% | 0% |

[a] UNFCCC Reported Data for 2002 as re-submitted in 2004

[b] A zero declaration may not always reflect non-use but could reflect reporting under other categories.

G*ood practice guidance* in this section deals with variations of the Tier 2 method. Tier 1 methods, covered previously, are generally seen as default methods where the application is not a *key category* and data availability is limited. (Exceptionally, for Fire Protection, Tier 1a method with country-specific activity data and emission factor will be used in the case it is identified as *key category*.) Each sub-section of Sections 7.2 to 7.7 discusses how to apply these methods to specific ODS applications, reviews existing data sources, and identifies gaps therein.

### Tier 2a – Emission-factor approach

The country-specific data required for a Tier 2a approach are derived from the number of products and end-uses relevant to each sub-application in which ODS substitutes are contained and from which ODS substitutes are ultimately emitted. This approach seeks information on the number of equipment units or products that use these chemicals, average chemical charges, average service life, emission rates, recycling, disposal, and other pertinent parameters. This information is generally collected at the level of distinct groups of products or equipment (e.g., for rigid foams: integral skin, continuous panel, discontinuous panel, appliance, injected foam products and others). Annual emissions are then estimated as a function of these parameters through the life of the units or products by the application of emission factors that are relevant to the lifecycle phases. Since equipment and other products vary significantly in the amount of chemical used, service life, and emission rates, the characterisation of this equipment can be a resource intensive task. The longer-lived the end-use equipment or product, and the more diverse the types of equipment or product within a particular sub-application, the more complex the sourced data approach has to be in order to account for emissions. However, the approach can provide an accurate estimate of emissions if the data called for by the following equation are available for all relevant types and vintages of equipment or product:

**EQUATION 7.4**
**SUMMARY EMISSIONS EQUATION BASED ON PHASES OF THE LIFECYCLE**

$$\begin{aligned} \textit{Total Emissions of Each PFC or HFC} &= \textit{Assembly/Manufacturing Emissions} \\ &\quad + \textit{Operation Emissions} \\ &\quad + \textit{Disposal Emissions} \end{aligned}$$

*Manufacturing or Assembly Emissions* occur as fugitives when new equipment is filled for the first time with a chemical or when a product is manufactured. *Operational Emissions* from equipment and products occur as leaks or by diffusion during the use phase of the product or equipment (including servicing). In some cases, there can even be intentional releases during operation. Finally, *Disposal Emissions* can occur when the equipment or product reaches its end-of-life and is decommissioned and disposed of. In this case, the remaining HFC/PFC in the product or equipment may escape to the atmosphere, be recycled, or possibly destroyed.

As with the Tier 1a method, there is a need to make provision for the development of banks in some applications. This can lead to complex multiple calculations at the sub-application level, since the dynamics of banks may vary considerably. However, because the individual algorithms rely on a simple sequential calculation of non-emitted consumption (i.e., consumption – emissions for each successive year), excellent emission assessments can result from a well-constructed and well-maintained national model.

The need to update equipment and product inventories on an annual basis can be a major implementation challenge for inventory compilers with limited resources. This challenge is made somewhat easier because it may not be necessary to collect annual chemical consumption if a comprehensive set of other market parameters is available (e.g., number of domestic refrigerators produced, etc.) In some countries or regions, trade associations can be a significant source of such data. Otherwise, specific market research may be necessary. Where such market parameters are the primary source of activity data, the potential magnitude of errors that can be introduced by small discrepancies at unit level makes it *good practice* to carry out a chemical consumption data cross-check to act as a means of providing quality assurance. The relevant QA/QC sections of this chapter give guidance on how to conduct such cross-checks for each relevant application.

In order to limit the burden of data management for both annual consumption data and the status of banks, it is possible to access international and regional databases of such information to gain the necessary inputs of globally or regionally validated data to maintain a national model. These databases can also help to overcome any confidentiality barriers that may exist in collecting and/or publishing data at a national level, particularly where the number of suppliers is low. More information on the use of such databases is contained in Section 7.1.2.4 and Box 7.1.

Even where comprehensive country-specific activity data exists at a country level, it is *good practice* to benchmark outputs against assessments made from databases of globally or regionally derived data. This need not be done on an annual basis but could reasonably be conducted every 2-3 years. Significant discrepancies can then be analysed and suitable actions taken to reconcile differences.

### Tier 2b – Mass-balance approach

Tier 2 mass-balance approaches are similar to those described for Tier 1b, except that the process is applied at the sub-application level. This is a particularly valuable approach for the refrigeration sector where there are a significant number of relatively heterogeneous sub-applications. As is also the case for Tier 1 methods, it is not uncommon to see mass-balance approaches used in combination with emission-factor approaches to ensure that the outputs achieved are as robust as possible. Such approaches can realistically be described as hybrid Tier 2a/b methods and they will be identified as such, where they occur in the relevant application-specific sections that follow.

Since mass-balance approaches also require activity data at the sub-application level, it may be more resource-efficient to use global or regional databases to obtain appropriate globally or regionally validated data. The same criteria for selection as set out for Tier 2a methods also apply for Tier 2b methods. Accordingly, equal care should be taken in selecting validated datasets.

#### 7.1.2.3 CHOICE OF EMISSION FACTORS

Emission factors are required for all methods following Approach A. In general terms, emission factors can be of two distinct types:

1. Emission factors derived from actual measurements of products or equipment at a national level during the various phases of their lifecycle (*country-specific*),

or

2. Emission factors inferred from wider regional or global sub-application experience (e.g., *default*).

The type of emission factor required will depend on the level of homogeneity within the sub-application, the Tier approach being implemented, the dependence of emission factors on field practices applied, the role of banks and the likelihood of specific national circumstances. In some cases, the application will be or may be reasonably considered to be totally emissive, in which case the net consumption for a given year will become the emissions estimate for that year (e.g., many aerosol applications). In such a situation, a default emission factor would normally be more than adequate. However, in most cases involving ODS substitutes, some delay in emission is anticipated. Accordingly emission factors may need to be more sophisticated, particularly when applied at the sub-application level (Tier 2).

Because Tier 1 methods typically operate at the application level, it is necessary to use composite emission factors, which can be either based on weighted averages of known sub-application emission factors (country-specific or default) or on validated approximation approaches. Since Tier 1 methods are intended to be simple in their application, inventory compilers have the option of using existing composite emission factors based on the work of others. The Tier 1a approaches outlined in Sections 7.2 to 7.7 make such provision.

For Tier 2 methods, inventory compilers need to be aware of the specific circumstances surrounding the sub-applications in their countries. Although product and equipment types can be similar throughout a region or, even globally, there can be significant differences in emission factors over the lifetime of the product or equipment. Such differences can arise from climatic factors, construction methods, regulatory approaches and, in particular, from servicing methods where these apply. An additional factor to be considered in many countries is the management of the disposal of products and equipment at the end of its service life, which can have a profound effect on the total emissions. The chemical remaining in systems at that stage can be 90 percent or more of the original quantity used. Specific issues related to emission factors are discussed in the relevant application sections.

Therefore, inventory compilers should ensure that their derivation takes into consideration these potential sources of variation. This is often best done by comparing selections with those chosen by other countries with similar circumstances. Where emission factor variation is seen to be significant (e.g., distinction between developed and developing country experience with refrigeration equipment), the item is highlighted in relevant application-specific sections of this chapter.

As an additional support to inventory compilers, the most significant emission factors are included in the Emissions Factor Database (EFDB) administered by IPCC. The extensive editorial review process ensures that listed emission factors in the EFDB are properly examined to insure their robustness. Since emission factors in the EFDB tend to be adjusted less frequently than globally or regionally derived activity data, the review process can usually keep up with developments, thereby ensuring that listed values are broadly current.

#### 7.1.2.4 CHOICE OF ACTIVITY DATA

For ODS substitutes, activity data consist of the net amount of each chemical consumed annually in a country in an application, sub-application or more detailed equipment/product type. When adopting a Tier 2a method, it is often necessary to collect activity data for the number of units of a particular equipment or product type in existence to estimate the amount of chemical consumed or in banks.

Where banks of chemical are likely to occur, it is also necessary to have information on historical annual net consumption patterns, either since the year of introduction of the chemical or over the average lifetime of products or equipment within the application or sub-application. This allows for the calculation of the cumulative bank in cases where emission factors must then be applied (Tier 1a or Tier 2a methods).

As noted previously, reprocessing of recovered fluid should not be included in consumption estimates. Imports and exports include not only bulk chemicals, but, for Tier 2 methods in particular, may also include the quantity of chemical contained in products, such as refrigerators, air-conditioners, packaging materials, insulating foams, fire extinguishers, etc., depending on whether regional allocation has been used or not. Usually, it is notoriously difficult to obtain data on HFCs and PFCs contained in equipment or products unless a specific customs regime has been set up to address this issue. This will only likely be practiced, if at all, in conjunction with the implementation of a Tier 2 method and is unlikely to be available for Tier 1 methods, making the availability of globally or regionally derived data particularly important, at least as a cross-check, if significant product or equipment trade is expected.

Such globally or regionally derived net consumption (activity) data can be obtained from the datasets contained in regional and global databases. Under this approach, chemical sales data are sometimes assigned from wider regional consumption information on the basis of some geo-economic factor such as population, GDP or number of dwellings. When using this market-based allocation method, it might not be necessary to take account of HFCs and PFCs contained in products being imported or exported, if the regional treatment causes netting out of intra-regional trade (i.e., imports and exports of products containing HFCs and PFCs within a region are roughly balanced). Where extra-regional trade is significant, then the HFCs and PFCs contained in products will need more careful consideration.

Since activity data will be more prone to annual change than emissions factors, the source of globally or regionally derived data used by the inventory compilers needs to be updated regularly. Reliable global databases carrying this information are regularly cross-checked with global sales data for individual chemicals and sub-applications, thereby ensuring regular validation. When accessing such databases, it is *good practice* for inventory compilers to ensure that the information they are receiving has been so validated. As noted in Box 7.1, Global and Regional Databases for ODS Substitutes, inclusion in the IPCC EFDB will indicate general adherence to due process, but it is *good practice* for countries to ensure that all data taken from the EFDB are appropriate for their national circumstances.

### Specific considerations when collecting country-specific activity data

The collection of country-specific activity data requires an inventory of HFC/PFC net consumption for each chemical and, where emissions lag behind consumption, an inventory of banked chemicals. Some inventory compilers may have access to national data published in trade magazines or technical reports. If these data are not available directly, they can be estimated by means of a special study to estimate the inventory of existing units or chemicals. Expert panels can also facilitate the generation of this information. Care must be taken to ensure that the scope of any datasets cited is understood and that any remaining gaps are identified.

Inventory compilers may also decide to conduct annual studies to update their inventories of different types of equipment/products. An alternative to this may be to calculate or estimate production growth for each one of the sub-applications under consideration. Data need to reflect new units that are introduced each year, and old or poorly functioning units that are retired.

Data on national chemical use are more easily obtained than data for the amount of equipment responsible for emissions, provided that confidentiality constraints do not intervene. It is always *good practice* to obtain data on the total annual sales from the chemical manufacturers or importers. The best source of data on the total charge of new equipment is likely to be the equipment manufacturers or the trade associations that represent them. For the total charge of retiring equipment, it is essential to obtain information on or estimate (i) equipment/product lifetime, and (ii) either (a) the historical sales of equipment/product and the historical average charge size or formulation, or, (b) the growth rate of such sales and charge sizes over the period in question, where such information is known for the current year.

Inventory compilers in countries that import all or the majority of new chemicals consumed are likely to encounter different issues of data availability than those in countries with significant domestic chemicals production. If the majority of chemicals are imported, either in bulk or in equipment and products, some form of import data will be necessary for calculating emissions. Ideally, customs officials should track and make available chemical import statistics. For some products, such as foam and aerosols, it may not be possible for customs officials to track the type of chemical in the product (e.g., Hydrocarbons vs. HFCs in aerosols), or the presence of the product in the imported equipment (e.g., closed cell foam in refrigerators). In such cases, it may be necessary to collect or estimate data with the assistance of major distributors and end-users.

As noted previously in this Section, the ability to obtain relevant country-specific activity data and banking information on a consistent basis at a country level can be constrained by such issues as confidentiality, lack of downstream industry networks and lack of trade information in products-containing HFCs and/or PFCs. Reconciliation is therefore often better achieved at regional level or even global level in some cases. In making this comment, it should be noted that the use of country-specific and globally or regionally derived data is not specifically an 'either/or' choice. In many cases, the development of a country's overall inventory may rely on a combination of data from both sources. In any event, the use of one to verify the other is actively encouraged as *good practice*.

#### Specific considerations when using the mass-balance approach (Tier 1b or 2b)

Activity data for a mass balance approach (Tier 1b or 2b) focus on chemical deployment rather than sources of emissions. These activity data include annual sales of new chemical, the total charge of new equipment, and the total charge of retiring equipment. If these data are not available at the national level, then globally or regionally derived data can be used, as for Approach A (emission-factor approach). Since the mass-balance approach is generally reserved for pressurised equipment in the refrigeration, air conditioning and fire protection applications, it is useful to know that comprehensive global databases already exist for these.

#### Time dependency of data contained in these Guidelines

The products and equipment in which ODS substitutes are used have changed significantly over time, and are expected to continue to change. As a result, where information on activity data and default emission factors is contained in these *Guidelines*, it should be noted that activity data will be a more volatile component than emission factors in determining overall emissions. Accordingly, any default activity information contained herein will 'age' more rapidly and will lead to greater inaccuracies with the passage of time unless appropriate adjustments are made for market growth in the interim. Global and regional databases for ODS substitutes noted in Box 7.1 will generally reflect these changes. Where ODS transitions are still in the future, the adoption of static activity data could lead to very significant errors in emission projections.

### 7.1.2.5 COMPLETENESS

Completeness is assured to a large extent for ODS Substitutes as a result of well-documented use patterns for ODSs themselves and by the fact that activity data, assessed at the application and sub-application levels, can be validated against total chemical sales. This is particularly the case for those HFCs and PFCs which are only used as ODS substitutes. However, it is still important to be able to identify all potential HFCs and PFCs in use. Table 7.1 gives an overview of the main HFCs and PFCs to be considered, but this may not be exhaustive, particularly when it comes to the components of blends, which can often be complex in their composition.

One set of emissions which is not covered routinely within this source category are those arising from chemical production itself. However, methods for assessing these emissions are covered within Chapter 3, Section 3.10.

It is possible for emissions to exceed consumption (activity) in a given year owing to emission of previously accumulated banks and therefore completeness of emissions reporting can only be established in Tier 2 approaches by plotting cumulative emission versus cumulative activity for the total period over which consumption and resulting emissions have occurred (i.e., cumulative consumption equals cumulative emissions plus current bank less cumulative destruction).

### 7.1.2.6 DEVELOPING A CONSISTENT TIME SERIES

Inventory compilers that have prepared basic (Tier 1) estimates in the past are encouraged to develop the capacity to prepare Tier 2 estimates in the future. It is *good practice* to ensure that only actual emission estimates are included in the same time series. Inventory compilers should recalculate historical emissions with the preferred actual method, if they change approaches. Since all Tier 1 and Tier 2 approaches are now actual emission methods, there is no problem in mixing these approaches for different applications or sub-applications. However, if potential emission methods have previously been used, the time series needs to be recalculated. If data are unavailable, the two methods should be reconciled to ensure consistency, following the guidance on recalculation provided in Volume 1, Chapter 5. It is *good practice* to provide full documentation for the recalculation, thereby ensuring transparency.

Emission factors generally come from historical data on other chemicals (e.g., CFCs) used in established markets. These factors need to be adapted to new chemicals (e.g., ODS substitutes) where new uptake occurs. National data on base year deployment is now available (or can be calculated with known uncertainty).

## 7.1.3 Uncertainty assessment

Over a long time (greater than 50 years in some applications) cumulative emissions of ODS substitutes within a country will tend to equal cumulative consumption in the same time frame unless significant end-of-life recovery has been practised. For a given year, the quantification of uncertainty for ODS is very difficult to estimate, due to the large number of different sources and the diversity of emission patterns. For the Tier 1b and 2b methods, the overall uncertainty will be directly related to quality and completeness of chemical sales and import data at either the application or the sub-application level. These factors will be equally important for Tier 1a methods but there will be additional sources of uncertainty arising from the use of composite emission factors and other assumptions required to complete specific algorithms. For the Tier 2a method, the uncertainty will reflect the completeness of the equipment survey, and the appropriateness of the emission factors developed at the sub-application level to characterise emissions. Further advice on uncertainties is provided in the separate sections on the six application areas that follow.

## 7.1.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation for all ODS substitutes applications

### 7.1.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) FOR ALL ODS SUBSTITUTES APPLICATIONS

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from these applications or sub-applications. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4. In addition to the guidance in Volume 1, specific procedures of relevance to this source category are outlined below.

Even with such provisions in place to deal with activity data, the real emission data for a given year will never be exactly known, irrespective of the refinement of the estimation methods. Hence, cross checking of integrated emission figures against real net consumption of HFC/PFC, together with judgement of banking over the same period of time must be performed at regular intervals, and the input factors have to be adjusted to achieve agreement over time.

#### Comparison of emissions estimates using different approaches

Inventory compilers should compare equipment/product based estimates at the sub-application level (Tier 2a) with the mass-balance Tier 1b or 2b approach, where appropriate, since emission factors at the product level have an inherent associated uncertainty. This technique will also minimise the possibility that certain end-uses are not accounted for in the equipment/product based approaches.

#### Potential emissions estimates as a reference scenario

Inventory compilers may also choose to use the potential emissions reference scenario as a check on the Tier 1 or Tier 2 actual estimates. Inventory compilers may consider developing accounting models that can reconcile potential and actual emissions estimates and may improve determination of country-specific emission factors over time. When taken alongside estimates of actual emission from determinations of atmospheric concentrations, this scenario can assist in monitoring the growth of banked greenhouse gases caused through delays in emission and, thereby, keeps track of likely future environmental burdens. This ultimate means of mass balance verification is particularly powerful for HFCs and PFCs because of their unique identities and lack of natural sources.

Potential emissions of a certain chemical are equal to the amount of virgin chemical consumed annually in the country minus the amount of chemical recovered for destruction or export in the year of consideration. (See Annex 2 of this volume.) All chemicals consumed will eventually be emitted to the atmosphere over time if not permanently encapsulated, chemically converted, or destroyed[7], and in the long term (in excess of 50 years for

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[7] The destruction of fluorocarbons can be costly but there are several destruction processes recommended by the Parties to the Montreal Protocol: liquid injection incineration; reactor cracking; gaseous/fume oxidation; rotary kiln incinerators; cement kilns; plasma destruction; municipal solid waste incinerators (foams only).

some applications), cumulative potential emissions will equal cumulative actual emissions for those applications which ultimately cease use of HFCs and/or PFCs and where capture and destruction are not practised.

Since accumulation is thought to be the dominant process at the present time in the major areas of usage, such as refrigeration and foams, potential emission calculations will strongly overestimate emissions and are inappropriate as a formal annual reporting method.

The error is minimised when enough time has passed for HFC/PFC-containing equipment and products to begin to be retired, although, even then, the rate of subsequent emission may depend on the end-of-life strategy chosen. However, as long as emissions lag behind consumption and consumption continues to grow, the overestimation will persist. The error is zero only if there is no delay in emissions or if the consumption growth rate is zero for a long period of time.

#### National activity data check

For the Tier 2 method, inventory compilers should evaluate the QA/QC procedures associated with estimating equipment and product inventories, whether country-specific, regionally or globally derived, to ensure that they meet the general procedures outlined in the QA/QC plan and that representative sampling procedures were used. This is particularly important for the ODS substitutes equipment/product types because of the large populations of equipment and products.

For the Tier 1b (mass balance) method, inventory compilers should evaluate and reference QA/QC procedures conducted by the organisations responsible for producing chemical deployment information. Sales data may come from gas manufacturers, importers, distributors, or trade associations. If the QC associated with the secondary data is inadequate, then the inventory compiler should establish its own QC checks on the secondary data, reassess the uncertainty of the emissions estimates derived from the data, and reconsider how the data are used.

#### Emission factors check

Emission factors used for the Tier 2a method should ideally be based on country-specific studies. Where such an approach is used, inventory compilers should compare these factors with the defaults and any values which may be contained in the EFDB or elsewhere in support of Tier 2a methods. They should determine if the country-specific values are reasonable, given similarities or differences between the national circumstances surrounding the sub-application in question and those assumed within the defaults. Any differences between country specific factors and default factors should be explained and documented.

### 7.1.4.2 REPORTING AND DOCUMENTATION FOR ALL ODS SUBSTITUTES APPLICATIONS

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11.

As discussed above, inventory compilers should prepare and report actual emissions estimates for as many sub-applications as possible. This is now aided by the availability of globally or regionally derived activity data in regional and global databases (see Box 7.1) together with emission factors for several sub-applications contained in the EFDB. For those equipment/product types where it is not possible to prepare actual emissions estimates at the sub-application level (i.e., Tier 2 estimates), even with this additional support, inventory compilers should prepare and report actual emission estimates using Tier 1 methods at the application level.

The balance between preservation of confidentiality and transparency of the data needs to be carefully addressed. Careful aggregation may solve some problems but will require that results are validated by other means (e.g., third party audit). Where data have been aggregated to preserve the confidentiality of proprietary information, qualitative explanations should be provided to indicate the method and approach for aggregation.

# 7.2 SOLVENTS (NON-AEROSOL)

## 7.2.1 Chemicals covered in this application area

HFCs are now used in solvent applications to a much lower extent than CFC-113 was used prior to phase-out, and PFCs are still only very rarely used. HFC/PFC solvent uses occur in four main areas as follows:

(i) Precision Cleaning;

(ii) Electronics Cleaning;

(iii) Metal Cleaning;

(iv) Deposition applications

HFCs are typically used in the form of an azeotrope or other blend for solvent cleaning. The most commonly used HFC solvent is HFC-43-10mee, with some use of HFC-365mfc, HFC-245fa (as an aerosol solvent[8]), and heptafluorocyclopentane (U.S. EPA, 2004b). This allows for tailoring the balance between effective cleaning and compatibility with materials of construction of the work-piece. The pure material does not have the cleaning power of CFC-113, since no chlorine atoms are present in the molecule.

In general, perfluorocarbons have little use in cleaning, as they are essentially inert, have very high GWPs and have very little power to dissolve oils - except for fluoro-oils and fluoro-greases for even deposition of these materials as lubricants in disk drive manufacture. Accordingly, PFCs only find rare uses in the solvent sector as blanketing fluids for 2-propanol cleaning systems (per British Aerospace military section) or in the now obsolete Advanced Vapour Degreasing (AVD) heterogeneous co-solvent system. Such PFCs can be used as blanketing fluids to prevent the loss of the more costly primary fluids in dual-fluid vapour phase soldering systems. PFCs can be used as the only working fluid in single-fluid vapour phase soldering systems. In the component manufacturing sector, PFCs are used to test the hermeticity of sealed components. Further information on the use of PFCs in the electronics industry is found within Chapter 6 of this volume.

In general, the major PFC manufacturers converted all former PFC users to HFC or hydrofluoroether (HFE) use in cleaning applications.

## 7.2.2 Methodological issues

### 7.2.2.1 CHOICE OF METHOD

Historically, emissions from solvent applications generally have been considered *prompt* emissions because 100 percent of the chemical is typically emitted within two years of initial use. (IPCC, 2000). In order to estimate emissions in such cases, it is necessary to know the total amount of each HFC or PFC chemical sold in solvent products each year. Emissions of HFCs and PFCs from solvent use in year t can be calculated as follows.

**EQUATION 7.5**

**EMISSION ESTIMATION METHOD FOR SOLVENT USES**

$$Emissions_t = S_t \bullet EF + S_{t-1} \bullet (1 - EF) - D_{t-1}$$

Where:

$Emissions_t$ = emissions in year *t*, tonnes

$S_t$ = quantity of solvents sold in year *t*, tonnes

$S_{t-1}$ = quantity of solvents sold in year *t*–1, tonnes

EF = emission factor (= fraction of chemical emitted from solvents in the year of initial use), fraction

$D_{t-1}$ = quantity of solvents destroyed in year *t*–1, tonnes

Table 7.1 indicates the known HFCs and PFCs used in solvent applications, although *good practice* is to research the country-specific situation in case any previously unidentified applications have arisen. The scope of

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[8] Emissions of aerosol solvents are included as an aerosol (see Section 7.3).

the search is aided by the fact that the inventory compiler is only looking for applications where ODSs were previously used.

The approach set out in Equation 7.5 can be applied as either a Tier 1a or a Tier 2a method, based as it is on Approach A (emission-factor approach). Whether the approach qualifies as a Tier 1 or Tier 2 method will depend on whether there are identifiable sub-applications within the solvent usages in the reporting country (e.g., the four main areas identified above). As trends have developed towards more controlled solvent environments, the need for a Tier 2 approach has increased. In some cases, there may be highly controlled sub-applications (e.g., in the precision electronics industry) where specific emission factors are fully characterised. These would be treated differently from more general solvent applications which may remain based on the default emission factor. It should be noted that Equation 7.5 assumes total release of solvent within two years regardless of the emission factor applied in year t. Additionally, there is no consideration of recovery and recycling, which may be a factor in some situations. However, it would be assumed that recovery and recycling would, in general, be reflected in reduced sales of virgin materials. Solvent recovered and subsequently destroyed is considered, but is an unlikely course in practice bearing in mind the cost of the chemicals involved.

### 7.2.2.2 CHOICE OF EMISSION FACTORS

The emission factor EF represents the fraction of chemical emitted from solvents in year t. The product lifetime is assumed to be two years, and thus any amount not emitted during the first year is assumed by definition to be emitted during the second and possibly final year. A decision tree for estimating actual emissions is included in Figure 7.2, Decision Tree for Actual Emissions from the Solvents application. The data collection process is described in Section 7.2.2.3.

In the absence of country-specific data, it is *good practice* to use a default emission factor of 50 percent of the initial charge/year for solvent applications.[9] In certain applications with new equipment incorporating low emission design features, it is very possible that much lower loss rates will be achieved and that emissions will occur over a period of more than two years. Alternative emission factors can be developed in such situations, using data on the use of such equipment and empirical evidence regarding alternative emission factors.[10] Such country-specific emission factors should be documented thoroughly (Tier 2a). The 'mix' of hand operated batch cleaning systems and automated conveyorised systems within a country or region may result in very different emissions. Attention to proper work practices, setup of the work area and proper training of the workers will significantly lower solvent emissions. Within such groups (batch or conveyorised), there is a wide range of equipment age, low emission design sophistication, workpiece design, workpiece load size and maintenance diligence. All of these factors will affect emissions from a particular piece of equipment or region.

Modifications for the recovery and recycling of solvents can be applied if an appropriate estimate of retrofitted equipment can be obtained. While HFC and PFC solvents may be recovered and recycled multiple times during their use owing to their high costs, in most emissive end uses (sub-applications) these chemicals will be released considerably more quickly after being placed in use than those in sealed refrigeration applications.

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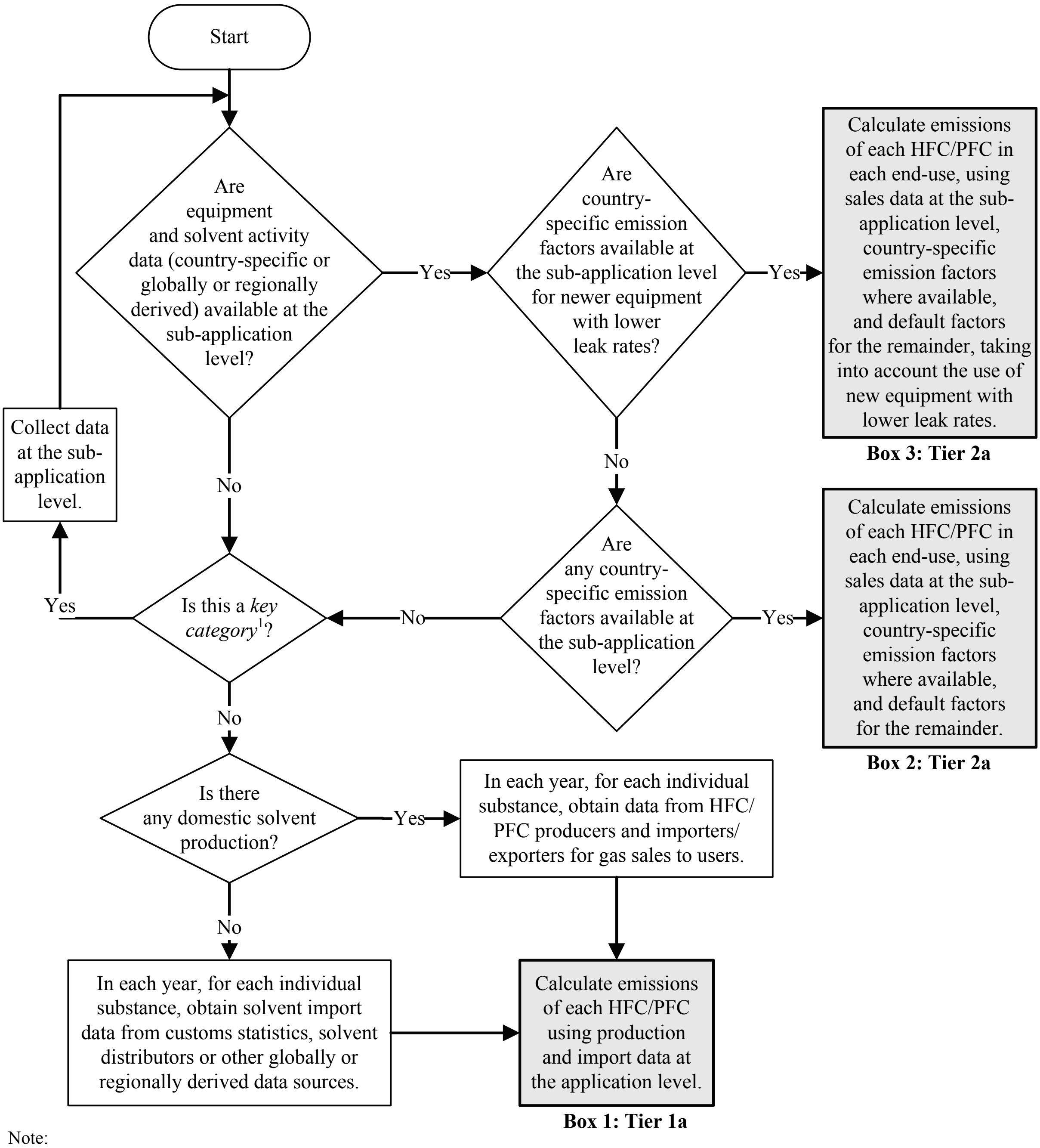
[9] *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC, 2000).

[10] As guidance, for sales to new equipment, approximately 10-20 percent may be emitted with the rest of the solvent used to fill the equipment. In subsequent years sales are for replenishment and can eventually be considered 100 percent emitted.

**Figure 7.2 Decision tree for actual emissions from the solvents application**



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.

### 7.2.2.3 CHOICE OF ACTIVITY DATA

Equation 7.5 should be applied to each chemical individually and, depending on the disaggregation in available data, it may be appropriate to assess net consumption of each chemical by sub-application (Tier 2a). Wherever possible, activity data should be collected directly from the suppliers of solvent or the users in support of either Tier 1a or 2a methods. However, where this is not possible, globally or regionally derived activity data at the application level or the sub-application level can be used where this is available.

The activity data for this end-use are equal to the quantity of each relevant chemical sold as solvent in a particular year. Accordingly, data on both domestic and imported solvent quantities should be collected from suppliers. Depending on the character of the national solvent industry, this can then be cross-checked with users where this is practicable. In most countries, the end-users will be extremely diverse and a supplier-based approach would be most practical. Nonetheless, a combination of both approaches is often the most effective.

#### SUPPLIER DATA

Supplier activity data refers to the amount of chemical solvent sold or imported annually into a country. Domestic solvent sales should be available directly from chemical manufacturers. As solvents are only produced in a few countries, most countries will import some or all of their consumption. Data on imported solvents can be collected from the exporting manufacturers, although information on exports to individual countries may be considered confidential. Alternatively, import statistics from customs agencies or the distributors of imported solvents can be used. Solvent import data are generally more easily obtained than aerosol import data because solvent is usually imported in bulk rather than in small containers.

If specific emission factors are developed for particular types of equipment, it will be necessary to disaggregate the consumption data into these equipment classes. In general, this will require a bottom-up approach.

#### USER DATA

User activity data include the number of pieces of equipment or canisters containing solvent and their charge. The bottom-up approach is suitable where large corporations consume most of the solvent sold, because it should be possible to obtain detailed solvent end-use data from a few large entities. The bottom-up approach may also be most appropriate when equipment-specific emission factors are available.

### 7.2.2.4 COMPLETENESS

Completeness depends on the availability of activity data. Inventory compilers in countries without domestic solvent production may need to use expert judgement in estimating activity data, because import statistics are likely to be incomplete (see Volume 1, Chapters 2 and 3).

There is a potential for double-counting with Volume 3 Chapter 6 which deals with HFC and PFC use in the electronics industry. This should not occur if care is taken to identify previous ODS consumption patterns. It is always *good practice* to cross-reference of both parts of a submission by inventory compilers to confirm that no double-counting has occurred.

With respect to double-counting, care should also be taken where HFCs and PFCs acting as solvents are contained in aerosols. A clear policy should be established as to how these are accounted. It is normally *good practice* to account for these uses under consumption in aerosols to avoid problems in making distinctions between solvents and propellants, particularly where one chemical can act in both roles. This matter is covered further in Section 7.3.

As noted in Section 7.2.2.1, it is also *good practice* to carry out some research to confirm that no HFCs or PFCs other than those listed in Table 7.1 are being used for solvent applications. Producers, importers and distributors should be able to confirm the situation.

### 7.2.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from the solvent sector should be calculated using the same method and data sources for every year in the time series. Where consistent data are unavailable for any years in the time series, gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5.

## 7.2.3 Uncertainty assessment

The assumption that all solvent may be emitted within approximately two years (50 percent in Year t and 50 percent in Year t+1) has been widely accepted by experts as a reasonable default (IPCC *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*, 2000). However, the magnitude of the error caused by this assumption will depend on the nature of solvent usage patterns in the country being reported. In general, the default assumption will over-estimate emissions for a given year as leak tightness of equipment improves, although not on a cumulative basis unless destruction is being practised. Conversely, growth in the destruction of recovered or recycled solvent over time will influence the assumption of 100 percent eventual release. Activity data should be reliable at the application level because of the small number of chemical manufacturers, the high cost of the solvent, and the 100 percent emissive nature of the use over time in most applications. However, uncertainty at the sub-application level will depend largely on the quality of data provided by users and the level of completeness achieved in surveying them.

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

### 7.2.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this application. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this application are outlined below:

- For accurate quality control/assurance both top-down and end-use data should be compiled. To allow independent assessment of the level of quality of the data reporting, the number of manufacturers and distributors plus end users interviewed should be quantified.
- When applying emission factors and activity data specific to various solvent applications, the activity data should be obtained at the same level of detail.

### 7.2.4.2 REPORTING AND DOCUMENTATION

Inventory compilers should report the emission factor used, and the empirical basis for any country-specific factors. For activity data, chemical sales and imports should be reported, unless there are confidentiality concerns arising from the limited number and location of manufacturers. (At present, for example, there may be only one producer of each compound.) Where there are less than three manufacturers of specific chemicals used as solvents, reporting could be aggregated into the aerosol section, because both are considered 100 percent emissive applications (see Section 7.3.4.2 below). In this case, to preserve confidentiality, emissions of individual gases should not be specified and emissions should be reported in $CO_2$-equivalent tonnes.

# 7.3 AEROSOLS (PROPELLANTS AND SOLVENTS)

## 7.3.1 Chemicals covered in this application area

Most aerosol packages contain hydrocarbon (HC) as propellants but, in a small fraction of the total, HFCs and PFCs may be used as propellants or solvents. Emissions from aerosols usually occur shortly after production, on average six months after sale. However, the period between manufacture and sale could vary significantly depending on the sub-application involved. During the use of aerosols, 100 percent of the chemical is emitted (Gamlen *et al.*, 1986; U.S. EPA, 1992b). The 5 main sub-applications are as follows:

(i) Metered Dose Inhalers (MDIs);

(ii) Personal Care Products (e.g., hair care, deodorant, shaving cream);

(iii) Household Products (e.g., air-fresheners, oven and fabric cleaners);

(iv) Industrial Products (e.g., special cleaning sprays such as those for operating electrical contact, lubricants, pipe-freezers);

(v) Other General Products (e.g., silly string, tyre inflators, klaxons).

The HFCs currently used as propellants are HFC-134a, HFC-227ea, and HFC-152a, as shown in Table 7.1. The substances HFC-245fa, HFC-365mfc, HFC-43-10mee and a PFC, perfluorohexane, are used as solvents in industrial aerosol products. Of these, HFC-43-10mee is the most widely used.[11] HFC-365mfc is also expected to be used within aerosols in the near future.

## 7.3.2 Methodological issues

### 7.3.2.1 CHOICE OF METHOD

Aerosol emissions are considered *prompt* because all the initial charge escapes within the first year or two after manufacture, typically six months after sale for most sub-applications. Therefore, to estimate emissions it is necessary to know the total amount of aerosol initially charged in product containers prior to sale. Emissions of each individual aerosol in year t can be calculated as follows:

**EQUATION 7.6**
**EMISSION ESTIMATION METHOD FOR AEROSOL USES**

$$Emissions_t = S_t \bullet EF + S_{t-1} \bullet (1 - EF)$$

Where:

$Emissions_t$ = emissions in year *t*, tonnes

$S_t$ = quantity of HFC and PFC contained in aerosol products sold in year *t*, tonnes

$S_{t-1}$ = quantity of HFC and PFC contained in aerosol products sold in year *t*–1, tonnes

EF = emission factor (= fraction of chemical emitted during the first year), fraction

This equation should be applied to each chemical individually. Wherever possible, activity data should be collected directly from the manufacturers or distributors of aerosols, ideally at the sub-application level to facilitate a Tier 2a approach. Globally or regionally derived activity data can be used to provide sub-application analysis where country-specific data does not exist. If data at the sub-application level is not available from either source, activity data at the application level should be obtained and applied using Equation 7.6 (Tier 1a).

Since the lifetime of the product is assumed to be no more than two years, any amount not emitted during the first year must by definition be emitted during the second and final year. In reality, most emissions occur within the first year after product purchase, but Equation 7.6 rightly accounts for the lag period between the time of manufacture and the time of purchase and use. When applying Equation 7.6, however, care must be taken to define the Point of Sale which, for the purposes of emission estimation, is viewed as sales by the manufacturer to

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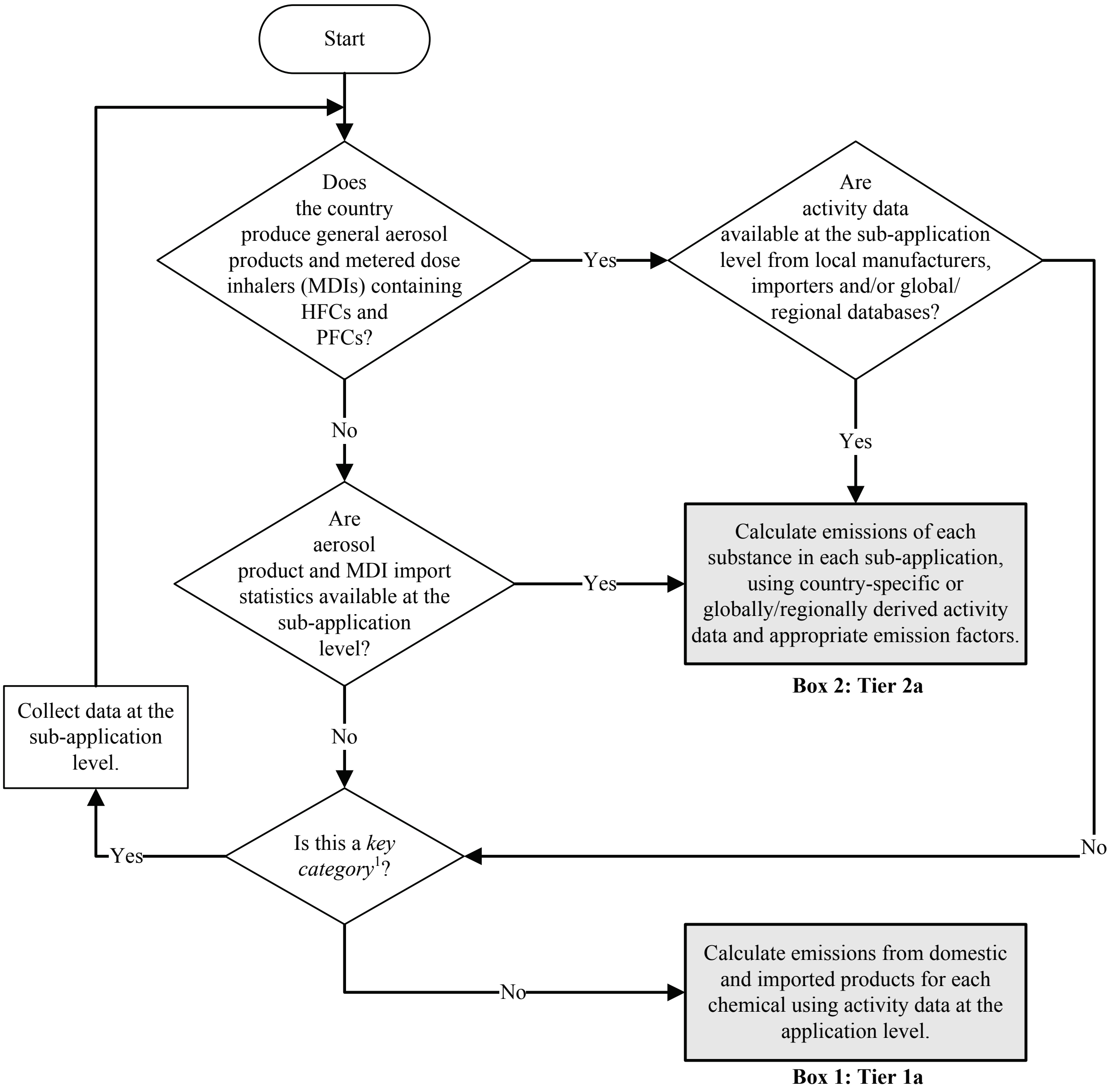
[11] HFC-43-10mee is used solely as a solvent, but is counted as an aerosol when delivered through aerosol canisters.

the supply chain and not by the retailer to the end-user. This approach is most appropriate because sales data will normally be collected from manufacturers and major distributors.

In contrast with the situation for solvents, there is rarely a need to account for recovery, recycling or destruction, since this is only likely to occur when stockpiled product becomes out-of-date. Under normal supply-chain management conditions this is a rare event.

A decision tree for estimating actual emissions is included in Figure 7.3, Decision Tree for Actual Emissions from the Aerosol Application. The data collection process is described below.

**Figure 7.3 Decision tree for actual emissions from the aerosol application**



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.

#### 7.3.2.2 CHOICE OF EMISSION FACTORS

It is *good practice* to use a default emission factor of 50 percent of the initial charge per year for the broad spectrum of aerosol products when assessed at the application level (Tier 1a). This means that half the chemical charge escapes within the first year and the remaining charge escapes during the second year (Gamlen *et al.*, 1986). Inventory compilers should use alternative emission factors only when empirical evidence is available for the majority of aerosol products at either the application level (Tier 1a) or the sub-application level (Tier 2a). In any event, the percentage emission factors should in general sum to 100 percent over the time during which it is assumed that the charge will escape. The development of country-specific emission factors should be documented thoroughly. General aerosol and MDI manufacturers may be able to provide data on process losses.

As a general observation, the consistently emissive nature of aerosols makes the distinction between country-specific and the default emission factor on the one hand and any differences between emission factors in the various sub-applications on the other hand, less influential on overall emissions estimates than is the case in other application areas. Therefore the benefit of following a more disaggregated Tier 2a approach in favour of a Tier 1a approach is less pronounced in the case of aerosols. Inventory compilers should therefore consider carefully how much resource to invest in developing a Tier 2 approach. However, there may be other reasons for keeping reporting of some sub-applications separate and it is expected many countries may wish to monitor emissions from MDIs separately to other general aerosols for policy reasons.

### 7.3.2.3 CHOICE OF ACTIVITY DATA

For the Tier 1a method, the activity data required are the total quantity of each relevant chemical contained in all aerosol products consumed within a country (both domestic sales and imports). For countries that import 100 percent of aerosol products, activity data are equal to imports.

Activity data for this application can be collected at the sub-application level using either a supplier-based or a user-based approach, depending on the availability and quality of the data (Tier 2a). The user-based approach requires data on the number of aerosol products sold and imported at the sub-application level (e.g., number of individual metered dose inhalers, hair care products, and tyre inflators), and the average charge per container. This may require globally or regionally derived activity data for some sectors of use. The supplier-based approach involves collecting aerosol and MDI chemical sales data directly from chemical manufacturers where their sales analysis is sufficiently robust at a country level. In many cases, a mix of both sources of data may be necessary.

**Domestic aerosol production:** For countries with domestic production, general aerosol and MDI manufacturers can usually provide data on the quantity of aerosol products produced for consumption in the country, the number of aerosols exported, the average charge per aerosol, and the type of propellant or solvent used (i.e. which HFC/PFC). Total use of domestically produced aerosol products in each year can then be calculated as the number of aerosol products sold domestically in a given year times the charge of HFC/PFC in each product. Of course, imported aerosols will still need to be added to this assessment to provide the total picture. If sub-application data from indigenous aerosol producers are not available, domestic chemical producers can often provide data on the amount of HFCs sold to domestic manufacturers in metered dose inhalers, and aggregate sales data to producers of other aerosols (categories (ii), (iii), (iv) and (v) above). If domestic aerosol and MDI manufacturers import HFCs, information may also be sought from chemical importers or their overseas suppliers, although the latter may not be able to provide data on exports destined for individual countries because of confidential business concerns. Customs officials and chemical distributors are another possible source for chemical import data. Globally or regionally derived activity data may also have a role both to fill gaps in the existing dataset and to cross-check data obtained from aerosol manufacturers and chemical suppliers.

**Imported aerosol production:** Most countries will import a significant share of their total aerosol products. Data on imports of HFC-containing general aerosols may be difficult to collect because official import statistics for aerosol products do not typically differentiate HFC-containing aerosols from others. When usable import statistics are unavailable from customs agencies, data may be available from product distributors and specific end-users. For example, in the case of MDIs, a limited number of pharmaceutical companies typically import products, and these companies can be surveyed to obtain the required information. Again globally or regionally derived activity data may be helpful in certain cases.

### 7.3.2.4 COMPLETENESS

Completeness depends on the availability of activity data on each chemical to be covered. Section 7.3.1 (and Table 7.1) provides an assessment of HFCs and PFCs currently used, but inventory compilers should check the situation with in-country sources to confirm those chemical relevant to the local situation. Inventory compilers in countries without domestic aerosol production may need to use expert judgement in estimating activity data, because import statistics are likely to be incomplete (see Volume 1, Chapters 2 and 3), particularly with reference to the propellants and solvents contained. Globally or regionally validated activity databases may be particularly helpful in such instances, where these exist.

#### 7.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from aerosols should be calculated using the same method and data sources for every year in the time series. Where consistent data are unavailable for any year in the time series, gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5.

### 7.3.3 Uncertainty assessment

The use of HFCs in the general aerosol sector is typically larger than in the MDI sector. Data from HFC manufacturers and importers of sales to the general aerosol sector are, at the present time, not well-defined other than for HFC-134a on a global scale. These data can be improved through additional data collection activities and the development of global and regional databases. The diffuse nature of the general aerosol sector means that the acquisition of reliable bottom-up data (Tier 2a) requires specific study on a country basis through local industry experts, whose advice should be sought on uncertainties using the approaches to expert judgement outlined in Volume 1, Chapter 3.

There are several sources of reliable data for the MDI sector, leading to a high level of confidence in the data reported that should be reflected in inventory emissions estimates. However, in reporting for a single country, the absence of reliable data for the general aerosol sector could mean that emission data could be over or under estimated by a factor of between one third and three times.

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

#### 7.3.4.1 QUALITY ASSURANCE/QUALITY CONTROL (QA /QC)

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and to organise an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this application. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this application are outlined as follows. Aerosol manufacturing and importing data, on the one hand, and chemical supply data, on the other hand, can be used to cross-check one another during or after the development of an emission estimate. Data used to calculate emissions from year t–1 should be consistent with data used in the previous year's inventory estimate, so the two-year total sums to 100 percent. If this is not the case, then the reason for the inconsistency should be reported. Data collection carried out in accordance with the section on data collection above should provide adequate quality control. To allow independent assessment of the level of quality of the data reporting, the number of manufacturers of aerosols plus importers should be quantified.

#### 7.3.4.2 REPORTING AND DOCUMENTATION

The emission estimate for metered dose inhalers may be reported separately from the emission estimate for other aerosols by some inventory compilers. In such cases, the specific emission factor used should be documented. If a country-specific emission factor is used in preference to a default factor, its development should be documented. Detailed activity data should be reported to the extent that it does not disclose confidential business information. Where some data are confidential, qualitative information should be provided on the types of aerosol products consumed, imported, and produced within the country. It is likely that the type of HFC used as a propellant or solvent and the sales of MDIs and general aerosols into individual countries could be viewed as confidential.[12] Where there are less than three manufacturers of specific chemicals used as solvents, reporting could be aggregated into this section, because both are considered 100 percent emissive applications (see Section 7.2.4.2 above).

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[12] Quantification of use data for individual general aerosol sectors will enable more reliable future projections to be developed and emission reduction strategies to be considered.

# 7.4 FOAM BLOWING AGENTS

## 7.4.1 Chemicals covered in this application area

Increasingly, HFCs are being used as replacements for CFCs and HCFCs in foams and particularly in insulation applications. Compounds that are being used include HFC-245fa, HFC-365mfc, HFC-227ea, HFC-134a, and HFC-152a, as shown in Table 7.1. The processes and applications for which these various HFCs are being used are shown in Table 7.4 with predominantly open-celled foams being in shaded rows.

TABLE 7.4
USE OF HFCS IN THE FOAM BLOWING INDUSTRY (FOAM PRODUCT EMISSIONS BY GAS – ODS REPLACEMENTS)

| **Cell Type** | **Sub-application** | **HFC Foam Blowing Agent Alternatives** | | | |
|---|---|---|---|---|---|
| | | **HFC-134a** | **HFC-152a** | **HFC-245fa** | **HFC-365mfc (+ HFC-227ea)** |
| O P E N | PU[a] Flexible Foam | | | | |
| | PU Flexible Moulded Foam | | | | |
| | PU Integral Skin Foam | ✓ | | ✓ | |
| | PU One Component Foam | ✓ | ✓ | | |
| C L O S E D | PU Continuous Panel | ✓ | | ✓ | ✓ |
| | PU Discontinuous Panel | ✓ | | ✓ | ✓ |
| | PU Appliance Foam | ✓ | | ✓ | ✓ |
| | PU Injected Foam | ✓ | | ✓ | ✓ |
| | PU Continuous Block | | | ✓ | ✓ |
| | PU Discontinuous Block | | | ✓ | ✓ |
| | PU Continuous Laminate | | | ✓ | ✓ |
| | PU Spray Foam | | | ✓ | ✓ |
| | PU Pipe-in-Pipe | ✓ | | ✓ | ✓ |
| | Extruded Polystyrene | ✓ | ✓ | | |
| | Phenolic Block | | | ✓ | ✓ |
| | Phenolic Laminate | | | ✓ | ✓ |

[a] PU denotes polyurethane

The division of foams into open-cell or closed-cell relates to the way in which blowing agent is lost from the products. For open-cell foam, emissions of HFCs used as blowing agents are likely to occur during the manufacturing process and shortly thereafter. In closed-cell foam, only a minority of emissions occur during the manufacturing phase. Emissions therefore extend into the in-use phase, with often the majority of emission not occurring until end-of-life (de-commissioning losses). Accordingly, emissions from closed cell foams can occur over a period of 50 years or even longer from the date of manufacture.

Open-celled foams are used for applications such as household furniture cushioning, mattresses, automotive seating and for moulded products such as car steering wheels and office furniture. Closed-cell foams, on the other hand, are primarily used for insulating applications where the gaseous thermal conductivity of the chosen blowing agent (lower than air) is used to contribute to the insulating performance of the product throughout its lifetime.

## 7.4.2 Methodological issues

The previous *Guidelines* presented an equation for calculating emissions from closed cell foam that accounted for the first two emission points (i.e., manufacturing and during the in-use phase). This remains generally sufficient to account for the early stages of HFC uptake. However, in order to prepare a *complete* estimate of emissions from this source, it is *good practice* to add third and fourth terms to the equation to account for decommissioning losses and chemical destruction, where data are available. Thus, the relevant equation is:

**EQUATION 7.7**
**GENERAL EMISSION-FACTOR APPROACH (A) FOR FOAMS**

$$Emissions_t = M_t \bullet EF_{FYL} + Bank_t \bullet EF_{AL} + DL_t - RD_t$$

Where:

$\text{Emissions}_t$ = emissions from closed-cell foam in year *t*, tonnes

$M_t$ = total HFC used in manufacturing new closed-cell foam in year *t*, tonnes

$EF_{FYL}$ = first year loss emission factor, fraction

$\text{Bank}_t$ = HFC charge blown into closed-cell foam manufacturing between year t and year *t-n*, tonnes

$EF_{AL}$ = annual loss emission factor, fraction

$DL_t$ = docommissioning losses in year *t* = remaining losses of chemical at the end of service life that occur when the product/equipment is scrapped, calculated from the amount of remaining chemical and the end-of-life loss factor which depends on the type of end-of-life treatment adopted[13], tonnes

$RD_t$ = HFC emissions prevented by recovery and destruction of foams and their blowing agents in year *t*, tonnes

*n* = product lifetime of closed-cell foam

*t* = current year

(*t-n*) = The total period over which HFCs used in foams could still be present

It should be noted that Equation 7.7, although targeted at closed cell foams, can be equally applied to open celled foams. In this sense it is a universal equation for all foams. In the case of open-celled foams the first-year Loss Emission Factor is typically 100 percent and the equation simplifies to its first component only, which then further simplifies to Equation 7.8.

Accordingly, where the nature of a foam is uncertain, Equation 7.7 should be applied to each chemical and major foam sub-application individually when pursuing a Tier 2a method.

Since emission profiles vary substantially by sub-application within the overall foam application, there is significant incremental value in adopting a Tier 2 method wherever possible. Ideally, this should be achieved by the researching of individual country activities. However, in practice, the intra-regional trade in foams coupled with the significant difficulty in setting up systems to identify the blowing agents used in foams already manufactured, makes a method based on country-specific activity data very difficult to implement at the sub-application level. Recognising that both disaggregated activity data and the related emission factors may be difficult to obtain at a country level, there have been several efforts by the UNEP Foams Technical Options Committee (UNEP-FTOC, 1999; UNEP-FTOC, 2003) and others to provide globally or regionally derived activity data and default emissions factors by sub-application for CFCs, HCFCs and hydrocarbons (HCs). Although HFCs are only now being used significantly as additional ODS alternatives, it is expected that a similar approach can be carried forward for these chemicals, with emission factors being available within the EFDB in order to provide a helpful source of information for inventory compilers. Other databases are emerging from the original FTOC work for activity data, and will be particularly helpful for countries where the trade in products-containing HFCs is significant, but difficult to track.

As an additional methodological consideration, it should be noted that many of the emissions from closed-cell insulation foams arise from banks of blowing agent built up from previous years of consumption. This point was

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[13] Most decommissioning procedures will not result in the release of all remaining blowing agent. Even processing through an open auto-shredder has been found to result in emission of less than 50 percent of the remaining blowing agent at the point of processing (U.S. EPA/AHAM, 2005). Accordingly, blowing agent banks can accumulate further along the waste stream (e.g., landfills) – see Section 7.4.2.1.

highlighted in the IPCC Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons (IPCC/TEAP, 2005) where it was noted that CFC emissions could continue from banked blowing agents in foams until the middle of the 21st century. This illustrates the importance of using an emissions estimation method which adequately reflects the development of banks.

An additional characteristic of foam inventories is that a significant majority of emissions occur from closed cell foam at the point of decommissioning or thereafter. Therefore, inventory compilers should be careful to research decommissioning practices and any recovery and destruction practices within their country closely. As a further consequence, methods which assume total release of blowing agent over the manufacturing and use phases are likely to significantly over-estimate emissions for any given year. Accordingly, methods should typically assume complete release of blowing agent at decommissioning only where there is definite evidence to support this and should normally attribute emissions to subsequent years based on a more appropriate release function. The relevant columns in Tables 7.6 and 7.7 therefore represent 'maximum potential' losses. In practice such emissions are likely to be spread over a substantial number of years following decommissioning if the foam remains broadly intact (i.e., average particle size > 8mm) (U.S. EPA/AHAM, 2005).

As a general observation, the mass-balance approach (Approach B) is inappropriate for foams since there is no mechanism by which such products are serviced in practice.

### 7.4.2.1 CHOICE OF METHOD

*Open-Cell Foam*: Since HFCs used for open-cell foam blowing are released immediately, the emissions in almost all cases will occur in the country of manufacture. The only exception may be in the case of OCF (One Component Foams) where the filled container may be manufactured in one country but the emissions occur in another country because the containers are easily traded. Emissions are calculated according to the following equation:[14]

**EQUATION 7.8**
**GENERIC CALCULATION METHOD FOR EMISSIONS FROM OPEN-CELLED FOAMS**

$$Emissions_t = M_t$$

Where:

$Emissions_t$ = emissions from open-cell foam in year $t$, tonnes

$M_t$ = total HFC used in manufacturing new open-cell foam in year $t$, tonnes

This equation must be applied for each chemical used in open-celled foam applications. Although, there is little variation in emission factor across the open-cell sub-applications, it may still be advantageous to use a disaggregated Tier 2a method in order to make it easier to accurately assess net consumption activity data. Such an approach will naturally address the trade in one-component foams. Where there is little use of one-component foam, it could be logical to revert to a Tier 1a method where Equation 7.8 is applied at the application level.

*Closed-Cell Foam*: Emissions from closed-cell foam occur at three distinct points, which have already been highlighted in Equation 7.7:

(i) First Year Losses from Foam Manufacture and Installation: These emissions occur where the product is manufactured or installed.

(ii) Annual Losses (in-situ losses from foam use): Closed-cell foam will lose a fraction of its initial charge each year until decommissioning. These emissions occur where the product is used.

(iii) Decommissioning Losses: Emissions upon decommissioning also occur where the product is used.

To implement an approach which captures these three phases it is necessary to collect current and historical data on annual chemical sales to the foam industry for the full length of time HFCs have been used in this application period up to and including the average lifetime of closed-cell foam (as long as 50 years). The import or export of foam formulations which already include HFCs should be also taken into account. Similarly, there should be adjustments made for articles such as domestic or commercial refrigerators and freezers or of construction sector applications such as sandwich panels, boards, blocks and insulated pipes which are produced in one country but may be used in another country.

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[14] For these applications, actual emissions of each chemical are equal to potential emissions.

In earlier assessments the calculation of decommissioning losses has been based on the premise that all blowing agent remaining in a foam at end-of-life will be lost at the decommissioning stage. From an emissions standpoint, this is a worst case scenario, even for disposal methods which are not targeted at recovery and destruction (see footnote 13). In practice, recovery and destruction of blowing agent or direct destruction (e.g., incineration) will further alleviate these losses. Hence Equation 7.7 carries a fourth component to allow for HFC emissions prevented in this way. The UNEP TEAP Task Force Report on Foams End-of-Life (UNEP-TEAP, 2005) addresses the many of the potential ways in which foam blowing agent emissions can be avoided and introduces the concept of Recovery and Destruction Efficiency (RDE) to assess the effectiveness of such methods.

Even where active recovery and destruction methods are not practised, it is still unlikely that all blowing agent will be released at end of life, particularly when foams are typically left in tact during disposal (e.g. during land-filling). Under these circumstances, a considerable proportion of the blowing agent will remain in the waste stream and an additional *banked* emission source will be established. Since the emission rates from such a bank will be lower than 100 percent, Equation 7.7 will over-estimate emissions where a significant proportion of the foam containing HFCs used in the country has already been decommissioned. Although it would be possible to envisage a fifth component to Equation 7.7 to address this element of emission, it is not deemed of sufficient relevance to warrant such an approach for the global phase of HFC use being covered by these *Guidelines*. However, some of the more sophisticated globally or regionally-derived assessments may address this issue.

If it is not possible to collect data for potential losses upon decommissioning, it should be assumed that all chemical not emitted in manufacturing is emitted over the lifetime of the foam. However, particular care should be taken to check whether articles such as domestic or commercial refrigerators and freezers are exported to another country for re-use. Where the foam application cannot be disaggregated to the sub-application level and no globally or regionally derived activity data is available, a Tier 1a method needs to be followed. *Good practice* in the choice of a Tier 1 method is to assume that all closed cell foam emissions follow the Gamlen model (see Table 7.5)

TABLE 7.5
DEFAULT EMISSION FACTORS FOR HFC FROM CLOSED-CELL FOAM

| Emission Factor | Default Values |
|---|---|
| Product Lifetime | n = 20 years |
| First Year Losses | 10% of the original HFC charge/year, although the value could drop to 5% if significant recycling takes place during manufacturing. |
| Annual Losses | 4.5% of the original HFC charge/year |

Source: Gamlen *et al.* (1986).

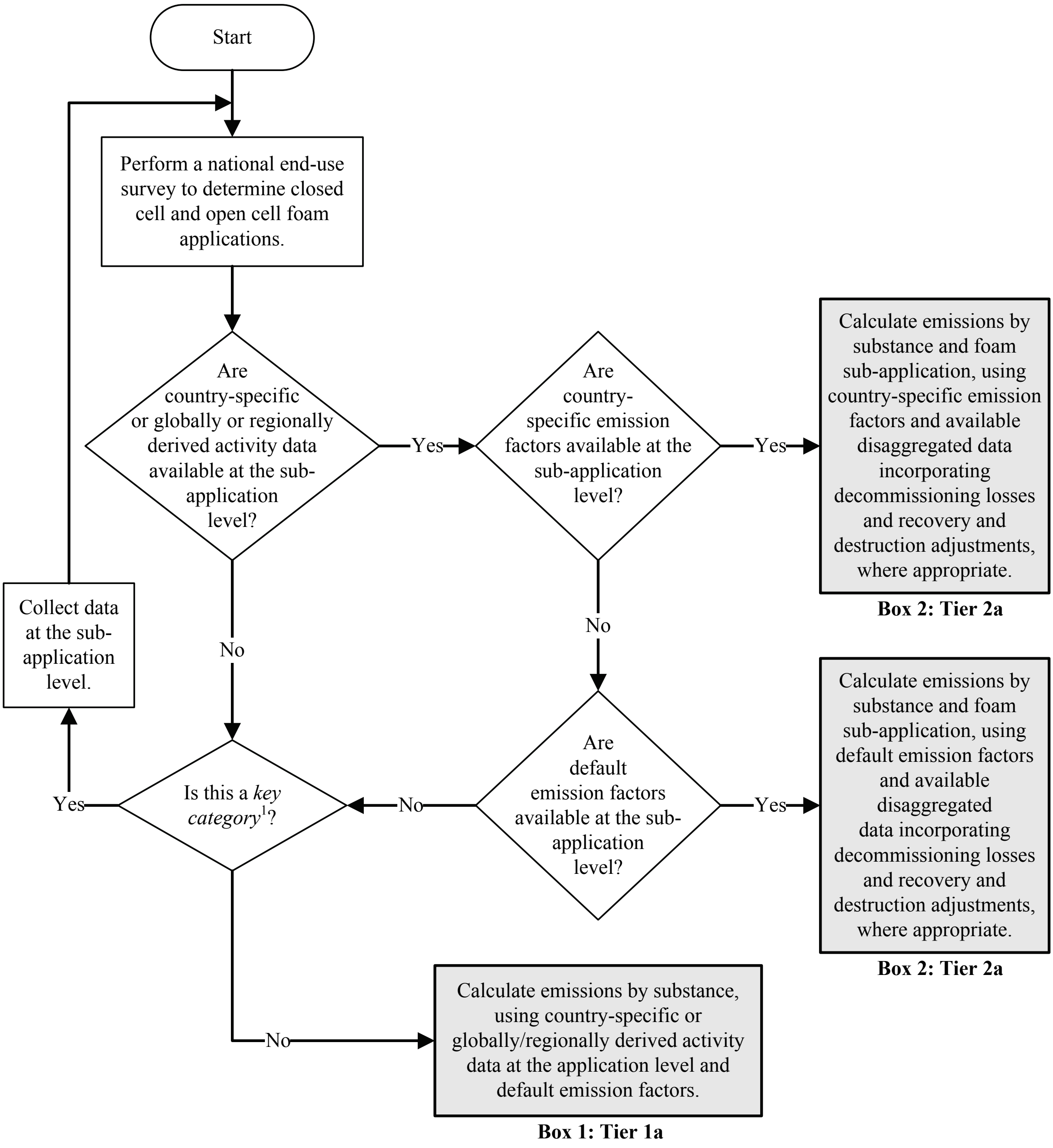
If both historical and current country-specific activity data is available for closed cell foams at the application level, it is possible to apply the Gamlen model to this information. However, the primary challenge for inventory compilers is usually in the characterisation of historic activity data at a country level. If such difficulties exist, it is usually possible to estimate activity data at a country level from the application of geo-economic factors provided that regional, globally or regionally-validated activity data are known. This approach is covered further in Section 7.4.2.3.

Where net consumption activity data is available at the sub-application level, either from sources of country-specific data or from globally or regionally derived activity datasets, it is *good practice* to use Tier 2 methods that reflect the level of disaggregation. This is particularly important for foams because of the heterogeneous nature of the various sub-applications involved. The decision tree in Figure 7.4 describes *good practice* in selecting methods for estimating emissions.

### 7.4.2.2 CHOICE OF EMISSION FACTORS

As in other applications, the first choice for emission factors is to develop and use peer-reviewed and well documented country-specific data based on field research on each foam type (open cell and closed cell) in support of a Tier 2a approach. As noted previously, if no information is available at the sub-application level, emission factors can be adopted from the Emission Factor Database (EFDB) or from the data contained in this section. However, it should be noted that the data contained in this section will not be replaced with updated values in the same way as may happen for the EFDB. Either country-specific or globally/regionally-derived approaches will lead to the necessary assessment of decommissioning losses.[15]

**Figure 7.4 Decision tree for emissions from the foam application**



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.

Table 7.6, Default Emission Factors for HFC-134a/HFC-152a (Foam Sub-Application) and Table 7.7, Default Emission Factors for HFC-245a/HFC-365mfc/HFC-227ea (Foam Sub-Application) lists default emission factors

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[15] It has also been noted that decommissioning may not necessarily involve total loss of blowing agent at that point, either because of a level of secondary use or because the item has been discarded intact (e.g., many refrigerators). These could be considered as some of the end-of-life management options available to nations, but are clearly less effective than proper destruction or recovery technologies. Emission models should focus proper attention to end-of-life issues.

assumptions for the most important current closed-cell foam applications. Use of these factors will require data on chemical sales at the sub-application level for both current and historic consumption in order that the bank of chemical in equipment/products for these sub-applications is properly considered.

**TABLE 7.6**
**DEFAULT EMISSION FACTORS FOR HFC-134a AND HFC-152a USES (FOAM SUB-APPLICATIONS )**
**(IPCC/TEAP, 2005)**

| Sub-Application | Product Life in years | First Year Loss % | Annual Loss % | Maximum Potential End-of-Life Loss % |
|---|---|---|---|---|
| Polyurethane – Integral Skin | 12 | 95 | 2.5 | 0 |
| Polyurethane – Continuous Panel | 50 | 10 | 0.5 | 65 |
| Polyurethane – Discontinuous Panel | 50 | 12.5 | 0.5 | 62.5 |
| Polyurethane – Appliance | 15 | 7 | 0.5 | 85.5 |
| Polyurethane – Injected | 15 | 12.5 | 0.5 | 80 |
| One Component Foam (OCF) [a] | 50 | 95 | 2.5 | 0 |
| Extruded Polystyrene (XPS)[b] - HFC-134a | 50 | 25 | 0.75 | 37.5 |
| Extruded Polystyrene (XPS) - HFC-152a | 50 | 50 | 25 | 0 |
| Extruded Polyethylene (PE) [a] | 50 | 40 | 3 | 0 |

Source:

[a] Ashford and Jeffs (2004) assembled from UNEP FTOC Reports (UNEP-FTOC, 1999; UNEP-FTOC, 2003).

[b] Vo and Paquet (2004): An Evaluation of Thermal Conductivity over time for Extruded Polystyrene Foams blown with HFC-134a and HCFC-142b

Some articles, such as reefers or insulated truck bodies, may spend almost all of their practical lives in transit between countries. Since these applications have very low in-use emissions it is reasonable if only the manufacturing and decommissioning losses are taken into account.

**TABLE 7.7**
**DEFAULT EMISSION FACTORS FOR HFC-245fa/HFC-365mfc/HFC-227ea USES (FOAM SUB-APPLICATION)**

| HFC-245a/HFC-365mfc Applications | Product Life in years | First Year Loss % | Annual Loss % | Maximum Potential End-of-Life Loss % |
|---|---|---|---|---|
| Polyurethane – Continuous Panel | 50 | 5 | 0.5 | 70 |
| Polyurethane – Discontinuous Panel | 50 | 12 | 0.5 | 63 |
| Polyurethane – Appliance | 15 | 4 | 0.25 | 92.25 |
| Polyurethane – Injected | 15 | 10 | 0.5 | 82.5 |
| Polyurethane – Cont. Block | 15 | 20 | 1 | 65 |
| Polyurethane – Disc. Block for pipe sections | 15 | 45 | 0.75 | 43.75 |
| Polyurethane – Disc. Block for panels | 50 | 15 | 0.5 | 60 |
| Polyurethane – Cont. Laminate / Boardstock | 25 | 6 | 1 | 69 |
| Polyurethane – Spray | 50 | 15 | 1.5 | 10 |
| Polyurethane – Pipe-in-Pipe | 50 | 6 | 0.25 | 81.5 |
| Phenolic – Discontinuous Block | 15 | 45 | 0.75 | 43.75 |
| Phenolic – Discontinuous Laminate | 50 | 10 | 1 | 40 |
| Polyurethane – Integral Skin | 12 | 95 | 2.5 | 0 |

Source: Ashford and Jeffs (2004) assembled from UNEP FTOC Reports (UNEP-FTOC, 1999; UNEP-FTOC, 2003)

If only aggregated chemical sales data for closed-cell foam are available and information on specific foam types cannot be obtained, the general default emission factors shown in Table 7.5 can be used in support of a Tier 1a method.[16] This replicates the previous Tier 2 guidance contained in the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC, 1997) but is now classified as a Tier 1a method following the exclusion of potential emission methods for ODS substitutes.

Use of these default emission factors will result in 90 percent of the initial charges being emitted over twenty years of annual use, after the initial 10 percent during the first year.

## 7.4.2.3 CHOICE OF ACTIVITY DATA

Two types of activity data are needed in order to prepare the emissions estimates:

1. the amount of chemical used in foam manufacturing in a country and not subsequently exported, and
2. the amount of chemical contained in foam imported into the country.

Data collection issues related to these two areas differ.

### Chemical used in foam manufacture

The amount of bulk chemicals used in the foam blowing industry should include both domestically produced and imported HFCs. Domestic chemical sales data to the foam industry should be available directly from chemical suppliers or foam manufacturers at the application level (Tier 1a) and may extend to a sub-application analysis (Tier 2a). As with other ODS substitute applications, imported chemical data may be available from customs officials or chemical distributors.

Historic consumption data is required to build an adequate picture of the development of blowing agent banks. However, this does not apply to open-celled foams which lose their blowing agents in the first year. For open-cell foam, all emissions will occur during manufacture, with the exception of the OCF sub-sector mentioned above. Thus, it is necessary to determine the share of chemical associated with the manufacture of open-celled foam. These data can be determined through an end-use survey, or approximated by reviewing similar end-use data gathered on CFCs and HCFCs.

### Chemical contained in imported and exported foams

Inventory compilers in countries that export closed-cell foam should subtract these volumes from their calculations of annual banks and ultimately decommissioning losses, since the in-use emissions will occur in the importing country. Data on the chemical charge of exported closed-cell foam may be available from large manufacturers. However, customs data itself is unlikely to yield relevant information on blowing agent type unless special provisions have been set up by the reporting country.

Similarly, inventory compilers in countries that import products containing closed-cell foam, should include estimates of emissions from these imported products for completeness. Since the inventory compiler will have even less knowledge and control of products manufactured outside of the country than for those manufactured and subsequently exported, information on the blowing agents contained in closed-cell foam products imported is even more difficult to collect. Accordingly, inventory compilers in countries whose emissions occur only from imported closed-cell foam may need to use expert judgement in estimating this data (see Volume 1, Chapters 2 and 3).

In the past, inventory compilers were not able to use international HFC production and consumption data sets to develop estimates of chemical contained in imported closed-cell foam because these data sets did not include regional use and trade pattern databases. For example, the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) statistics-gathering process compiled global activity data up until 1997 for HFC-134a in the foam sector[17] but regional breakdowns were unavailable.

To help resolve this problem, some databases now contain national mechanisms to assist inventory compilers by taking advantage of international HFC/PFC consumption and emission data sets to access globally or regionally derived activity data and bank estimates for blowing agents contained in closed cell foams within their own countries. These can be applied within Tier 2a assessments and will provide estimated consumption and bank data at the sub-application level, to which the default emission factors contained in Tables 7.6 and 7.7 (or updated versions thereof carried in the EFDB or elsewhere) can be applied.

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[16] No emission factors are provided for open-cell foams because all emissions occur during the first year.

[17] HFC-134a is the most commonly used HFC. AFEAS data can found at http://www.afeas.org.

### 7.4.2.4 SUMMARISING THE PRIMARY METHODS

#### Stepwise through the Tier 2a method using proxy data

The Box 7.2 illustrates the typical steps required to implement a Tier 2a method using proxy data:

**BOX 7.2**

**TIER 2a IMPLEMENTATION FOR THE FOAM APPLICATION USING GLOBALLY OR REGIONALLY DERIVED DATA**

There are up to 16 sub-applications in the foam sector. A reporting country needs to consider which of these sub-applications are relevant to its situation and carry out the following steps for each such process/application.

Consumption

1. Identify the tonnage of foam used in the process/application
2. Establish the average density for the foam used in the process/application and hence foam volume ('foam volume per unit' is the commonly used metric for houses and buildings)
3. Identify the number of houses built in the year or appliances manufactured/sold in the year to determine a nominal foam volume ratio (foam volume per unit)
4. Assess growth trends in both the number of units and the foam volume ratio and apply these trends to estimate the tonnage of foam for previous and future years (i.e., years in which data from Step 3 might not be available).
5. Assess the market split, or share of various blowing agents (chemicals) used for each process/application. Particular care should be taken when dealing with blends.
6. Identify typical foam formulations for each blowing agent type and apply these formulations to the proportion of the process/application using that blowing agent.
7. Multiply the foam tonnage by the formulation (weight/weight) and market share details to obtain blowing agent consumption by blowing agent type (typically up to 14 types).
8. Cross-check with any sales information available on specific blowing agents at country-level.

Emissions-in-Use

9. Establish the first year loss rate for the process/application. Multiply this loss rate by the chemical consumption to estimate losses emanating from this phase. *These emissions should be added to the other sources of emission.*
10. The balance of the non-emitted consumption for that year is added to the bank of blowing agent stored in that process/application.
11. Apply a linear emission rate to banked materials, thus eliminating the need to run parallel models based on the vintage of the bank contribution.
12. Apply the average in-use emission rate to the bank and *add the resulting emissions to the emissions total.*
13. Based on the predicted average product life, establish how much of the bank will be decommissioned in the current year and subtract it from the bank.

Decommissioning, recovery and destruction

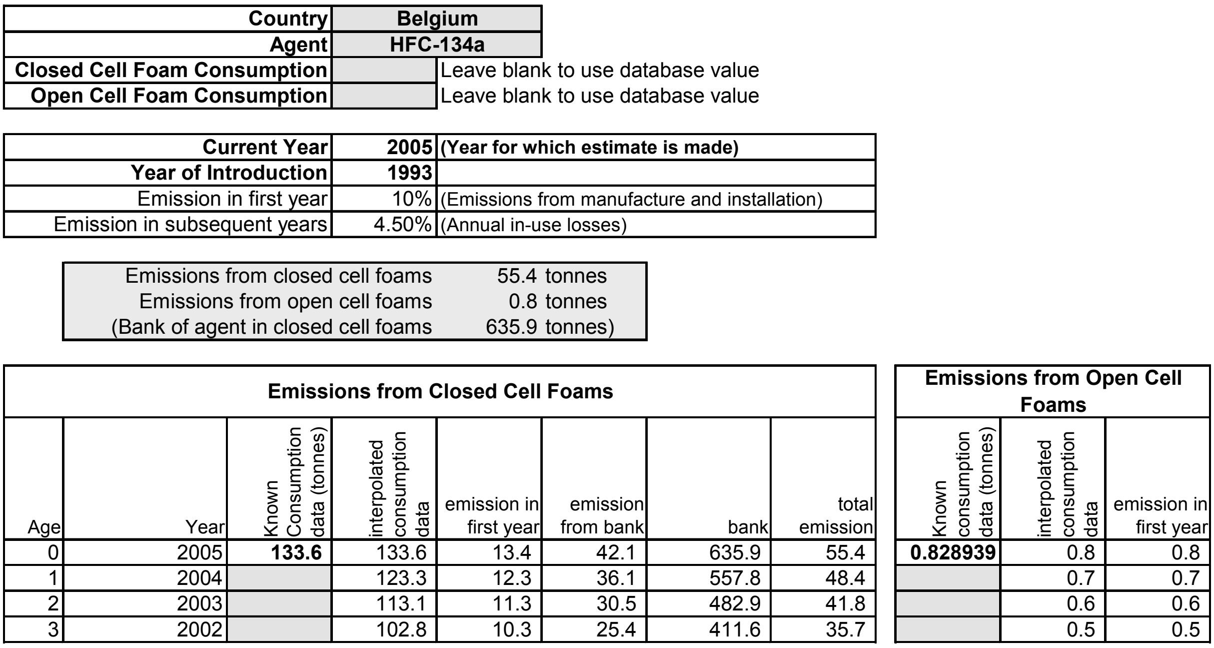
14. There are a number of end-of-life options for foams, but *good practice* suggests that four major options should be considered:
    a. Re-use
    b. Landfill without shredding
    c. Shredding without recovery
    d. Total recovery and capture (including shredding with recovery, direct incineration etc.)

15. The decommissioned portions of the banks for a given year should be ascribed to the four options outlined above in proportion to the practice of the country.
16. Emission factors during decommissioning and other end-of-life management steps should be established. These should then be applied to the decommissioned portions of the process/application. *These emissions should be added to the other sources of emission.* The maximum emission factors in Tables 7.6 and 7.7 should be applied only where instantaneous release can reasonably be assumed to occur.
17. Where emissions from end-of-life management may be on-going (e.g., re-use, landfill and shredding without recovery), further end-of-life banks should be established to keep track of accumulation of blowing agents and to estimate the on-going annual emissions from these sources.
18. Annual emission factors for each of these sources should be applied to the end-of-life banks. *These emissions should be added to the other sources of emission.*

### Using the Tier 1a method based on Gamlen model

As a more limited alternative, it is possible to use a Tier 1a method based on the Gamlen model (Table 7.5) to estimate emissions from the total bank of closed cell foam in a country. The following spreadsheet excerpt illustrates the method[18]:

**Figure 7.5 Example of spreadsheet calculation for Tier 1a method**



| | | |
|---|---|---|
| **Country** | **Belgium** | |
| **Agent** | **HFC-134a** | |
| **Closed Cell Foam Consumption** | | Leave blank to use database value |
| **Open Cell Foam Consumption** | | Leave blank to use database value |

| | | |
|---|---|---|
| **Current Year** | **2005** | **(Year for which estimate is made)** |
| **Year of Introduction** | **1993** | |
| Emission in first year | 10% | (Emissions from manufacture and installation) |
| Emission in subsequent years | 4.50% | (Annual in-use losses) |

| | | |
|---|---|---|
| Emissions from closed cell foams | 55.4 | tonnes |
| Emissions from open cell foams | 0.8 | tonnes |
| (Bank of agent in closed cell foams | 635.9 | tonnes) |

**Emissions from Closed Cell Foams**

| Age | Year | Known Consumption data (tonnes) | interpolated consumption data | emission in first year | emission from bank | bank | total emission |
|---|---|---|---|---|---|---|---|
| 0 | 2005 | **133.6** | 133.6 | 13.4 | 42.1 | 635.9 | 55.4 |
| 1 | 2004 | | 123.3 | 12.3 | 36.1 | 557.8 | 48.4 |
| 2 | 2003 | | 113.1 | 11.3 | 30.5 | 482.9 | 41.8 |
| 3 | 2002 | | 102.8 | 10.3 | 25.4 | 411.6 | 35.7 |

**Emissions from Open Cell Foams**

| Known consumption data (tonnes) | interpolated consumption data | emission in first year |
|---|---|---|
| **0.828939** | 0.8 | 0.8 |
| | 0.7 | 0.7 |
| | 0.6 | 0.6 |
| | 0.5 | 0.5 |

In this instance, Belgium is estimated to have consumed 133.6 tonnes of HFC-134a for closed cell foams in 2005 and to have emitted 13.4 tonnes from first year foam manufacturing activities, and 42.1 tonnes emissions from the accrued bank of foams, making a total of 55.4 tonnes of HFC-134a from closed cell foams in 2005. This assessment is based on the understanding that HFC-134a was introduced substantively in Belgium in 1993, so the estimate includes 13 years of data. The overall approach, when based on regionally derived data, assumes that the average uptake of HFC-134a-based technologies in Europe is reflected in the country in question.

This method has particular attraction for countries and regions that have low rates of foam consumption (e.g., developing countries), and where the foam volume ratio in buildings is low and emissions are likely to be minimal over the effective period of these *Guidelines*. However, for the regions consuming larger volumes of HFCs in buildings, Tier 2 methods are strongly recommended to avoid the misallocation of consumption and, in particular, emissions because of the assumptions implicit in the Gamlen model (Table 7.5) and the averaging of consumption patterns.

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[18] Where introduction is slow, the ‘year of introduction’ should be taken as the first year of substantive use.

### 7.4.2.5 COMPLETENESS

At least sixteen foam potential sub-applications and five potential chemicals used as blowing agents (HFC-134a, HFC-152a, HFC-245fa, HFC-365mfc and HFC-227ea) have been identified within the foam application. For completeness, inventory compilers should determine whether HFC blowing agents are used in each sub-application being practised in their countries, which suggests up to 80 theoretically possible combinations (see Table 7.4, Use of HFCs in the Foam Blowing Industry). In practice, this list reduces to 53 realistic potential chemical/application combinations, although there are some potential regional variations.

It should also be noted that, at this stage, the methods described do not explicitly address the use of blends, although, in theory, this should be covered in the chemical-by-chemical assessment. The challenge, as with refrigerants (see Section 7.5) will be one of activity monitoring and reporting. The use of blends is undoubtedly increasing and may include combinations of, for example, HFC-245fa and HFC-365mfc. Blends of HFC-365mfc with minor proportions of HFC-227ea are also being introduced by one manufacturer. However, it is premature at this stage to assign different emission factors to such systems.

### 7.4.2.6 DEVELOPING A CONSISTENT TIME SERIES

An inventory compiler should maintain a consistent method in assessing its emissions over the time period. If, for example, no system is established to monitor actual decommissioning at the outset of the inventory process, it will be very difficult to obtain data retrospectively if a change from globally or regionally-derived to country-specific data is considered. This decision should therefore be the subject of careful consideration at the outset of the reporting process. Any recalculation of estimates should be done according to the guidance provided in Volume 1, Chapter 5. In contrast, changes in approach for Activity Level determinations will be easier to implement retrospectively.

## 7.4.3 Uncertainty assessment

For net consumption activity data, current sales data indicate that the global estimates are accurate to within 10 percent, regional estimates are in the 30 - 40 percent range, and the uncertainty of country specific consumption information may be more than 50 percent. It should be noted that the calculation of the total emissions for a year will be only partially dependent on the accuracy of estimates of new consumption in that year. The remainder of the emissions will arise from banked blowing agent in installed foam and from those foams decommissioned in that year. The estimation of these contributors will depend fundamentally on the accuracy of historic consumption data.

Using Approach A (emission-factor approach), emission factors will add to the uncertainties, particularly if only default emission factors can be used. Since decommissioning will be the trigger for the majority of emissions in many cases, the product end-of-life assumptions may introduce the greatest degree of uncertainty. It is therefore very important that inventory compilers keep records of their estimates of HFC-containing products and develop some mechanism for monitoring actual decommissioning if possible. These records may help ensure that the summed emissions do not exceed total inputs over time.

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

### 7.4.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this application. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

One of the main concerns will be to ensure that the preservation of the integrity of regional and global data will be maintained by the summation of individual country estimates and a major part of the QA/QC review process will need to concern itself with this cross reference.

### 7.4.4.2 REPORTING AND DOCUMENTATION

Emissions factors should be reported, along with documentation for the development of country-specific data. Chemical sales to the foam blowing industry should be reported in a manner that addresses confidentiality concerns. Most confidentiality issues arising from any data collection process relate to the most highly concentrated activities. To deal with this, emissions from foam could be reported as a single number, provided that the development of the number could be reviewed under suitable terms of confidentiality. Of course, a declaration of consolidated emissions from manufacture (first year), use (product life) and decommissioning (end-of-life) will always be preferable to allow continued focus on improvements being made in each of these areas. If inventory compilers use activity data derived from global or regional databases, they should report the results of how they allocated emissions to the country level.

# 7.5 REFRIGERATION AND AIR CONDITIONING

## 7.5.1 Chemicals covered in this application area

Refrigeration and air-conditioning (RAC) systems may be classified in up to six sub-application domains or categories (UNEP-RTOC, 2003), although less sub-applications are typically used at a single country level. These categories correspond to sub-applications that may differ by location and purpose, and are listed below:

(i) Domestic (i.e., household) refrigeration,

(ii) Commercial refrigeration including different types of equipment, from vending machines to centralised refrigeration systems in supermarkets,

(iii) Industrial processes including chillers, cold storage, and industrial heat pumps used in the food, petrochemical and other industries,

(iv) Transport refrigeration including equipment and systems used in refrigerated trucks, containers, reefers, and wagons,

(v) Stationary air conditioning including air-to-air systems, heat pumps, and chillers[19] for building and residential applications,

(vi) Mobile air-conditioning systems used in passenger cars, truck cabins, buses, and trains.[20]

For all these sub-applications, different HFCs are progressively replacing CFCs and HCFCs. For example, in developed and several developing countries, HFC-134a has replaced CFC-12 in domestic refrigeration, high-pressure chillers and mobile air conditioning systems, and blends of HFCs such as R-407C (HFC-32/HFC-125/HFC-134a) and R-410A (HFC-32/HFC-125) are replacing HCFC-22 mainly in stationary air conditioning. HFC blends R-404A (HFC-125/HFC-143a/HFC-134a) and R-507A (HFC-125/HFC-143a) have replaced R-502 (CFC-22/CFC-115) and HCFC-22 in commercial refrigeration. Other, non-HFC substances are also used to replace CFCs and HCFCs such as iso-butane (HC-600a) in domestic refrigeration or ammonia in industrial refrigeration.

A large number of blends containing HFCs and/or PFCs are being used in Refrigeration and Air Conditioning applications. Table 7.8 shows the most common of these blends.

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[19] Comfort air conditioning in large commercial buildings (including hotels, offices, hospitals, universities, etc.) is commonly provided by water chillers coupled with an air handling and distribution system.

[20] The sub-application of mobile air conditioning systems is likely to represent the largest share of HFC emissions within the Refrigeration and Air Conditioning application for many countries. See Section 7.5.2.4, Applying Tier 2 Methods – The Example Of Mobile Air Conditioning (MAC), for an example of how to calculate these emissions. The reader will see that limited information is needed to approximate these emissions, and essentially becomes a simple multiplication of an average emission factor and the number of cars with HFC air conditioning, and possibly adding emissions relating to container management, charging and end-of-life.

**Table 7.8**
**Blends (many containing HFCs and/or PFCs)**

| Blend | Constituents | Composition (%) |
|---|---|---|
| R-400 | CFC-12/CFC-114 | Should be specified[1] |
| R-401A | HCFC-22/HFC-152a/HCFC-124 | (53.0/13.0/34.0) |
| R-401B | HCFC-22/HFC-152a/HCFC-124 | (61.0/11.0/28.0) |
| R-401C | HCFC-22/HFC-152a/HCFC-124 | (33.0/15.0/52.0) |
| R-402A | HFC-125/HC-290/HCFC-22 | (60.0/2.0/38.0) |
| R-402B | HFC-125/HC-290/HCFC-22 | (38.0/2.0/60.0) |
| R-403A | HC-290/HCFC-22/PFC-218 | (5.0/75.0/20.0) |
| R-403B | HC-290/HCFC-22/PFC-218 | (5.0/56.0/39.0) |
| R-404A | HFC-125/HFC-143a/HFC-134a | (44.0/52.0/4.0) |
| R-405A | HCFC-22/ HFC-152a/ HCFC-142b/PFC-318 | (45.0/7.0/5.5/42.5) |
| R-406A | HCFC-22/HC-600a/HCFC-142b | (55.0/14.0/41.0) |
| R-407A | HFC-32/HFC-125/HFC-134a | (20.0/40.0/40.0) |
| R-407B | HFC-32/HFC-125/HFC-134a | (10.0/70.0/20.0) |
| R-407C | HFC-32/HFC-125/HFC-134a | (23.0/25.0/52.0) |
| R-407D | HFC-32/HFC-125/HFC-134a | (15.0/15.0/70.0) |
| R-407E | HFC-32/HFC-125/HFC-134a | (25.0/15.0/60.0) |
| R-408A | HFC-125/HFC-143a/HCFC-22 | (7.0/46.0/47.0) |
| R-409A | HCFC-22/HCFC-124/HCFC-142b | (60.0/25.0/15.0) |
| R-409B | HCFC-22/HCFC-124/HCFC-142b | (65.0/25.0/10.0) |
| R-410A | HFC-32/HFC-125 | (50.0/50.0) |
| R-410B | HFC-32/HFC-125 | (45.0/55.0) |
| R-411A | HC-1270/HCFC-22/HFC-152a | (1.5/87.5/11.0) |
| R-411B | HC-1270/HCFC-22/HFC-152a | (3.0/94.0/3.0) |
| R-411C | HC-1270/HCFC-22/HFC-152a | (3.0/95.5/1.5) |
| R-412A | HCFC-22/PFC-218/HCFC-142b | (70.0/5.0/25.0) |
| R-413A | PFC-218/HFC-134a/HC-600a | (9.0/88.0/3.0) |
| R-414A | HCFC-22/HCFC-124/HC-600a/HCFC-142b | (51.0/28.5/4.0/16.5) |
| R-414B | HCFC-22/HCFC-124/HC-600a/HCFC-142b | (50.0/39.0/1.5/9.5) |
| R-415A | HCFC-22/HFC-152a | (82.0/18.0) |
| R-415B | HCFC-22/HFC-152a | (25.0/75.0) |
| R-416A | HFC-134a/HCFC-124/HC-600 | (59.0/39.5/1.5) |
| R-417A | HFC-125/HFC-134a/HC-600 | (46.6/50.0/3.4) |
| R-418A | HC-290/HCFC-22/HFC-152a | (1.5/96.0/2.5) |
| R-419A | HFC-125/HFC-134a/HE-E170 | (77.0/19.0/4.0) |
| R-420A | HFC-134a/HCFC-142b | (88.0/12.0) |
| R-421A | HFC-125/HFC-134a | (58.0/42.0) |
| R-421B | HFC-125/HFC-134a | (85.0/15.0) |
| R-422A | HFC-125/HFC-134a/HC-600a | (85.1/11.5/3.4) |
| R-422B | HFC-125/HFC-134a/HC-600a | (55.0/42.0/3.0) |
| R-422C | HFC-125/HFC-134a/HC-600a | (82.0/15.0/3.0) |
| R-500 | CFC-12/HFC-152a | (73.8/26.2) |
| R-501 | HCFC-22/CFC-12 | (75.0/25.0) |
| R-502 | HCFC-22/CFC-115 | (48.8/51.2) |
| R-503 | HFC-23/CFC-13 | (40.1/59.9) |
| R-504 | HFC-32/CFC-115 | (48.2/51.8) |
| R-505 | CFC-12/HCFC-31 | (78.0/22.0) |
| R-506 | CFC-31/CFC-114 | (55.1/44.9) |
| R-507A | HFC-125/HFC-143a | (50.0/50.0) |
| R-508A | HFC-23/PFC-116 | (39.0/61.0) |
| R-508B | HFC-23/PFC-116 | (46.0/54.0) |
| R-509A | HCFC-22/PFC-218 | (44.0/56.0) |

[1] R-400 can have various proportions of CFC-12 and CFC-114. The exact composition needs to be specified, e.g., R-400 (60/40).

## 7.5.2 Methodological issues

### 7.5.2.1 CHOICE OF METHOD

As discussed in the introductory section to this chapter, both Tier 1 and Tier 2 result in estimates of *actual* emissions rather than estimates of *potential* emissions. Actual estimates, which account for the lag between consumption and emissions, are particularly important for both the refrigeration and air conditioning sector because of the potentially long retention of refrigerants in products and equipment utilised in these applications.

The options available to the refrigeration and air conditioning application are shown in the decision tree shown in Figure 7.6.

#### TIER 1

#### Tier 1 a/b

It is expected that the refrigeration and air conditioning will be a *key category* for many countries. The implication of this conclusion from Table 7.2 and the decision tree in Figure 7.6 is that either country-specific or globally or regionally derived activity data will be required at the sub-application (disaggregated) level in order to complete the reporting task. However, in the rare instances that the refrigeration and air conditioning application is much less significant, there should be available a suitable Tier 1 method for aggregated data.

From experience of studying the dynamics of refrigerant consumption and banks in several countries (UNEP-RTOC, 2003; Ashford, Clodic, Kuijpers and McCulloch, 2004; and supporting materials), it is possible to derive assumptions that allow for the assessment of the use of refrigerant that may help in assessing sales of a given refrigerant at a country level. Such a hybrid Tier 1a/b approach may use the following assumptions:

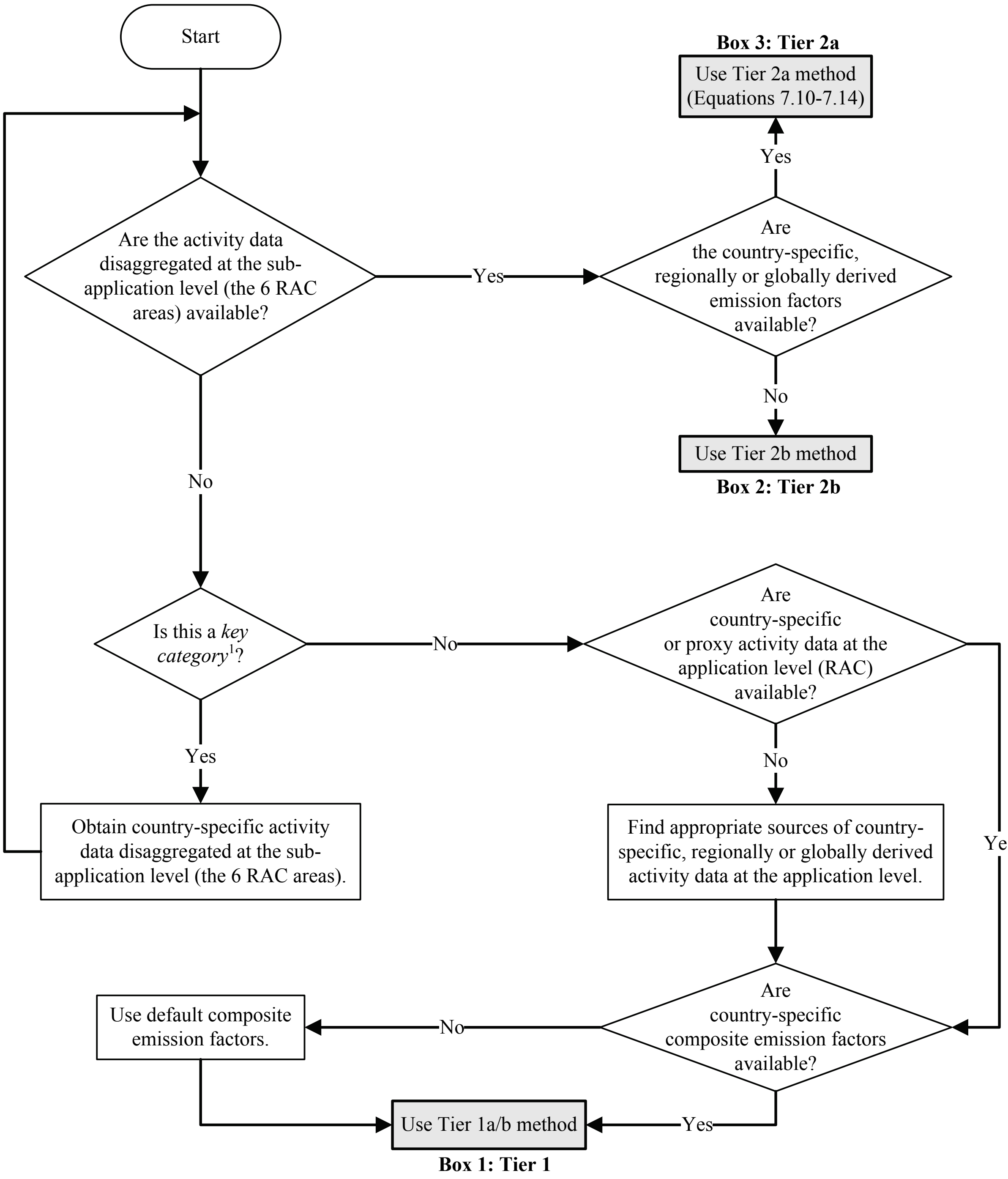
1. Servicing of equipment containing the refrigerant does not commence until 3 years after the equipment is installed.
2. Emissions from banked refrigerants average 15 percent annually across the whole RAC application area. This assumption is estimated to be a weighed average across all sub-applications, for which default emission factors are shown in Table 7.9.
3. In a mature market two thirds of the sales of a refrigerant are used for servicing and one third is used to charge new equipment. A mature market is one in which ODS substitute-employing refrigeration equipment is in wide use, and there are relationships between suppliers and users to purchase and service equipment.
4. The average equipment lifetime is 15 years. This assumption is also estimated to be a weighed average across all sub-applications.
5. The complete transition to a new refrigerant technology will take place over a 10 year period. From experiences to date, this assumption is believed to be valid for a single chemical in a single country.

With these assumptions in place, it is possible to derive emissions, if the following data can be provided:

- Sales of a specific refrigerant in the year to be reported
- Year of introduction of the refrigerant
- Growth rate in sales of new equipment (usually assumed linear across the period of assessment)
- Assumed percentage of new equipment exported
- Assumed percentage of new equipment imported

The Tier 1a/b method then back-calculates the development of banks of a refrigerant from the current reporting year to the year of its introduction. In mapping this period, the method also models the transition from sales to new equipment (100 percent initially) to the mature market position assumed based on experience to be 33 percent to new equipment and 67 percent to servicing requirements. It is assumed that the transition to new refrigerant technology is reflected identically in any imported equipment.

**Figure 7.6 Decision tree for actual emissions from the refrigeration and air conditioning (RAC) application**



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.

The following spreadsheet example indicates how the Tier 1a/b method would estimate a seven-year time series of emissions of the selected refrigerant, following its initial introduction in 1998, with the knowledge that there were sales of 1 000 tonnes in 2005. The spreadsheet contained in the *2006 Guidelines* CDROM mirrors this calculation, and globally or regionally derived datasets[21] at both application and consolidated sub-application levels should be available at a country level to assist in completion of this spreadsheet.

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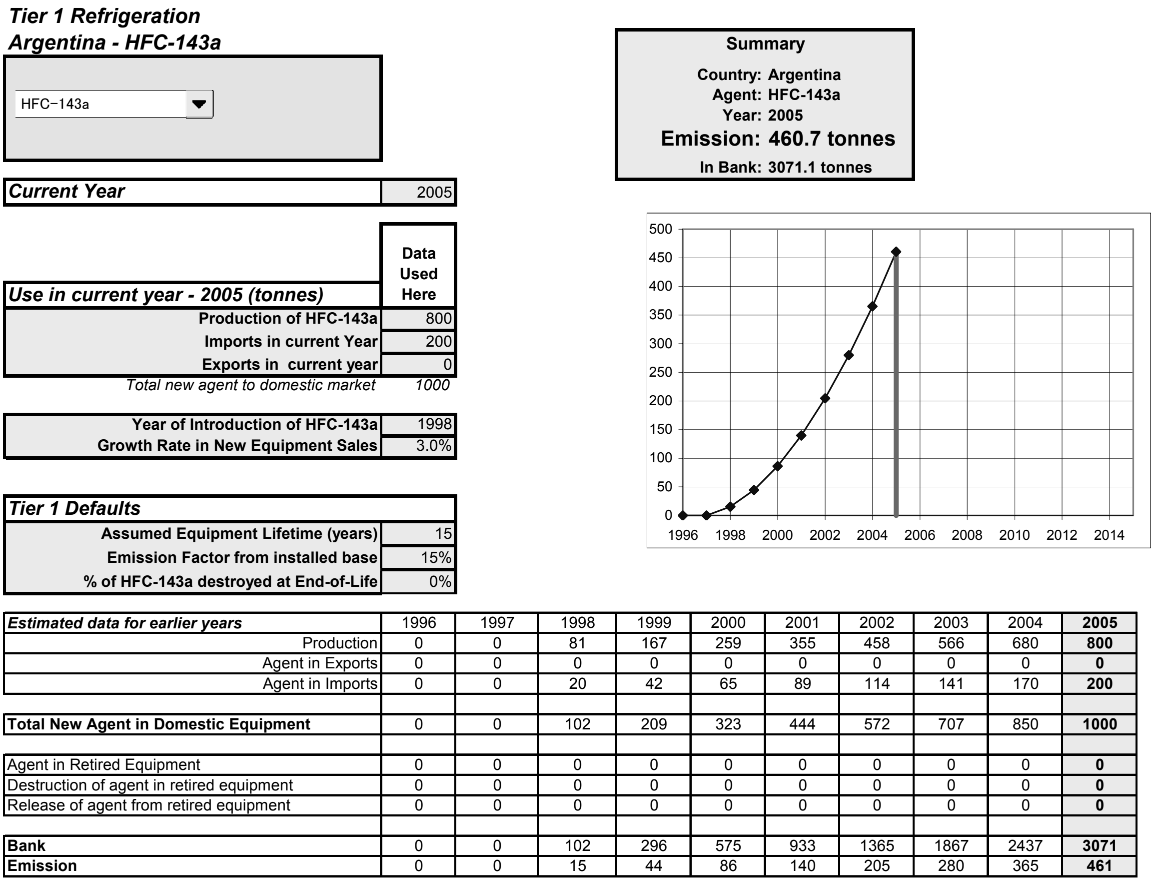
[21] As noted in Box 7.1, inclusion in the IPCC Emission Factor Database (EFDB) will indicate general adherence to due process, but it is *good practice* for countries to ensure that all data taken from the EFDB are appropriate for their national circumstances.

**Figure 7.7 Example of spreadsheet calculation for Tier 1a/b assessments**



***Tier 1 Refrigeration***
***Argentina - HFC-143a***

**Summary**
**Country: Argentina**
**Agent: HFC-143a**
**Year: 2005**
**Emission: 460.7 tonnes**
**In Bank: 3071.1 tonnes**

| | |
|---|---|
| ***Current Year*** | 2005 |

| ***Use in current year - 2005 (tonnes)*** | **Data Used Here** |
|---|---|
| **Production of HFC-143a** | 800 |
| **Imports in current Year** | 200 |
| **Exports in current year** | 0 |
| *Total new agent to domestic market* | *1000* |

| | |
|---|---|
| **Year of Introduction of HFC-143a** | 1998 |
| **Growth Rate in New Equipment Sales** | 3.0% |

| ***Tier 1 Defaults*** | |
|---|---|
| **Assumed Equipment Lifetime (years)** | 15 |
| **Emission Factor from installed base** | 15% |
| **% of HFC-143a destroyed at End-of-Life** | 0% |

| ***Estimated data for earlier years*** | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | **2005** |
|---|---|---|---|---|---|---|---|---|---|---|
| Production | 0 | 0 | 81 | 167 | 259 | 355 | 458 | 566 | 680 | **800** |
| Agent in Exports | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| Agent in Imports | 0 | 0 | 20 | 42 | 65 | 89 | 114 | 141 | 170 | **200** |
| | | | | | | | | | | |
| **Total New Agent in Domestic Equipment** | 0 | 0 | 102 | 209 | 323 | 444 | 572 | 707 | 850 | **1000** |
| | | | | | | | | | | |
| Agent in Retired Equipment | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| Destruction of agent in retired equipment | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| Release of agent from retired equipment | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| | | | | | | | | | | |
| **Bank** | 0 | 0 | 102 | 296 | 575 | 933 | 1365 | 1867 | 2437 | **3071** |
| **Emission** | 0 | 0 | 15 | 44 | 86 | 140 | 205 | 280 | 365 | **461** |

In this hypothetical example, the production of a specific refrigerant are 800 tonnes with an additional 200 tonnes in imported equipment, in 2005 making a total consumption of 1 000 tonnes. Based on this consumption figure and knowledge of the year of introduction of the refrigerant, it can be seen that the Tier 1a/b method predicts emissions of 461 tonnes based on the development of banks over the previous seven years. The bank in 2005 is estimated at 3 071 tonnes.

It should be noted that, while such methods allow for the estimation of emissions when data are difficult to obtain, it is still necessary to have an accurate assessment of country-specific or globally or regionally derived net consumption activity data. When the content of Table 7.8 is considered (particularly when some of these blends may be being imported in equipment) it is clear that there needs to be considerable knowledge of technology selection in the market. Refrigerant suppliers should be able to assist inventory compilers in this area, but the burden of developing high quality activity datasets may lead inventory compilers to the conclusion that Tier 2 options provide more value with little extra work. Indeed, where globally or regionally validated data activity is sought, this will normally be a reconstitution of disaggregated data originally at the sub-application level, so it might be most logical to take full advantage of that versatility and pursue a Tier 2 approach from the outset.

## TIER 2

### Overview

The Tier 2a methodology:

a) Takes into account the phase out or the phase down of CFCs and HCFCs depending on the Montreal Protocol schedule and possible national or regional regulations, in order to establish the refrigerant choice for all applications;

b) Defines the typical refrigerant charge and the equipment lifetime per sub-application;

c) Defines the emission factors for refrigerant charge, during operation, at servicing and at end-of-life.

Calculation of emissions throughout the equipment lifetime requires deriving the total stock of equipment independent of their vintage. In doing so the refrigerant bank is established per sub-application.

In order to achieve consistency it is suggested to derive the annual market of refrigerants from the refrigerant quantities charged in the brand new equipment and from the refrigerant quantities used for servicing of the total stock of equipment.

The Tier 2b mass-balance approach relies on a knowledge of the annual sales of refrigerant, refrigerant destroyed and any changes in equipment stock that occur (i.e., new equipment sales and equipment decommissioned) on a sub-application basis. It does not require an absolute knowledge of equipment stocks or emission factors relating to each refrigeration and air conditioning sub-application.

Examples of how the Tier 2 methodology may be applied are given in the remainder of this section.

### Tier 2b - Mass-balance approach

The mass-balance approach is particularly applicable to the Refrigeration and Air Conditioning application because of the significant servicing component required to maintain equipment. The general approach to Tier 2b is introduced in Chapter 1 of Volume 3.

For the mass-balance approach, the four emission stages (charging, operation servicing and end-of-life) identified above are addressed in the following simplified equation:

**EQUATION 7.9**

**DETERMINATION OF REFRIGERANT EMISSIONS BY MASS BALANCE**

$$\begin{aligned} Emissions &= Annual\ Sales\ of\ New\ Refrigerant - Total\ Charge\ of\ New\ Equipment \\ &+ Original\ Total\ Charge\ of\ Retiring\ Equipment - Amount\ of\ Intentional\ Destruction \end{aligned}$$

*Annual Sales of New Refrigerant* is the amount of a chemical introduced into the refrigeration sector in a particular country in a given year. It includes all chemical used to fill or refill equipment, whether the chemical is charged into equipment at the factory, charged into equipment after installation, or used to recharge equipment at servicing. It does not include recycled or reclaimed chemical.

*Total Charge of New Equipment* is the sum of the full charges of all the new equipment that is sold in the country in a given year. It includes both the chemical required to fill equipment in the factory and the chemical required to fill the equipment after installation. It does not include charging emissions or chemical used to recharge equipment at servicing.

*Original Total Charge of Retiring Equipment* is the sum of the full charges of all the retiring equipment decommissioned in a country in a given year. It assumes that the equipment will have been serviced right up to its decommissioning and will therefore contain its original charge.

*Amount of Intentional Destruction* is that quantity of the chemical duly destroyed by a recognised destruction technology.

In each country there is a stock of existing refrigeration equipment that contains an existing stock of refrigerant chemical (*bank*). Therefore, annual sales of new chemical refrigerant must be used for one of three purposes:

- To increase the size of the existing chemical stock (bank) in use (including retrofitting equipment from a previous chemical to the given chemical)
- To replace that fraction of last year's stock of chemical that was emitted to the atmosphere (through, for example, leaks or servicing losses)
- To provide supply-chain priming or stockpiles

Since the third item in this list is rarely required in a steady-state market, it is not included in Equation 7.9. Terms to account for stockpiling and retrofitting could be added to Equation 7.9 if such situations exist.

The difference between the total quantity of gas sold and the quantity of that gas used to increase the size of the chemical stock equals the amount of chemical emitted to the atmosphere. The increase in the size of the chemical stock is equal to the difference between the total charges of the new and retiring equipment.

By using data on current and historical sales of gas, rather than emission factors referenced from literature, the equation reflects assembly, operation, and disposal emissions at the time and place where they occur. Default emission factors may not be accurate because emissions rates may vary considerably from country to country and even within a single country.

As discussed in Chapter 1, Section 1.5 of Volume 3, one drawback of the mass-balance approach is that it can underestimate emissions when equipment stocks are growing, because there is a lag between the time the emissions occur and the time they are detected (through equipment servicing). This underestimate will be relatively large in countries where HFCs have been used in equipment for less than ten years, because much of the equipment will have leaked without ever being serviced. Thus, countries where HFCs have been used for less than ten years are encouraged to estimate emissions using alternative approaches. In general, the longer HFCs are used in a country, the smaller the underestimate associated with the mass-balance approach. Once equipment containing HFCs begins to retire, the underestimate declines to a low level.

Equation 7.9 can be applied either to individual types of equipment (sub-applications), or more generally to all air conditioning and refrigeration equipment in a country (i.e., Tier 1b), depending on the level of disaggregation of available data. If disaggregated data are available, emissions estimates developed for each type of equipment and chemical are summed to determine total emissions for the application.

### Tier 2a – Emission-factor approach

In a Tier 2a calculation, refrigerant emissions at a year **t** from each of the six[22] sub-applications of refrigeration and air conditioning systems are calculated separately. These emissions result from:

- $E_{containers,t}$ = emissions related to the management of refrigerant containers
- $E_{charge,t}$ = emissions related to the refrigerant charge: connection and disconnection of the refrigerant container and the new equipment to be charged
- $E_{lifetime,t}$ = annual emissions from the banks of refrigerants associated with the six sub-applications during operation (fugitive emissions and ruptures) and servicing
- $E_{end\text{-}of\text{-}life,t}$ = emissions at system disposal

All these quantities are expressed in kilograms and have to be calculated for each type of HFC used in the six different sub-applications.

**EQUATION 7.10**
**SUMMARY OF SOURCES OF EMISSIONS**

$$E_{total,t} = E_{containers,t} + E_{Charge,t} + E_{lifetime,t} + E_{end-of-life,t}$$

Methods for estimating average emission rates for the above-mentioned sectors are outlined below and need to be calculated on a refrigerant by refrigerant basis for all equipment regardless of their vintage. If information on container and charging emissions is not available, inventory compilers can estimate these losses as a percent of the bank and revise the lifetime (operation plus servicing) emission factor in Equation 7.13 below to account for such losses.

### *Refrigerant management of containers*

The emissions related to the refrigerant container management comprises all the emissions related to the refrigerant transfers from bulk containers (typically 40 tonnes) down to small capacities where the mass varies from 0.5 kg (disposable cans) to 1 tonne (containers) and also from the remaining quantities - the so-called refrigerant *heels* (vapour and /or liquid) - left in the various containers, which are recovered or emitted.

**EQUATION 7.11**
**SOURCES OF EMISSIONS FROM MANAGEMENT OF CONTAINERS**

$$E_{containers,t} = RM_t \bullet \frac{c}{100}$$

Where:

$E_{containers,t}$ = emissions from all HFC containers in year *t*, kg

$RM_t$ = HFC market for new equipment and servicing of all refrigeration application in year *t*, kg

c = emission factor of HFC container management of the current refrigerant market, percent

The emissions related to the complete refrigerant management of containers are estimated between 2 and 10 percent of the refrigerant market.

### *Refrigerant charge emissions of new equipment*

The emissions of refrigerant due to the charging process of new equipment are related to the process of connecting and disconnecting the refrigerant container to and from the equipment when it is initially charged.

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[22] More than six sub-applications can be used, depending on the level of disaggregated data available.

### EQUATION 7.12
### SOURCES OF EMISSIONS WHEN CHARGING NEW EQUIPMENT

$$E_{charge,t} = M_t \bullet \frac{k}{100}$$

Where:

$E_{charge,t}$ = emissions during system manufacture/assembly in year *t*, kg

$M_t$ = amount of HFC charged into new equipment in year *t* (per sub-application), kg

k = emission factor of assembly losses of the HFC charged into new equipment (per sub-application), percent

Note: the emissions related to the process of connecting and disconnecting during servicing are covered in Equation 7.13.

The amount charged ($M_t$) should include all systems which are charged in the country, including those which are produced for export. Systems that are imported pre-charged should not be considered.

Typical range for the emission factor k varies from 0.1 to 3 percent. The emissions during the charging process are very different for factory assembled systems where the emissions are low (see Table 7.9) than for field-erected systems where emissions can be up to 2 percent.

### *Emissions during lifetime (operation and servicing)*

Annual leakage from the refrigerant banks represent fugitive emissions, i.e., leaks from fittings, joints, shaft seals, etc. but also ruptures of pipes or heat exchangers leading to partial or full release of refrigerant to the atmosphere. Besides component failures, such as compressor burn-out, equipment is serviced mainly when the refrigerating capacity is too low due to loss of refrigerant from fugitive emissions. Depending on the application, servicing will be done for instance every year or every three years, or sometimes not at all during the entire lifetime such as in domestic refrigeration sub-applications. For some sub-applications, leaks have to be fixed during servicing and refrigerant recovery may be necessary, so the recovery efficiency has to be taken into account when estimating emission factors. In addition, knowing the annual refrigerant needs for servicing per sub-application allows the determination of the national refrigerant market by adding the refrigerant quantities charged in new equipment (see Paragraph Quality assurance/Quality control). The following calculation formula applies:

### EQUATION 7.13
### SOURCES OF EMISSIONS DURING EQUIPMENT LIFETIME

$$E_{lifetime,t} = B_t \bullet \frac{x}{100}$$

Where:

$E_{lifetime,t}$ = amount of HFC emitted during system operation in year *t*, kg

$B_t$ = amount of HFC banked in existing systems in year *t* (per sub-application), kg

x = annual emission rate (i.e., emission factor) of HFC of each sub-application bank during operation, accounting for average annual leakage and average annual emissions during servicing, percent

In calculating the refrigerant bank ($B_t$) all systems in operation in the country (produced domestically and imported) have to be considered on a sub-application by sub-application basis.

Examples of typical leakage rates (x) for various types of equipment describing the respective refrigeration sub-applications are given in Table 7.9.

### *Emissions at end-of-life*

The amount of refrigerant released from scrapped systems depends on the amount of refrigerant left at the time of disposal, and the portion recovered. From a technical point of view, the major part of the remaining fluid can be recovered, but recovery at end-of-life depends on regulations, financial incentives, and environmental consciousness.

The following calculation formula (Equation 7.14) is applicable to estimate emissions at system disposal:

EQUATION 7.14

EMISSIONS AT SYSTEM END-OF-LIFE

$$E_{end-of-life,\,t} = M_{t-d} \bullet \frac{p}{100} \bullet (1 - \frac{\eta_{rec,\,d}}{100})$$

Where:

$E_{end\text{-}of\text{-}life,\,t}$ = amount of HFC emitted at system disposal in year *t*, kg

$M_{t-d}$ = amount of HFC initially charged into new systems installed in year (*t-d*), kg

p = residual charge of HFC in equipment being disposed of expressed in percentage of full charge, percent

$\eta_{rec,d}$ = recovery efficiency at disposal, which is the ratio of recovered HFC referred to the HFC contained in the system, percent

In estimating the amount of refrigerant initially charged into the systems ($M_{t-d}$), all systems charged in the country (for the domestic market) and systems imported pre-charged should be taken into account.

### 7.5.2.2 CHOICE OF EMISSION FACTORS

#### Tier 1a/b method

As explained within Section 7.5.2.1, Choice of Method, a composite emission factor is required to complete a Tier 1 method. Since the sub-applications within the refrigeration and air conditioning application are relatively heterogeneous, the validity of any single composite emission factor must be in doubt unless it takes into consideration the particular mix of sub-applications in the country. It is therefore *good practice* to develop composite emission factors on the basis of research within the country. The over-arching default emissions factor of 15 percent of the bank annually is used in the example of spreadsheet calculation contained in the *2006 Guidelines* CDROM attached to these *Guidelines*.

#### Tier 2a method

*Good practice* for choosing emission factors is to use country-specific data, based on information provided by equipment manufacturers, service providers, disposal companies, and independent studies. When national data are unavailable, inventory compilers should use the default emission factors shown in Table 7.9, Estimates for Charge, Lifetime and Emission Factors, which summarises best estimates of equipment charge, lifetime, and emission factors. These default values reflect the current state of knowledge about the industry, and are provided as ranges rather than point estimates. The lower end of the lifetime and emission factor ranges is intended to indicate the status within developed countries, while the upper end of each range is intended to indicate the status within developing countries. Inventory compilers should choose from the range according to country-specific conditions, and document the reasons for their choices. If data collected from the field cannot be broken down into the sub-applications as in Table 7.9, it is *good practice* to use expert judgement to estimate the relative share of each type of equipment, and calculate composite emission factors weighted according to that relative share, as proposed for Tier 1a/b, or use the emission factor appropriate to the most common type(s) of equipment.

### TABLE 7.9
### ESTIMATES[1] FOR CHARGE, LIFETIME AND EMISSION FACTORS FOR REFRIGERATION AND AIR-CONDITIONING SYSTEMS

| Sub-application | Charge (kg) | Lifetimes (years)[2] | Emission Factors (% of initial charge/year)[3] | | End-of-Life Emission (%) | |
|---|---|---|---|---|---|---|
| **Factor in Equation** | **(M)** | **(d)** | **(k)** | **(x)** | **($\eta_{rec,d}$)** | **(p)** |
| | | | **Initial Emission** | **Operation Emission** | **Recovery Efficiency[4]** | **Initial Charge Remaining** |
| Domestic Refrigeration | $0.05 \leq M \leq 0.5$ | $12 \leq d \leq 20$ | $0.2 \leq k \leq 1$ | $0.1 \leq x \leq 0.5$ | $0 < \eta_{rec,d} < 70$ | $0 < p < 80$ |
| Stand-alone Commercial Applications | $0.2 \leq M \leq 6$ | $10 \leq d \leq 15$ | $0.5 \leq k \leq 3$ | $1 \leq x \leq 15$ | $0 < \eta_{rec,d} < 70$ | $0 < p < 80$ |
| Medium & Large Commercial Refrigeration | $50 \leq M \leq 2000$ | $7 \leq d \leq 15$ | $0.5 \leq k \leq 3$ | $10 \leq x \leq 35$ | $0 < \eta_{rec,d} < 70$ | $50 < p < 100$ |
| Transport Refrigeration | $3 \leq M \leq 8$ | $6 \leq d \leq 9$ | $0.2 \leq k \leq 1$ | $15 \leq x \leq 50$ | $0 < \eta_{rec,d} < 70$ | $0 < p < 50$ |
| Industrial Refrigeration including Food Processing and Cold Storage | $10 \leq M \leq 10{,}000$ | $15 \leq d \leq 30$ | $0.5 \leq k \leq 3$ | $7 \leq x \leq 25$ | $0 < \eta_{rec,d} < 90$ | $50 < p < 100$ |
| Chillers | $10 \leq M \leq 2000$ | $15 \leq d \leq 30$ | $0.2 \leq k \leq 1$ | $2 \leq x \leq 15$ | $0 < \eta_{rec,d} < 95$ | $80 < p < 100$ |
| Residential and Commercial A/C, including Heat Pumps | $0.5 \leq M \leq 100$ | $10 \leq d \leq 20$ | $0.2 \leq k \leq 1$ | $1 \leq x \leq 10$ | $0 < \eta_{rec,d} < 80$ | $0 < p < 80$ |
| Mobile A/C | $0.5 \leq M \leq 1.5$ | $9 \leq d \leq 16$ | $0.2 \leq k \leq 0.5$ | $10 \leq x \leq 20$[5] | $0 < \eta_{rec,d} < 50$ | $0 < p < 50$ |

[1] Based on information contained in UNEP RTOC Reports (UNEP-RTOC, 1999; UNEP-RTOC, 2003)

[2, 3] Lower value for developed countries and higher value for developing countries

[4] The lower threshold (0%) highlights that there is no recovery in some countries.

[5] Schwarz and Harnisch (2003) estimates leakage rates of 5.3% to 10.6%; these rates apply only to second generation mobile air conditioners installed in European models in 1996 and beyond.

## 7.5.2.3 CHOICE OF ACTIVITY DATA

### Tier 1a/b method

Inventory compilers in countries that manufacture refrigerant chemicals should estimate Annual Sales of New Refrigerant using information provided by chemical manufacturers. Data on imported chemical should be collected from customs statistics, importers, or distributors.

Total Charge of New Equipment can be estimated using either:

- Information from equipment manufacturers/importers on the total charge of the equipment they manufacture or import; or
- Information from chemical manufacturers/importers on their sales to equipment manufacturers and distributors.

Ensure this information only includes sales as refrigerant, not feedstock or other uses. The difference between the total sales of new refrigerant and that charged in new equipment is assumed to be used for servicing. Where information on new equipment charges is unavailable, it can be assumed that, in a mature market, two thirds of refrigerant is used for servicing while one third is used for new equipment. However, the adoption of such assumptions must be accompanied by some justification about the state of the market and how well these assumptions are likely to apply.

### Tier 2 methods

Both Tier 2a and Tier 2b methods require the development of a matrix for each sub-application based on equipment type on the one hand and refrigerant type on the other hand. In order to derive the number of pieces of equipment for all the vintages, historic net consumption activity data is also required. The annual update of the matrix makes it possible to recalculate all emission types as detailed in Equations 7.10 to 7.14 each year. Moreover, the refrigerant choice has to be assessed on a year-by-year basis owing to changing national regulations (often relating to CFC and HCFC phase-out at different dates) and changing technological choices. In some countries HFC refrigerant regulations have started to enter into force.

Where country-specific data cannot be analysed to this level, globally or regionally validated activity data can be obtained from reputable databases based on refrigerant charges and lifetimes provided in Table 7.9, for all sub-applications, to facilitate Tier 2 methods. A number of refinements are usually necessary dependent on the particular circumstances of the country. Assistance for this can be obtained from application experts.

### Other shared issues

Whether collecting country-specific activity data in support of a Tier 1 or a Tier 2 method, inventory compilers must take care in dealing with refrigerant blends. Table 7.8 illustrates the complexity already existing and blends are only expected to increase in popularity as manufacturers of equipment seek for further improvements in performance, particularly in respect of energy efficiency. Where blends contain both HFCs and other components, only the reportable elements need to be considered. This is even the case for other components with significant GWPs (e.g., CFCs and HCFCs).

Inventory compilers also need to consider how to monitor the movement of trade in equipment and products containing HFCs and/or PFCs. The Box 7.3 below sets out some of the measures required to estimate imports and exports adequately.

### BOX 7.3
### ACCOUNTING FOR IMPORTS AND EXPORTS OF REFRIGERANT AND EQUIPMENT

In estimating *Annual Sales of New Refrigerant*, *Total Charge of New Equipment*, and *Original Total Charge of Retiring Equipment*, as required for Tier 2b, inventory compilers should account for imports and exports of both chemicals and equipment. This will ensure that they capture the actual domestic consumption of chemicals and equipment. For example, if a country imports a significant share of the HFC-134a that it uses, the imported quantity should be counted as part of **Annual Sales**. Alternatively, if a country charges and then exports a significant number of household refrigerators, the total charge of the exported refrigerators should be subtracted from the total charge of the household refrigerators manufactured in the country to obtain **Total Charge of New Equipment**.

***GENERAL APPROACH***: In general, the quantity Annual Sales should be estimated using the following formula:

**Annual Sales = Domestically Manufactured Chemical**
**+ Imported Bulk Chemical**
**− Exported Bulk Chemical**
**+ Chemical Contained in Factory-Charged Imported Equipment**
**− Chemical Contained in Factory-Charged Exported Equipment**

All quantities should come from the year for which emissions are being estimated. Similarly, the quantity of **Total Charge of New Equipment** should be estimated using the following:

**Total Charge of New Equipment**
**= Chemical to Charge Domestically Manufactured Equipment that is not Factory-Charged**
**+ Chemical to Charge Domestically Manufactured Equipment that is Factory-Charged**
**+ Chemical to Charge Imported Equipment that is not Factory-Charged**
**+ Chemical Contained in Factory-Charged Imported Equipment**
**− Chemical Contained in Factory-Charged Exported Equipment**

*Original Total Charge of Retiring Equipment* should be estimated the same way as *Total Charge of New Equipment*, except all quantities should come from the year of manufacture or import of the retiring equipment.

***SIMPLIFIED APPROACH***: In estimating *Annual Sales* and *Total Charge of New Equipment*, it is possible to ignore the quantities of chemical imported or exported inside of factory-charged equipment if these quantities cancel out in the calculation of emissions. However, inventory compilers that use the simplified calculation should ensure that: (1) they treat imports and exports of factory-charged equipment consistently in estimating both *Annual Sales* and *Total Charge New of Equipment*; and (2) they continue to account for imports and exports of factory-charged equipment in estimating *Original Total Charge of Retiring Equipment.* As new equipment will eventually become retiring equipment, countries may wish to track imports and exports of factory-charged equipment even if this information is not strictly necessary to develop the current year's estimate.

The simplified formula for **Annual Sales** is:

**Annual Sales = Domestically Manufactured Chemicals**
**+ Imported Bulk Chemicals**
**− Exported Bulk Chemicals**

The simplified formula for **Total Charge of New Equipment** is:

**Total Charge of New Equipment**
**= Chemicals to Charge Domestically Manufactured Equipment**
**+ Chemical to Charge Imported Equipment that is not Factory-Charged**

The full formula, accounting for imports and exports of pre-charged equipment, must be used to calculate *Original Total Charge of Retiring Equipment.*

### 7.5.2.4 APPLYING TIER 2 METHODS – THE EXAMPLE OF MOBILE AIR CONDITIONING (MAC)

The Box 7.4 below sets out the step-by-step approach required to assess the emissions from the mobile air conditioning sub-application of a hypothetical country's inventory. The method adopted is primarily a Tier 2a approach, although there are also elements which would be equally applicable to Tier 2b. This example, therefore, highlights the reality that pure approaches and methods are rare in practice. There will often be a mix of emission-factor approach and mass–balance approach as well as a mix of country-specific data and globally or regionally derived data. As pointed out in Section 7.1.2.1, one method, approach or dataset will often be used to cross-check another. This example also demonstrates that a detailed implementation of the Tier 2a method requires a significant amount information gathering about a sub-application. Once established, it is less burdensome to implement the approach in subsequent years. Also note that assumptions made are for example only; inventory compilers should collect country-specific information rather than using the assumptions shown.

**BOX 7.4**
**EXAMPLE OF THE APPLICATION OF A TIER 2a CALCULATION FOR MOBILE AIR CONDITIONING**

**Introduction**

National inventories and other studies to date show that emissions of HFC-134a from mobile air conditioners (MACs) contribute significantly to the Refrigeration and Air Conditioning (RAC) Application emissions and the ODS Substitutes Category emissions. For many countries, emissions from MACs will comprise 50 percent or more of the RAC emissions and possibly more than 50 percent of the total ODS Substitutes Category emissions. This is due to many factors, including:

- The phaseout of ODSs to HFCs in MACs occurred earlier and more quickly than other Sub-Applications, such as residential (stationary) air conditioning and commercial refrigeration (supermarkets), which still rely substantially on ODSs.
- MACs are subject to extremes in terms of physical shock and vibration and hence emissions tend to be large.
- The lifetime of MACs tends to be shorter than many other RAC Sub-Applications, so that end-of-life emissions are seen earlier and equipment stocks relying on ODSs are replaced sooner with HFCs.
- Due to the small charge of refrigerant involved, recovery from MACs is often seen as uneconomical and hence is not often practiced during service and disposal.

In addition, data on vehicle purchases and registrations in a country are often known to a higher degree of quality or are easily obtained. Hence, it is *good practice* to estimate emissions from this Sub-Application. The following text describes how the general equations for the RAC Application can be applied to the MAC Sub-Application.

**Data Gathering and Assumptions**

An accurate estimate of MAC emissions may be obtained by collecting some data at the Sub-Application level and applying a few basic assumptions to simplify the data and calculations required, as follows:

*Refrigerant Type.* It will be important to separate each data point by refrigerant, so that emissions of each refrigerant are calculated separately. For MACs, this may be simplified by the fact that all MACs produced since the mid- to late-1990s use HFC-134a as the refrigerant. However, CFC-12 was used in the past and still exists in some operating systems. Furthermore, for the future other refrigerants such as HFC-152a and R-744 (carbon dioxide) are being considered.

*Refrigerant Sold in Containers* ($RM_t$). For MACs, refrigerant generally comes in three basic types of containers – 'bulk containers' sent to vehicle manufacturers to fill new MACs, 'small cans' containing about 300-500 grams of refrigerant generally used by individuals servicing their own equipment, and 'cylinders' containing about 10-15 kilograms of refrigerant used by shops that service many vehicles. If one assumes no losses from bulk containers (see below), then in order to calculate $E_{containers}$, one needs to know the total refrigerant sold in small cans ($RM_{sc}$) and cylinders ($RM_{cy}$). It will be important to distinguish the refrigerant sold into different Sub-Applications (e.g., HFC-134a is also used in the chillers and domestic refrigeration Sub-Applications) so that only the refrigerant sold for MACs is used in the calculations. This data may be obtained from small can packagers and refrigerant producers/distributors.

*Container Heels* (*c*). For this example, we assume the heels from service containers are not recovered (e.g., the cylinders are discarded, not reused) and are $c_{sc}$ = 20% for the small can and $c_{cy}$ = 2% for the cylinder. Because bulk refrigerant containers generally go back to the refrigerant producer and are refilled, we can assume there are no heels that would be emitted and hence $c_{bulk}$ = 0%.

*MACs Produced Each Year* (*$N_t$*). If the number of MACs placed in service each year is not known, an estimate can be made by multiplying the number of cars placed in service each year by an estimate of the percentage that were sold with MACs. These data may be available from automobile manufacturers, MAC producers/suppliers, or government agencies involved in transportation, infrastructure and highway safety. If more than one type of refrigerant is used, it is important to separate each Nt into the different refrigerants, e.g., $N_{1994} = N_{1994,CFC\text{-}12} + N_{1994,HFC\text{-}134a}$.

*Nominal Charge of Each MAC* (*$m_t$*). This factor would likely vary by the type of vehicle; for instance small passenger cars will likely have lower refrigerant charges than buses or larger cars, especially those with multiple evaporators. Likewise, this could vary over time, for instance decreasing as manufacturers make smaller systems for the same vehicle size, or increasing as larger cars and more multiple-evaporator units enter the market. For this example, we assume a constant over time at an average m = 0.7 kg, which is typical of small to medium-sized passenger cars.

*Refrigerant Charged into New Equipment* (*$M_t$*). This is easily calculated as $M_t = N_t \bullet m_t = 0.7 \bullet N_t$.

*Assembly Losses* (*k*). This is used to calculate the Charge Emissions, also referred to as 'First-Fill Emissions.' The loss rate is often small, on the order of k = 0.5% or smaller. For simplicity, we assume k = 0 in this example.

*Lifetime* (*d*). The presumed lifetime of a MAC. This variable can be based on national data and can be different for different types of MACs (passenger cars, buses, etc.) For this example, we assume the lifetime of all MACs is d = 12 years.

*Bank in Existing Equipment* (*B*). The bank will be the amount of refrigerant in MACs put into service, minus the amount of refrigerant in MACs disposed, plus the amount of refrigerant used to service MACs, minus the amount that has leaked. In actuality, a given MAC will probably leak over several years before being serviced. Rather than attempting to account for this, for this example we apply Equation 7.13 which assumes all MACs are serviced each year such that the estimated charge of each MAC is the same as the nominal charge. The annual emission rate is averaged to account for this assumption. This will only produce small errors unless the year-to-year sales of MACs fluctuate widely. Hence the bank in any given year is the sum of the Refrigerant Charged into New Equipment each year from the current year back to the assumed average lifetime of the equipment. Thus,

$$B_t = \sum_{i=1}^{d} M_{t-i+1}$$

For example, using d = 12 years, the bank in 2006 would be $B_{2006} = M_{2006} + M_{2005} + M_{2004} + \ldots + M_{1997} + M_{1996} + M_{1995}$.

*Annual Emission Rate* (*x*). This factor accounts for both leaks from equipment as well as any emissions during service. Both of these items can be different for different types of MACs and can also vary by when the MAC was produced (i.e., older MACs may leak more than newer MACs). If annual servicing does not occur, the amount emitted at any servicing event needs to be average over the number of years between servicing event to obtain the annual rate. This amount is likely to vary considerably depending on national conditions and what type(s) of service is (are) performed. Whether recovery of the given charge before service is performed must be considered, and may be deduced in part by examining the amount of refrigerant sold in small cans versus cylinders. For this example, we assume that 15% of the nominal charge is leaked each year and 11% on average is emitted during servicing. Hence, x = 26%.

*Residual Charge in MACs Disposed* (*p*). Assuming that the MAC is serviced the year before it is disposed, and that the annual emission rate is estimated, this is easily calculated as p = 1 – x. In our example, p = 1 – 26% = 0.74

*Recovery Efficiency* (*nrec*). If no regulations or incentives exist to require recovery of refrigerant from MACs disposed, then likely very little will occur. So, for this example, we assume that nrec = 0.

**Calculation of Different Types of Emissions**

Now that these data have been gathered and assumptions have been made, calculating the emissions may be performed. An example for year t = 2006 follows:

*Container Emissions (Equation 7.11).*

$$E_{containers,2006} = RM_{cy,2006} \bullet c_{cy} + RM_{sc,2006} \bullet c_{sc} = 0.02 \bullet RM_{cy,2006} + 0.2 \bullet RM_{sc,2006}$$

*Charging Emissions (Equation 7.11).*

$$E_{ch\arg e,2006} = M_{2006} \bullet k = 0$$

*Lifetime (Operating and Servicing) Emissions (Equation 7.13).*

$$\begin{aligned} E_{operation,2006} &= B_{2006} \bullet x = 0.26 \bullet B_{2006} = 0.26 \bullet \sum_{i=1}^{d} M_{t-i+1} \\ &= 0.26 \bullet (M_{2006} + M_{2005} + M_{2004} + \cdots + M_{1997} + M_{1996} + M_{1995}) \\ &= 0.26 \bullet m \bullet (N_{2006} + N_{2005} + N_{2004} + \cdots + N_{1997} + N_{1996} + N_{1995}) \\ &= 0.26 \bullet 0.7 \bullet (N_{2006} + N_{2005} + N_{2004} + \cdots + N_{1997} + N_{1996} + N_{1995}) \\ &= 0.182 \bullet (N_{2006} + N_{2005} + N_{2004} + \cdots + N_{1997} + N_{1996} + N_{1995}) \end{aligned}$$

*End-of-Life Emissions (Equation 7.14).*

$$\begin{aligned} E_{end-of-life,2006} &= M_{2006-d} \bullet p \bullet (1 - n_{rec}) = M_{2006-12} \bullet 0.74 \bullet (1-0) \\ &= 0.74 \bullet M_{1994} = 0.74 \bullet 0.7 \bullet N_{1994} = 0.518 \bullet N_{1994} \end{aligned}$$

**Calculation of Total Emissions**

*Total MAC Emissions (Equation 7.8).*

$$\begin{aligned} E_{total,2006} &= E_{containers,2006} + E_{ch\arg e,2006} + E_{lifetime,2006} + E_{servicing,2006} + E_{end-of-life,2006} \\ &= 0.02 \bullet RM_{cy,2006} + 0.2 \bullet RM_{sc,2006} + 0 \\ &\quad + 0.182 \bullet (N_{2006} + N_{2005} + N_{2004} + \cdots + N_{1997} + N_{1996} + N_{1995}) + 0.518 \bullet N_{1994} \\ &= 0.02 \bullet RM_{cy,2006} + 0.2 \bullet RM_{sc,2006} \\ &\quad + 0.182 \bullet (N_{2006} + N_{2005} + N_{2004} + \cdots + N_{1997} + N_{1996} + N_{1995}) + 0.518 \bullet N_{1994} \end{aligned}$$

The only unknowns are:

- $RM_{sc}$ – refrigerant (in kilograms) sold in small cans to service MACs, which may be obtained from small can packagers;
- $RM_{cy}$ – refrigerant (in kilograms) sold in cylinders to service MACs, which may be obtained from refrigerant producers/distributors; and,
- $N_t$ – the number of MACs put in service each year, which may be available from automobile manufacturers, MAC producers/suppliers, or government agencies involved in transportation, infrastructure and highway safety.

If the emissions from refrigerant containers and from end-of-life are not included, for example if it is believed that service cylinders are completely evacuated and minimal MACs reach their end-of-life in the given year, this equation becomes simply an activity (the number of MACs) multiplied by an emission factor (annual emission rate times average charge size, in this case 0.182 kg per MAC). This calculation yields the total emissions in kilograms of refrigerant. Keeping each refrigerant separate and multiplying each sum by the refrigerant's GWP will yield kilograms of $CO_2$ equivalent emissions. Dividing by 1 billion ($10^9$) will yield emissions in teragrams of $CO_2$ equivalent ($TgCO_2eq$).

#### 7.5.2.5 COMPLETENESS

Completeness for the Tier 1a/b method can be achieved if data for new refrigerants, and refrigerants in equipment that is retired in the current year, are available. For the Tier 2a and 2b methods, completeness depends on a thorough accounting of the existing equipment banks, and this may involve tracking large amounts of data.

#### 7.5.2.6 DEVELOPING A CONSISTENT TIME SERIES

Emissions from refrigeration and air conditioning should be calculated using the same method and data sources for every year in the time series. Where consistent data are unavailable for the more rigorous method for any years in the time series, these gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5.

### 7.5.3 Uncertainty assessment

Table 7.8, Estimates for Charge, Lifetime and Emission Factors for Refrigeration and Air-Conditioning Systems, presents emission factor ranges that highlight the uncertainty associated with this sector. Generally, disaggregated methods (Tier 2) have less uncertainty than Tier 1 methods because of the heterogeneous nature of the sub-applications. Those Tier 2 methods that rely on emission factors (Tier 2a) have more uncertainty than mass balance methods that use chemical sales data (Tier 2b). This occurs largely because of the small unit size of most equipment and the potential for the multiplication of a small unit error. Inventory compilers should seek industrial advice on uncertainties, using the approaches to obtaining expert judgements outlined in Volume 1, Chapter 3.

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

#### 7.5.4.1 QUALITY ASSURANCE/QUALITY CONTROL

In order to conduct a quality control for Tier 2 method, it is possible, but not necessary in order to satisfy the requirements of *good practice,* to compare the annual national HFC refrigerant market as declared by the chemical manufacturers or the refrigerant distributors with the annual HFC refrigerant needs as derived by the Tier 2 method. Refrigerant will be needed for either charging new equipment or servicing existing equipment. What is needed (i.e., purchased) to charge equipment includes the refrigerant that is actually charged in the equipment plus any associated emissions (either during the charging process or from containers that are used for charging but not completely emptied before they are discarded). What is needed for service is refrigerant to replace that which is lost from existing equipment due to leaks and lost during servicing, as well as refrigerant from containers that are not completely emptied before they are discarded. The following formula leads to this verification.

**EQUATION 7.15**
**VERIFICATION OF SUPPLY AND DEMAND ASSESSMENTS**

$$RN_t = \sum_{j=1}^{6}\left(S_{prod\_t,j} \bullet m_{t,j}\right) + \sum_{j=1}^{6}\left(M_{t,j} \bullet k_j\right) + \sum_{j=1}^{6}\left(B_{t,j} \bullet x_j\right) + RM_t \bullet c$$

Where:

$RN_t$ = HFC refrigerant needs in year *t*, kg

*j* = counter from 1 to 6 (or the number of sub-applications chosen for the Tier 2 method)

$S_{prod\_t,j}$ = national production of equipment using HFC refrigerant for sub-application domain *j* in year *t*, number of equipment

$m_{t,j}$ = initial average charge of HFC in sub-application *j* type of equipment, kg

$M_{t,j}$ = amount of HFC charged into the equipment of sub-application *j* at manufacturing in year *t*, kg

$k_j$ = emission factor of assembly losses of the HFC charged into new equipment of sub-application *j*, fraction

$B_{t,j}$ = amount of HFC banked in existing systems of sub-application *j* in year *t* (per sub-application), kg

$x_j$ = annual emission rate (i.e., emission factor) of HFC banked in sub-application *j* during operation, accounting for average annual leakage and average annual emissions during servicing, fraction

$RM_t$ = HFC market for new equipment and servicing of all refrigeration sub-applications in year *t*, kg

c = emission factor of HFC container management of the refrigerant market, fraction

The first term corresponds to the refrigerant charge of new refrigerating and air conditioning system produced in the country at the current year *t* including exports.

The second term corresponds to the refrigerant emitted during the initial charging of new refrigeration and air conditioning systems produced in the country at the current year *t* including exports.

The third term corresponds to the refrigerant charge used for servicing, assuming the refrigerant emitted from leaks and during servicing is topped-off each year.

The final term represents the refrigerant emitted from containers across the entire refrigeration and air conditioning market in the given year *t*.

Refrigerant recovered and recharged directly to the same owner's equipment are not seen as a need; however, refrigerant recovered and sent for reclamation is accounted for in the declared market.

The annual refrigerant market as declared by chemical manufacturers or refrigerant distributors RD is calculated by Equation 7.16

**EQUATION 7.16**
**CALCULATION OF ANNUAL REFRIGERANT MARKET**

$$RD_t = R_{prod\_t} - R_{exp\_t} + R_{imp\_t} + R_{recl\_t} - R_{dest\_t}$$

Where:

$R_{prod\_t}$ = quantities of HFC refrigerant production in the country, kg

$R_{exp\_t}$ = quantities of HFC refrigerant produced in the country and exported, kg

$R_{imp\_t}$ = quantities of imported HFC refrigerant, kg

$R_{recl\_t}$ = quantities of HFC refrigerant recovered and reprocessed for sale as reclaimed HFC refrigerant less quantities going to reclaimers that have not yet been sold, kg

$R_{dest\_t}$ = quantities of HFC refrigerant destroyed, kg

All quantities are calculated for the current year *t*.

Comparing $RN_t$ that is the HFC refrigerant needs as derived from the inventory method and $RD_t$ the HFC refrigerant market as declared by refrigerant manufacturers and distributors gives a clear quality control of the inventory method, and also of the global emissions. $RN_t$ and $RD_t$ are calculated for each HFC type.

Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

It is difficult to provide adequate QA/QC procedures for the Tier 1 a/b method without carrying out a Tier 2 analysis to verify the choice of composite emission factor. Since this defeats the object of the Tier 1 approach, the most appropriate strategy is to seek external evaluation of the derivation of the composite emission factor where it is country-specific. An alternative will be to compare Tier 1 outputs with the predictions of regional or global databases.

### 7.5.4.2 REPORTING AND DOCUMENTATION

The supporting information necessary to ensure transparency in reported emissions estimates is shown in Table 7.10, Good Practice Documentation for Refrigerating and Air-Conditioning Systems.

TABLE 7.10
GOOD PRACTICE DOCUMENTATION FOR REFRIGERATION AND AIR-CONDITIONING SYSTEMS

| Data Source | Data to be Reported | Tier 1a/b | Tier 2a and 2b |
|---|---|---|---|
| Regulation for phase-out of CFCs and HCFCs | Schedule of phase out for charging of brand new equipment and for servicing | X | X |
| Government Statistics or Disposal Companies | Number of equipment disposed of for each type of application | X | X |
| Refrigerant Manufacturers and Distributors | All virgin refrigerants sold for charging new equipment and for servicing in the different sectors | X | X |
| Manufacturer Association or Marketing Studies | Equipment produced on a national level using HFC refrigerants (for the six sub-applications) | X | X |
| Import/Export Companies, Governement Statistics, Manufacturer Association or Marketing Studies | Number of equipment using HFCs (imported and exported) | X | X |
| Government or Refrigerant Distributors | HFC refrigerants recovered for re-processing or for destruction | X | X |
| Manufacturer Association | Average equipment lifetime | NA | X |
| Manufacturer Association | Initial charge of systems | X | X |

# 7.6 FIRE PROTECTION

## 7.6.1 Chemicals covered in this application area

There are two general types of fire protection (fire suppression) equipment that use HFCs and/or PFCs as partial replacements for halons: portable (streaming) equipment, and fixed (flooding) equipment. HFCs, PFCs and more recently a fluoroketone are mainly used as substitutes for halons, typically halon 1301, in flooding equipment. PFCs played an early role in halon 1301 replacement but current use is limited to replenishment of previously installed systems. HFCs in portable (streaming) equipment, typically replacing halon 1211, are available but have achieved very limited market acceptance due primarily to their high cost. PFC use in new portable extinguishers is currently limited to a small proportion (few percent) in an HCFC blend.

While actual emissions from the fire protection sub-sector are expected to be quite small, the use is normally non-emissive in provision of stand-by fire protection and is growing. This results in an accumulating bank of future potential emissions.

HFCs and PFCs that might still be involved in fire protection are shown in Table 7.1.

## 7.6.2 Methodological issues

### 7.6.2.1 CHOICE OF METHOD

As with the refrigeration and air conditioning application, the fire protection application offers the possibility of using both Approach A (emission-factor approach) and Approach B (mass–balance approach). The latter is justified by the fact that a considerable proportion of net consumption is likely to be targeted at equipment servicing rather than new equipment. However, the fire protection application differs from the refrigeration and air conditioning application in that the sub-applications are less numerous and more homogeneous. This means that the Tier 1a or Tier 1b method may be sufficient to provide appropriate emissions reporting, although, to be strictly correct, the inclusion of end-of-life considerations would normally warrant a Tier 2 approach.

However, as with both foam and refrigeration/air conditioning, it is necessary in the fire protection application to deal with the development and tracking of banks. This means that an historical time series of country-specific or globally or regionally derived activity data is required dating back to the introduction of any new HFC or PFC.

Since HFCs and PFCs in fire protection are emitted over a period longer than one year, countries need to represent emissions from equipment charged during previous years. Choosing an annual production-based emission factor to reflect a multi-year emission process can lead to considerable error and is not considered *good practice*.

Equation 7.17 indicates how the approach should be modified to consider the time dependence of the emissions and to consider what activity data could most likely be made available.

**EQUATION 7.17**
**TIME DEPENDENCE OF EMISSIONS FROM FIRE PROTECTION EQUIPMENT**

$$Emissions_t = Bank_t \bullet EF + RRL_t$$

and

$$Bank_t = \sum_{i=t_0}^{t} \left( Production_i + Imports_i - Exports_i - Destruction_i - Emissions_{i-1} \right) - RRL_t$$

Where:

$Emissions_t$ = emissions of agent from fire protection equipment in year $t$, tonnes

$Bank_t$ = bank of agent in fire protection equipment in year $t$, tonnes

EF = fraction of agent in equipment emitted each year (excluding emissions from retired equipment or otherwise removed from service), dimensionless

$RRL_t$ = Recovery Release or Loss: emissions of agent during recovery, recycling or disposal at the time of removal from use of existing fire protection equipment in year $t$, tonnes

$\text{Production}_t$ = amount of newly supplied agent (i.e., excluding recycled agent) in fire protection equipment produced in year *t*, tonnes

$\text{Imports}_t$ = amount of agent in fire protection equipment imported in year *t*, tonnes

$\text{Exports}_t$ = amount of agent in fire protection equipment exported in year *t*, tonnes

$\text{Destruction}_t$ = amount of agent from retired fire protection equipment that is collected and destroyed, tonnes

*t* = year for which emissions are being estimated (e.g., 2006, 2007, etc.)

$t_0$ = first year of chemical production and/or use

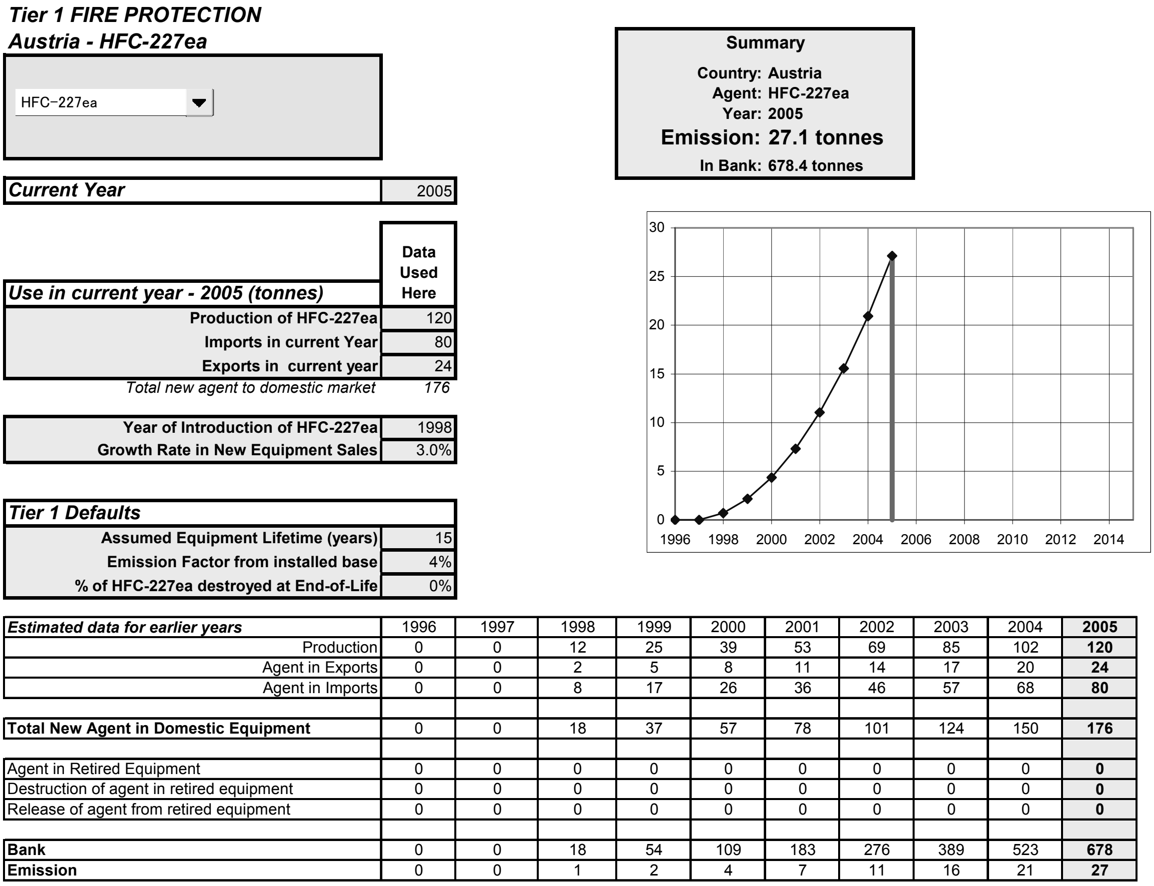
*i* = counter from first year of chemical production and/or use $t_0$ to current year *t*

It is *good practice* to apply Equation 7.17 to each individual greenhouse gas used in fire protection equipment. The calculation of the emissions must be performed for each year and applied to the next year's calculation.

With this background in mind, the decision tree for the fire protection application as set out in Figure 7.9 becomes very straight-forward.

As with Tier 1 methods adopted in both foams and refrigeration and air conditioning, it is possible to create a simple spreadsheet that accounts for the development of banks and the subsequent emissions from them. The following spreadsheet extract provides an example:

**Figure 7.8 Example of spreadsheet calculation for Tier 1 method**



***Tier 1 FIRE PROTECTION***
***Austria - HFC-227ea***

**Summary**
**Country: Austria**
**Agent: HFC-227ea**
**Year: 2005**
**Emission: 27.1 tonnes**
**In Bank: 678.4 tonnes**

| | |
|---|---|
| ***Current Year*** | 2005 |

| ***Use in current year - 2005 (tonnes)*** | **Data Used Here** |
|---|---|
| **Production of HFC-227ea** | 120 |
| **Imports in current Year** | 80 |
| **Exports in current year** | 24 |
| *Total new agent to domestic market* | *176* |

| | |
|---|---|
| **Year of Introduction of HFC-227ea** | 1998 |
| **Growth Rate in New Equipment Sales** | 3.0% |

| ***Tier 1 Defaults*** | |
|---|---|
| **Assumed Equipment Lifetime (years)** | 15 |
| **Emission Factor from installed base** | 4% |
| **% of HFC-227ea destroyed at End-of-Life** | 0% |

| ***Estimated data for earlier years*** | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | **2005** |
|---|---|---|---|---|---|---|---|---|---|---|
| Production | 0 | 0 | 12 | 25 | 39 | 53 | 69 | 85 | 102 | **120** |
| Agent in Exports | 0 | 0 | 2 | 5 | 8 | 11 | 14 | 17 | 20 | **24** |
| Agent in Imports | 0 | 0 | 8 | 17 | 26 | 36 | 46 | 57 | 68 | **80** |
| | | | | | | | | | | |
| **Total New Agent in Domestic Equipment** | 0 | 0 | 18 | 37 | 57 | 78 | 101 | 124 | 150 | **176** |
| | | | | | | | | | | |
| Agent in Retired Equipment | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| Destruction of agent in retired equipment | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| Release of agent from retired equipment | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| | | | | | | | | | | |
| **Bank** | 0 | 0 | 18 | 54 | 109 | 183 | 276 | 389 | 523 | **678** |
| **Emission** | 0 | 0 | 1 | 2 | 4 | 7 | 11 | 16 | 21 | **27** |

It is intended that such a spreadsheet facilitates the calculation for the Fire Protection application, supported, where necessary, by activity data from an appropriate globally or regionally derived dataset[23].

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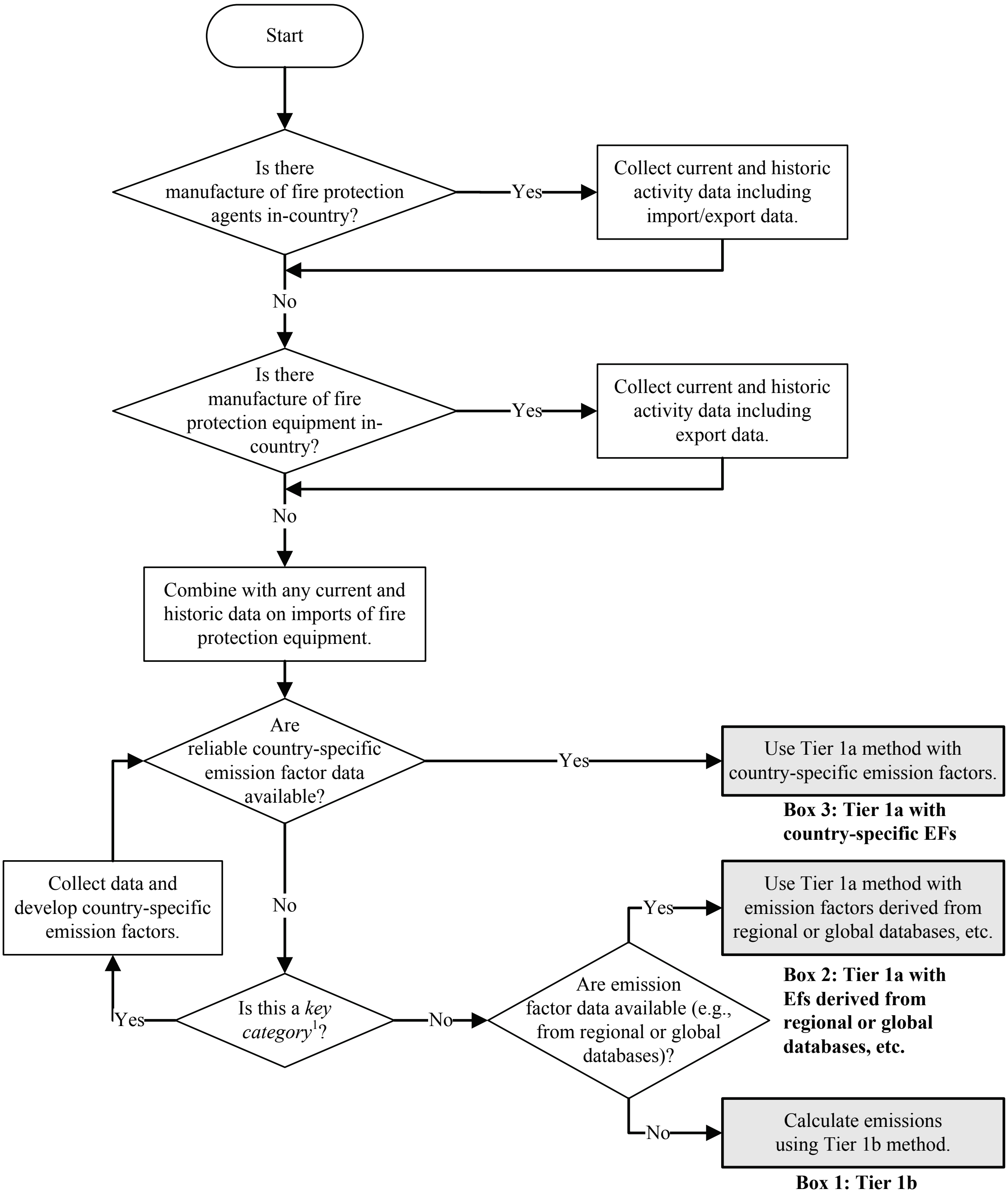
[23] As noted in Box 7.1, inclusion in the IPCC Emission Factor Database (EFDB) will indicate general adherence to due process, but it is *good practice* for countries to ensure that all data taken from the EFDB are appropriate for their national circumstances.

**Figure 7.9 Decision tree for actual emissions from the fire protection application**



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.

## 7.6.2.2 CHOICE OF EMISSION FACTORS

Experience gained during the phase-out of halons substances has taught some valuable lessons regarding use and emission patterns, and it is reasonable to expect that these lessons are relevant for greenhouse gases used for similar purposes. Fire protection equipment is designed to release its initial charge during an actual fire incident. A recent study shows that annual emissions from installed flooding systems are in the range of 2 ± 1 percent of the installed base (Verdonik and Robin, 2004). For halon 1211 portable extinguishers, the Halons Technical

Options Committee (2003) estimated that the emission rate for 2000 is approximately twice that of fixed systems. Applying that factor provides a range of 2 to 6 percent (that is, 4% ±2%) of the in-use quantities.

Given the nature of this application, there are opportunities to recover the gas at the end of life of the equipment (or whenever removed from service). The recovered gas may be destroyed or recycled. Therefore, the default assumption of zero end-of-life recovery may overestimate end-of-life emissions. The inventory compiler should establish contacts with relevant industries to collect information on recovery that may occur due to legislation, Industry Codes of Practice or other measures. It is *good practice* to document this information and report any assumptions.

For those countries without a national Industry Code of Practice, it is *good practice* to assume that the agent will not be recovered at the end of the system life and is emitted. Typical lifetimes for flooding systems are 15 to 20 years. In specialised applications, such as aircraft and military systems, systems can remain in use for 25 to 35 years or longer (UNEP-HTOC, 1994).

### 7.6.2.3 CHOICE OF ACTIVITY DATA

For countries that produce the fire protection agent, it is *good practice* to assign all of the production of that agent to that country unless known to have been 1) exported in bulk or 2) destroyed. For countries that do not produce the agent but produce and fill fire protection systems, all of the bulk agent imported into the country is considered to remain in the country unless known to have been 1) re-exported in bulk or 2) destroyed. Countries that do not produce the agent or systems would use the activity data developed by the producer countries to develop their inventory or, baring evidence of export into the country, estimate the emissions from fire protection as below the significance of their overall greenhouse gas emissions, i.e., essentially zero. This default methodology places the major responsibility on the countries that produce the agent or use them for the manufacture of systems. In order for producer countries to use this methodology, activity data would need to be developed on production, bulk imports and exports, and destruction.

In summary, activity data comes from countries that are producers of fire protection agents or systems, with the exception of destruction. In order for the producer country to decrease the amount credited toward that country from production of agent, bulk exports must be demonstrated. These bulk exports while reducing the producer countries installed base would also serve as activity data for importing countries to determine their installed base.

### 7.6.2.4 COMPLETENESS

Inventory compilers should ensure that all greenhouse gases used in the fire protection industry are included in the estimate. It is also necessary to apply Equation 7.17 beginning in the first year that greenhouse gas fire protection agents were employed in the country.

### 7.6.2.5 DEVELOPING A CONSISTENT TIME SERIES

In some countries, historical activity data for the greenhouse gases charged into new equipment or used to service existing equipment may be difficult to determine because of the recent introduction of these substances. If inventory compilers use preliminary emission factors for these years based on historical data for halons, and then switch they should follow *good practice* in ensuring time series consistency, as described in Volume 1, Chapter 5.

## 7.6.3 Uncertainty assessment

On the global level, a high degree of certainty could be expected because assessments will be based on production and provides for a complete material balance. At any time, Aggregate Global Production will always equal Aggregate Global Emissions plus the Aggregate Total Contained in Equipment. There is more uncertainty in the country-specific data. A small error is built into the method as importing and exporting of filled systems is not included in the method. However, based on experience with halon and their greenhouse gas substitutes, accurate data on filled system import/export is likely not obtainable at a reasonable level of effort.

Verdonik (2004) compared reports on halon consumption against the manufacturers' reports of global halon production from CEFIC[24], reported developing country production and reported CEIT[25] production. The results

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[24] CEFIC – European Chemical Industry Association

[25] CEIT – Countries with Economies in Transition

were a standard deviation of 16 percent for developed countries, 15 percent for developing countries and 13 percent globally. It is anticipated that the uncertainty in HFC/PFC emission estimates would be comparable or higher than the uncertainty seen in halon consumption estimates.

## 7.6.4 Quality Assurance/Quality control (QA/QC), Reporting and Documentation

### 7.6.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. This may involve direct reference to global or regional databases for parallel assessments which allow benchmarking. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures would be applicable, if higher tier methods were used to determine emissions from this application. However, if this is not the case, the basic QA/QC approaches outlined in Volume 1, Chapter 6 can be adopted.

In addition to the guidance in Volume 1, specific procedures of relevance to this application are outlined in the references at the end of the chapter.

### 7.6.4.2 REPORTING AND DOCUMENTATION

Access to data such as chemical sales may depend on the ability of inventories to preserve confidentiality. The balance between preservation of confidentiality and transparency of the data is an important issue, especially in a low use application such as fire protection. These ODS substitutes are manufactured by a few producers, in quantities very much lower than ODS substitutes used in other applications. Careful aggregation of GWP-weighted data may be a means to resolve this issue.

# 7.7 OTHER APPLICATIONS

## 7.7.1 Chemicals covered in this application area

HFCs and PFCs represent a large range of gases whose properties make them attractive for a variety of niche applications not covered separately in this Chapter. These include electronics testing, heat transfer, dielectric fluid, medical applications and potentially many new applications not yet developed. There are also some historical uses of PFCs, as well as emerging use of HFCs, in these applications. These applications have leakage rates ranging from 100 percent emissive in year of application to around 1 percent per annum. However, this chapter is specifically focused on those uses of HFCs and PFCs which directly replace Ozone Depleting Substances and these are much more limited in scope.

There is a need to be sure that double-counting does not occur with the electronics category covered in Chapter 6 of this Volume, including electronics testing, heat transfer and dielectric applications. Other double-counting is possible in the coverage of solvents or where HFCs and/or PFCs are contained as solvents in industrial aerosols. This is a prime example where the delineation between what is acting as an ODS Substitute and what is not can be very fine. To avoid confusion, this chapter has taken the approach that only those technology transitions which occur directly from ODSs to HFC and/or PFC technologies should be considered.

Bearing in mind that ODS phase-out (both CFCs and HCFCs) is moving towards completion in developed countries, the number of new applications emerging is expected to be very limited. However, in theory at least, new applications could emerge right up until the final global phase-out of ODSs in 2040.

## 7.7.2 Methodological issues

### 7.7.2.1 CHOICE OF METHOD

The choice of *good practice* methods depends on national circumstances (see decision tree in Figure 7.10, Decision Tree for Actual Emissions from the Other Applications).

When choosing a method for this application area, there is a need to consider whether to treat each *Other Application* as a separate application or whether to address them as a group. The former will lead to a series of Tier 2 methods, while the latter will lead to a single Tier 1 approach.

The end-users for these niche applications will be extremely diverse. As a result, investigating each of these applications separately may not be feasible. Instead, it is suggested that these other miscellaneous applications be divided into highly emissive applications similar to solvents and aerosols, and less emissive contained applications similar to closed-cell foam and refrigerators. The breakdown of annual gas consumption going to either category should be determined by a survey of end-use applications.

The split of usage will be:

- Emissive = X% of total consumption (where X would normally be expected to be typically >50%)
- Contained = (100 – X)% of total consumption

The consequence of this approach is that, depending on the number of sub-applications in each class, it could be possible to follow an exclusively Tier 1 approach or alternatively adopt a Tier 2 method. Since the primary differentiator is the rate of emission, and it is not known whether sub-applications will require servicing or not, it is recommended that exclusively Approach A (emission-factor approach) be used (i.e., Tier 1a and/or Tier 2a).

Modelling of these two classes of sub-application is considered in turn.

#### EMISSIVE APPLICATIONS

It is *good practice* to use a Tier 1a method, similar to the methods described for aerosols and solvents. During use of fluids in these applications, 100 percent of the chemical is emitted on average six months after sale. In other words emissions in year t can be calculated according to the equation for solvents and aerosols as follows:

**EQUATION 7.18**
**ASSESSMENT OF PROMPT EMISSION SOURCES FROM OTHER APPLICATIONS**

$$Emissions_t = S_t \bullet EF + S_{t-1} \bullet (1 - EF)$$

Where:

$Emissions_t$ = emissions in year *t*, tonnes

$S_t$ = quantity of HFC and PFC sold in year *t*, tonnes

$S_{t-1}$ = quantity of HFC and PFC sold in year *t*–1, tonnes

EF = emission factor (= fraction of chemical emitted during the first year after manufacture), fraction

The emission factor (EF) represents that fraction of chemical emitted during the first year after manufacture. By definition, emissions over two years must equal 100 percent. This equation should be applied to each chemical individually.

### CONTAINED APPLICATIONS

Certain applications have much lower loss rates. Where appropriate data are available, a separate emissions model will be required to adjust for this lower leakage rate. Where no data exist, globally or regionally derived activity data and emission factors can be used. Thus, the equation for annual emissions is as follows:

**EQUATION 7.19**
**ASSESSMENT OF EMISSIONS FROM OTHER CONTAINED APPLICATIONS**

$$\begin{aligned} Emissions = {} & Product\ Manufacturing\ Emissions + Product\ Life\ Emissions \\ & + Product\ Disposal\ Emissions \end{aligned}$$

Where:

*Product Manufacturing Emissions = Annual Sales ● Manufacturing Emission Factors*

*Product Life Emissions = Bank ● Leakage Rate*

*Product Disposal Emissions = Annual Disposal ● Disposal Emission Factors*

## 7.7.2.2 CHOICE OF EMISSION FACTORS

Emission factors for those sub-applications with prompt emissions will follow similar selection criteria to those for solvents (Section 7.2.2.2) and aerosols (Section 7.3.2.2).

Emission factors for contained sub-applications will depend on the particular nature of that sub-application. If a series of sub-applications is fairly homogeneous in nature it may still be possible to work with a composite emission factor and adopt a Tier 1a method. However, where there is considerable variation in the nature of contained sub-applications, it will be more appropriate to research these specifically, if appropriate emission factors are not available. In either case, the need for separate emission factors will lead to the adoption of a Tier 2a method.

## 7.7.2.3 CHOICE OF ACTIVITY DATA

Activity data will always be difficult to establish for small niche applications and inventory compilers will be reliant on the co-operation of chemical suppliers to identify qualifying sub-applications. However, once identified, they should be relatively easy to quantify at a country level because they are likely to be fairly specialist in nature.

As indicated in Figure 7.10, it is *good practice* to conduct an end-use survey periodically.

## 7.7.2.4 COMPLETENESS

As noted in Section 7.7.2.3, the key challenge will be to keep updated with new *Other Application* as they emerge. Regular cross-reference with ODS Substitution Reviews (e.g., UNEP Technical & Economic Assessment Panel Reports) will assist in this respect.

### 7.7.2.5 DEVELOPING A CONSISTENT TIME SERIES

Emissions from *Other Application* should be calculated using the same method and data sources for every year in the time series. Where consistent data are unavailable for any year in the time series, gaps should be recalculated according to the guidance provided in Volume 1, Chapter 5.

## 7.7.3 Uncertainty assessment

There may be a wide range of *other applications* and therefore it is not possible to give default uncertainties for these sources. However, procedures should be put in place to assess levels of uncertainty in accordance with the practices outlined in Volume 1 Chapter 3.

## 7.7.4 Quality assurance/quality control (QA/QC), reporting and documentation

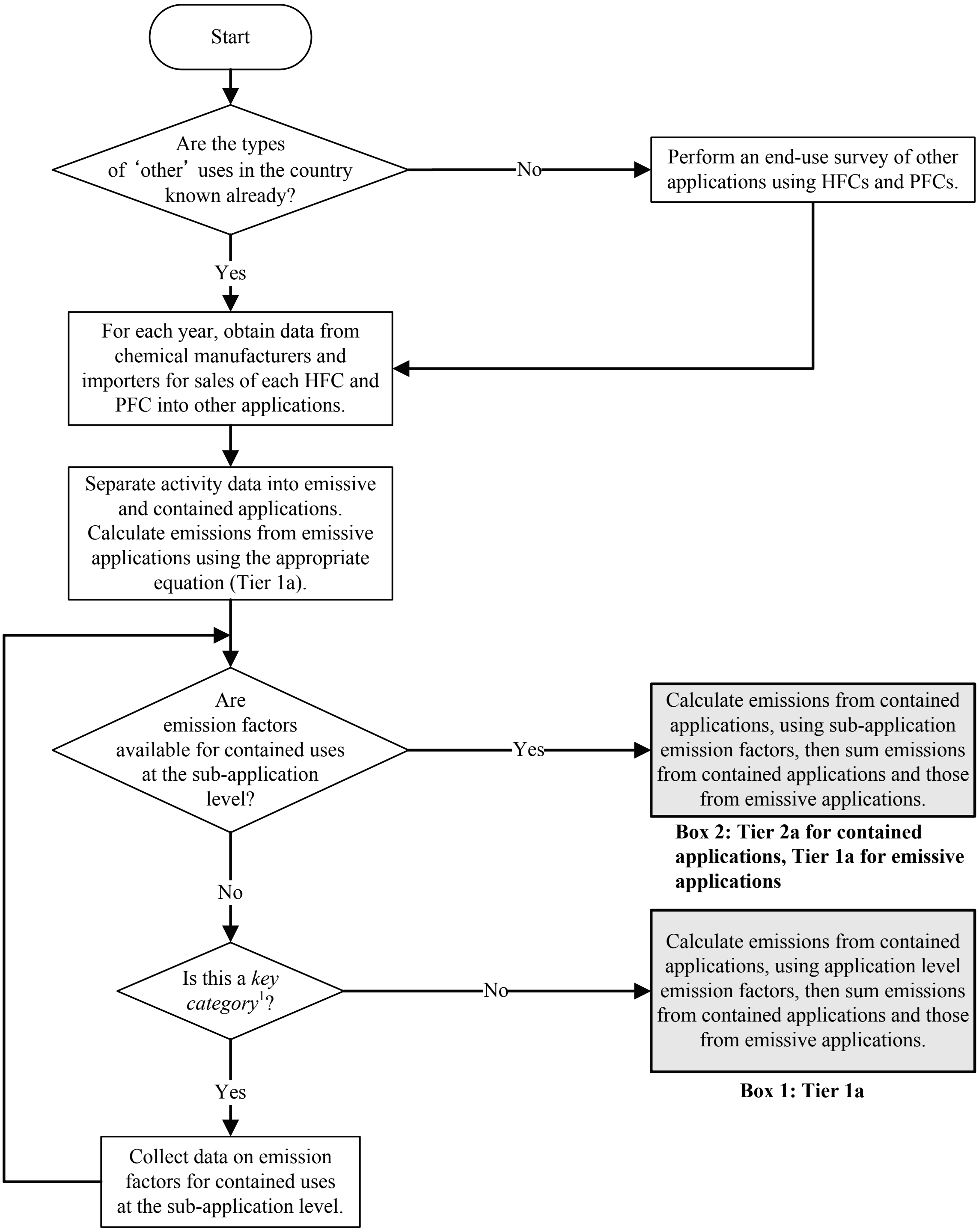
### 7.7.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. This may involve direct reference to global or regional databases for parallel assessments which allow benchmarking. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may be applicable, if higher tier methods are used to determine emissions from these sub-applications. However, if this is not the case, the basic QA/QC approaches outlined in Volume 1, Chapter 6 can be adopted.

### 7.7.4.2 REPORTING AND DOCUMENTATION

The balance between preservation of confidentiality and transparency of the data is an important issue, especially in low-use sub-applications. Specialist ODS substitutes are often manufactured by only a few producers, in quantities very much lower than ODS substitutes used in other applications. Careful aggregation of GWP-weighted data may be a means to resolve this issue.

**Figure 7.10 Decision tree for actual emissions from the other applications**



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.

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# CHAPTER 8

# OTHER PRODUCT MANUFACTURE AND USE

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# 8 OTHER PRODUCT MANUFACTURE AND USE

## 8.1 INTRODUCTION

This chapter outlines methods for estimating emissions of sulphur hexafluoride ($SF_6$) and perfluorocarbons (PFCs) from the manufacture and use of electrical equipment and a number of other products. It also provides methods for estimating emissions of nitrous oxide ($N_2O$) from several products. In most of these applications, the $SF_6$, PFC, or $N_2O$ is deliberately incorporated into the product to exploit one or more of the physical properties of the chemical, such as the high dielectric strength of $SF_6$, the stability PFCs, and the anaesthetic effect of $N_2O$. However, the applications discussed here have a wide range of emission profiles, ranging from immediate and unavoidable release of all of the chemical (e.g., use of PFCs as atmospheric tracers) to largely avoidable, delayed release from leak-tight products after 40 years of use (e.g., manufacture and use of sealed-pressure electrical equipment). The estimation methods presented in the chapter have been tailored to reflect these differences in emission profiles.

Section 8.2 details methods for estimating $SF_6$ and PFC emissions from electrical equipment. Section 8.3 details methods for estimating emissions from the manufacture and use of a wide variety of other industrial, commercial, and consumer products that contain $SF_6$ and PFCs, excluding those discussed elsewhere in this volume (e.g., PFC emissions from electronics manufacturing, which are discussed in Chapter 6). (Please see the introduction to Section 8.3 for the list of excluded sources.) Finally, Section 8.4 discusses methods for estimating $N_2O$ emissions from anaesthetics, propellants, and other product uses.

## 8.2 EMISSIONS OF $SF_6$ AND PFCs FROM ELECTRICAL EQUIPMENT

### 8.2.1 Introduction

Sulphur hexafluoride ($SF_6$) is used for electrical insulation and current interruption in equipment used in the transmission and distribution of electricity. Emissions occur at each phase of the equipment life cycle, including manufacturing, installation, use, servicing, and disposal. Most of the $SF_6$ used in electrical equipment is used in gas insulated switchgear and substations (GIS) and in gas circuit breakers (GCB), though some $SF_6$ is used in high voltage gas-insulated lines (GIL), outdoor gas-insulated instrument transformers and other equipment. The aforementioned applications may be divided into two categories of containment. The first category is 'Sealed Pressure Systems' or 'Sealed-for-life Equipment', which is defined as equipment that does not require any refilling (topping up) with gas during its lifetime and which generally contains less than 5 kg of gas per functional unit.[1] Distribution equipment normally falls into this category. The second category is 'Closed Pressure Systems', which is defined to include equipment that requires refilling (topping up) with gas during its lifetime. This type of equipment generally contains between 5 and several hundred kg per functional unit. Transmission equipment normally falls into this category. Both categories of equipment have lifetimes of more than 30 to 40 years. In Asia, significant quantities of $SF_6$ are used in gas-insulated power transformers (GIT).

Electrical equipment is the largest consumer and most important use of $SF_6$, globally. It significantly contributes to worldwide $SF_6$ emissions. However, the importance of this source varies considerably from region to region and from country to country. The emissions from this category depend not only on the installed (banked) or consumed quantities of $SF_6$, but also very much on the tightness of the products and the handling processes applied. Regional average emission rates presently vary between far less than 1 percent to more than 10 percent. In general, emission rates have declined significantly since 1995. Targeted industry actions have reduced emissions by 50 to 90 percent in Europe and Asia (Ecofys, 2005; Aoyama, 2004). These actions include (1)

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[1] Formal definitions of 'sealed-pressure system' and 'closed-pressure system' are contained in International Electro-technical Commission (IEC) Standard 60694. (IEC, 1996)

designing equipment to require a smaller charge of $SF_6$ and to be more leak tight and (2) improving handling processes and handling equipment for all life cycle stages.[2]

In some regions (e.g., North America and Japan), perfluorocarbons (PFCs) are used as dielectrics and heat transfer fluids in power transformers. PFCs are also used for retrofitting CFC-113 cooled transformers. One PFC used in this application is perfluorohexane ($C_6F_{14}$). In terms of both absolute and carbon-weighted emissions, PFC emissions from electrical equipment are generally believed to be much smaller than $SF_6$ emissions from electrical equipment; however, there may be regional exceptions to this pattern.

## 8.2.2 Methodological issues

### 8.2.2.1 CHOICE OF METHOD

Emissions of $SF_6$ from electrical equipment can be estimated in a variety of ways with varying degrees of complexity and data intensity. This section describes *good practice* for using a Tier 1 method (the default emission‑factor approach), a Tier 2 method (the country-specific emission-factor approach), and a Tier 3 method (a hybrid that can use either mass-balance or emission-factor approaches for different life cycle stages, depending on country-specific circumstances). Generally, emissions estimates developed using the Tier 3 method, which is implemented at the facility level, will be the most accurate. Estimates developed using the Tier 1 method will be the least accurate.

As is true for other emission sources, the tier selected will depend on data availability and whether or not the category is *key*. Figure 8.1, Decision Tree for $SF_6$ from Electrical Equipment, summarises the process for choosing among Tiers 3, 2, and 1. *Good practice* in choosing between the mass-balance and emission-factor variants of the Tier 3 approach is discussed in detail in Section 1.5 of Chapter 1. This choice will depend both on data availability and on country-specific circumstances. As a first step in assessing the importance of $SF_6$ emissions from electrical equipment and the other categories discussed in this chapter, inventory compilers are encouraged to contact chemical producers and suppliers as well as electrical equipment manufacturers and utilities and/or their industry associations. These organisations can provide basic information on chemical consumption and on equipment stocks and applications that can help the inventory compiler estimate emissions and identify sources that merit further investigation. They can also provide important advice and support in establishing more extensive data collection systems to support Tier 2 and Tier 3 estimates.

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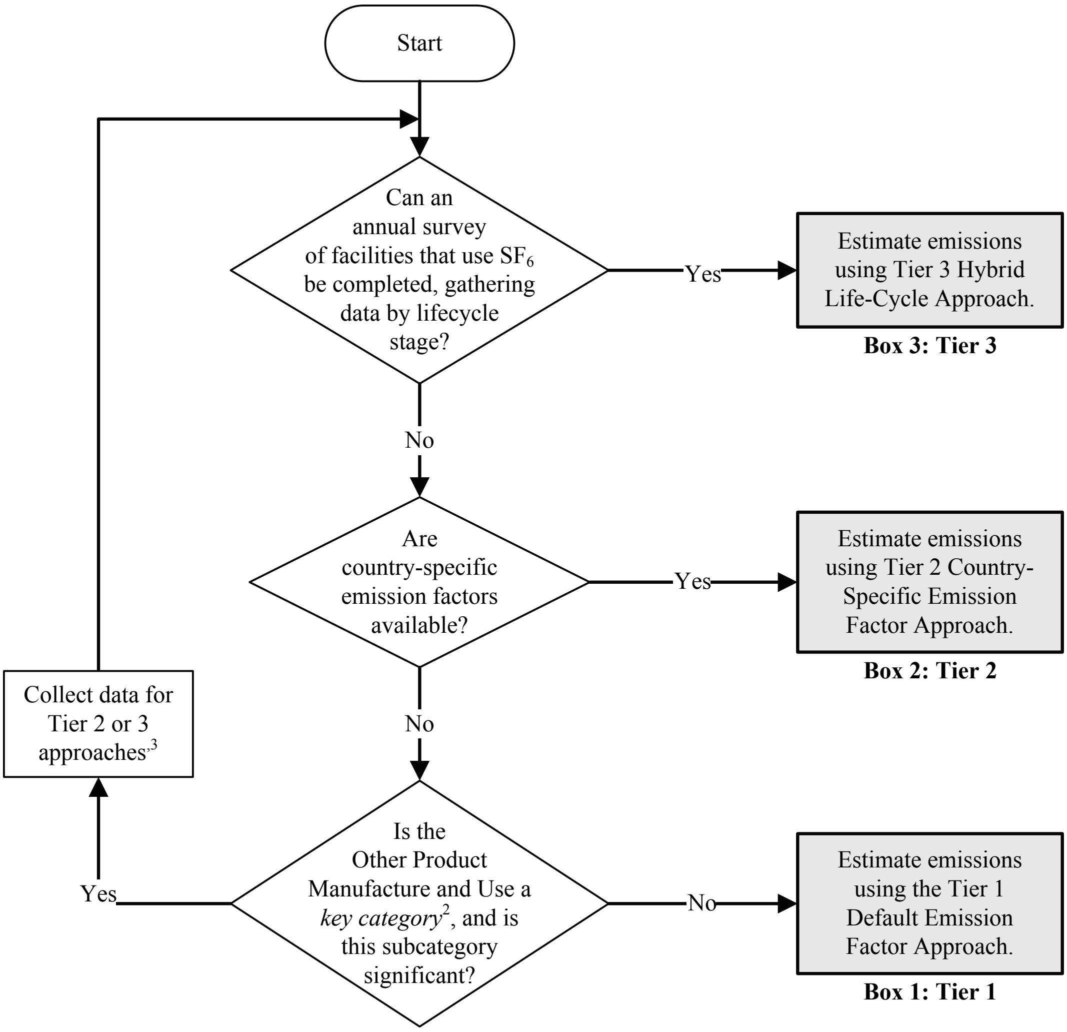
[2] International Council on Large Electric Systems (CIGRE) has published a guide on $SF_6$ handling, Guide for the Preparation of customized “Practical $SF_6$ Handling Instructions,” Task Force B3.02.01, CIGRE Publication No.276, August 2005. (CIGRE, 2005)

**Figure 8.1 Decision tree for $SF_6$ from electrical equipment[1]**



Note:
1. In selecting an estimation method, it is *good practice* also to consider the criteria presented in Table 1.7, Chapter 1, Section 1.5 of this volume for choosing between the mass-balance and emission-factor variants of each tier.
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.
3. It is *good practice* to contact National/Regional associations of utilities/users and manufacturers to collect, check, and aggregate actual and historical data.

### TIER 1 METHOD – DEFAULT EMISSION FACTORS

The Tier 1 approach is the simplest approach for estimating $SF_6$ and PFC emissions from electrical equipment. (Henceforth in this section, '$SF_6$' will be used to denote '$SF_6$ and/or PFCs.') In this method, emissions are estimated by multiplying default regional emission factors by, as appropriate, the $SF_6$ consumption of equipment manufacturers and/or by the nameplate $SF_6$ capacity of the equipment at each life cycle stage beyond manufacturing in the country. The term Installation Emissions may be omitted if (1) installation emissions are not expected to occur (i.e., for closed-pressure equipment) or (2) installation emissions are included in the emission factor for emissions from Manufacturing or Use. Default emission factors are given in Tables 8.2 to 8.4.

*It is good practice* to use the following equation:

**EQUATION 8.1**
**DEFAULT EMISSION FACTOR METHOD**

$$\text{Total Emissions} = \text{Manufacturing Emissions} + \text{Equipment Installation Emissions} + \text{Equipment Use Emissions} + \text{Equipment Disposal Emissions}$$

Where:

*Manufacturing emissions* = Manufacturing Emission Factor • Total $SF_6$ consumption by equipment manufacturers

*Equipment installation emissions* = Installation Emission Factor • Total nameplate capacity of new equipment filled on site (not at the factory).

*Equipment use emissions* = Use Emission Factor • Total nameplate capacity of installed equipment. The 'use emission factor' includes emissions due to leakage, servicing, and maintenance as well as failures

*Equipment disposal emissions* = Total nameplate capacity of retiring equipment • Fraction of $SF_6$ remaining at retirement

## TIER 2 METHOD – COUNTRY-SPECIFIC EMISSION FACTOR METHOD

The Tier 2 method uses the same basic equation as Tier 1, but requires reliable country-specific emission factors for each life cycle stage. Country-specific emission factors will be more accurate because they reflect the unique circumstances in which electrical equipment is used in a given country. In addition, if detailed data for equipment retirement are available, emissions due to retirement can be estimated more accurately. The expression for Equipment Disposal Emissions in the Tier 2 method includes terms accounting for $SF_6$ recovery at retirement and disposal, as follows:

**EQUATION 8.2**
**EQUIPMENT DISPOSAL EMISSIONS UNDER COUNTRY-SPECIFIC EMISSION FACTOR METHOD**

Equipment disposal emissions = Total nameplate capacity of retiring equipment • Fraction of $SF_6$ remaining at retirement • (1 – fraction of retiring equipment whose $SF_6$ is recovered • recovery efficiency • fraction of recovered $SF_6$ recycled, reused with no further treatment, or destroyed*)

*This final term is intended to account for emissions during chemical recycling and destruction.

Note that to be considered Tier 2, estimates must be developed using only country-specific emission factors.

## TIER 3 HYBRID METHOD – EMISSIONS BY LIFE CYCLE STAGE OF EQUIPMENT

The Tier 3 method is the most accurate approach for estimating actual emissions of $SF_6$ from electrical equipment. This method is detailed but flexible, accommodating a wide range of national circumstances. The method is implemented at the facility level and includes separate equations for each phase of the life cycle of equipment, including equipment manufacture, installation, use, and disposal. Depending on the type of equipment, the life cycle stage, and country-specific circumstances, either a mass-balance approach or country- (or facility-) specific emission factors may be used. In general, it is *good practice* to use the mass-balance approach, except where (1) emission rates from a process are near or below the precision of the measurements required for the mass-balance approach (e.g., 3 percent of nameplate capacity per year or less), (2) equipment is never serviced during its lifetime (as is expected to be the case for sealed pressure equipment), or (3) equipment stocks are growing very rapidly, as may be the case in countries where electrical equipment has been introduced within the last 10-20 years.

The hybrid approach enhances accuracy by permitting use of the mass-balance approach for some processes and life cycle stages and the emission-factor approach for other processes and life cycle stages. However, the combination of different approaches also introduces opportunities for double-counting or overlooking emissions. Inventory compilers need to be aware of this problem and take steps to avoid it. Table 8.1, Avoiding Double-Counting or Overlooking Emissions, provides examples of both the problem and some potential solutions.

The annex to this chapter (Annex 8A) briefly describes an example of the Tier 3 approach as it has been applied in Germany. This example is intended to illustrate rather than prescribe; the precise approach taken by any given country will depend on country-specific circumstances.

Ideally, data are obtained for every equipment manufacturer, electricity transmission and distribution facility (utility), equipment disposer (which may be a manufacturer, electric utility, or other entity), and $SF_6$ recycling or destruction facility in the country, and the emissions of all manufacturers, utilities, disposers, and recycling or destruction facilities are summed to develop the national estimate. The basic equation is:

**EQUATION 8.3**
**TIER 3 TOTAL EMISSIONS**

$$\begin{aligned} Total\ Emissions = & \sum Equipment\ Manufacturing\ Emissions \\ & + \sum Equipment\ Installation\ Emissions \\ & + \sum Equipment\ Use\ Emissions \\ & + \sum Equipment\ Disposal\ and\ Final\ Use\ Emissions \\ & + \sum Emissions\ from\ SF_6\ Recycling\ and\ Destruction \end{aligned}$$

Where:

*Equipment Manufacturing Emissions* at the facility level can be estimated by Equations 8.4A and 8.4B.

*Equipment Installation Emissions* at the facility level can be estimated by Equations 8.5A and 8.5B.

*Equipment Use Emissions* at the facility level can be estimated by Equations 8.6A and 8.6B.

*Equipment Disposal and Final Use Emissions* at the facility level can be estimated by Equations 8.7A and 8.7B.

*Emissions from $SF_6$ Recycling and Destruction* at the facility level can be estimated by Equations 8.8 and 8.9.

In the above equation, national emissions for each phase are equal to the sum of the emissions of all equipment manufacturers, equipment users, equipment disposers, or $SF_6$ recyclers/destroyers at that phase. In practice, it is not always possible to obtain data for every facility; in these cases countries may use one of the extrapolation methods discussed in Section 8.2.2.3, Choice of Activity Data.

### *Equipment manufacturing emissions*

*Equipment manufacturing emissions* can be estimated using either a *pure mass-balance* approach or a mixture (*hybrid*) of a mass-balance approach for some processes and an emission-factor based approach for others. The pure mass-balance approach is preferred except where a substantial fraction of a manufacturer's emissions come from processes whose emission rates fall below the precision of the measurements required for the mass-balance approach (e.g., 3 percent of nameplate capacity per year or less). In these cases, it is *good practice* to use emission factors to estimate emissions from the processes with very low emission rates and to use the mass-balance approach to estimate emissions from the other manufacturing processes.

*Pure mass-balance approach*: Using the pure mass-balance approach, the total emissions of each equipment manufacturer can be estimated using the following equation:

**EQUATION 8.4A**
**EQUIPMENT MANUFACTURING EMISSIONS - PURE MASS-BALANCE**

$$\begin{aligned} Equipment\ Manufacturing\ Emissions = & Decrease\ in\ SF_6\ Inventory + Acquisitions\ of\ SF_6 \\ & - Disbursements\ of\ SF_6 \end{aligned}$$

Where:

*Decrease in $SF_6$ Inventory* = $SF_6$ stored in containers at the beginning of the year – $SF_6$ stored in containers at the end of the year

*Acquisitions of $SF_6$* = $SF_6$ purchased from chemical producers or distributors in bulk + $SF_6$ returned by equipment users or distributors with or inside of equipment + $SF_6$ returned to site after off-site recycling

*Disbursements of $SF_6$* = $SF_6$ contained in new equipment delivered to customers + $SF_6$ delivered to equipment users in containers + $SF_6$ returned to suppliers + $SF_6$ sent off-site for recycling + $SF_6$ destroyed

*Hybrid approach*: This method first requires that manufacturers separate the gas flows associated with processes for which the mass-balance approach will be used from the gas flows associated with processes for which the emission-factor approach will be used. Emissions from the former can then be estimated using the approach outlined in Equation 8.4A. Emissions from the latter can be estimated by multiplying the total nameplate capacity of equipment undergoing each process (e.g., filling) by the country- or facility-specific emission factor for that process. Total emissions for each manufacturer are then estimated by summing the emissions from both sets of processes, using the following equation:

**EQUATION 8.4B**
**EQUIPMENT MANUFACTURING EMISSIONS - HYBRID**

$$\begin{aligned}&\textit{Equipment Manufacturing Emissions} = \textit{Equation } 8.4A\\&+\sum \textit{Nameplate capacity of equipment undergoing each process}^{*}\\&\bullet \textit{Emission factor for that process}\end{aligned}$$

* Excluding that covered by Equation 8.4A

### *Equipment installation emissions*

*Equipment installation emissions* may be estimated using either a *mass-balance* or an *emission-factor* approach. Again, the mass-balance approach is preferred except where emission rates are very low.

*Pure Mass-balance approach*: Using the mass-balance approach, the total emissions of each equipment installer can be estimated using the following equation:

**EQUATION 8.5A**
**EQUIPMENT INSTALLATION EMISSIONS - PURE MASS-BALANCE**

$$\begin{aligned}\textit{Equipment Installation Emissions} &= SF_6 \textit{ used to fill equipment}\\&- \textit{Nameplate capacity of new equipment}\end{aligned}$$

*Hybrid approach*: This method first requires that users separate the gas flows associated with equipment for which the mass-balance approach will be used from the gas flows associated with equipment for which the emission-factor approach will be used. Emissions from the former can then be estimated using the approach outlined in Equation 8.5A. Emissions from the latter can be estimated by multiplying the newly installed nameplate capacity of each equipment type by the country- or facility-specific installation emission factor for that type. Total emissions for each installer are then estimated by summing the emissions from both sets of equipments, using the following equation:

**EQUATION 8.5B**
**EQUIPMENT INSTALLATION EMISSIONS - HYBRID**

$$\begin{aligned}&\textit{Equipment Installation Emissions} = \text{Equation 8.5A}\\&+\sum \textit{Nameplate capacity of new equipment filled on site}^{*} \bullet \textit{Installation emission factor}\end{aligned}$$

* Excluding that covered by Equation 8.5A

### *Equipment use emissions*

*Equipment use emissions* may be estimated using either a *pure mass-balance* or a *hybrid* approach. The pure mass-balance approach is likely to be appropriate for countries where (1) electrical equipment that uses $SF_6$ has been in use for 10-20 years or more, and (2) emissions from sealed-pressure systems are likely to be negligible. The hybrid approach is likely to be appropriate for other countries.

*Pure mass-balance approach*: Using the pure mass-balance approach, the total emissions of each equipment user can be estimated using the following equation:

**EQUATION 8.6A**
**EQUIPMENT USE EMISSIONS - PURE MASS-BALANCE**

$$\begin{aligned}\textit{Equipment Use Emissions} &= SF_6 \textit{ used to recharge closed pressure equipment at servicing}\\&- SF_6 \textit{ recovered from closed pressure equipment at servicing}\end{aligned}$$

*Hybrid approach*: This method first requires that users separate the gas flows associated with equipment for which the mass-balance approach will be used from the gas flows associated with equipment for which the emission-factor approach will be used. Emissions from the former can then be estimated using the approach outlined in Equation 8.6A. Emissions from the latter can be estimated by multiplying the total nameplate capacity of each type of equipment by the country- or facility-specific emission factor for that type of equipment. The emission-factor approach is likely to be more accurate for sealed-pressure equipment everywhere and for all types of equipment in countries where electrical equipment has been used for less than 10-20 years. Total emissions for each user are then estimated by summing the emissions from both sets of equipment, using the following equation:

**EQUATION 8.6B**
**EQUIPMENT USE EMISSIONS - HYBRID**

$$\begin{aligned} &\textit{Equipment Use Emissions} = \text{Equation 8.6A} \\ &+ \sum \textit{Nameplate capacity of equipment installed}^{*} \bullet \textit{Use emission factor} \end{aligned}$$

* Excluding that covered by Equation 8.6A

### *Equipment disposal and final use emissions*

*Equipment disposal and final use emissions* may be estimated using either a *pure mass-balance* or a *hybrid* approach, based on country-specific circumstances. In both the pure mass-balance and hybrid approaches, emissions from closed-pressure equipment are estimated using a mass-balance equation. In the pure mass-balance approach, emissions from sealed-pressure systems are also estimated using a mass-balance equation. In the hybrid approach, emissions from sealed-pressure systems are estimated using an emission-factor-based term.

*Pure mass-balance approach*: In countries where the gas-collection infrastructure (including recovery equipment, technician training, and economic or legal incentives to recover) is not very well-developed or widely applied, it is *good practice* to use the pure mass-balance approach, as follows:

**EQUATION 8.7A**
**EQUIPMENT DISPOSAL AND FINAL USE EMISSIONS - PURE MASS-BALANCE**

$$\begin{aligned} \textit{Disposal and Final Use Emissions} &= \textit{Emissions from closed} \cdot \textit{pressure equipment} \\ &+ \textit{Emissions from sealed} \cdot \textit{pressure equipment } (\textit{MB}) \end{aligned}$$

Where:

*Disposal and final use emissions from closed-pressure equipment* = Nameplate capacity of retired closed-pressure equipment – $SF_6$ recovered from retired closed-pressure equipment, and

*Disposal and final use emissions from sealed-pressure equipment* (*MB*) = Nameplate capacity of retired sealed-pressure systems – $SF_6$ recovered from retired sealed-pressure systems

Note that if the inventory compiler uses the emission-factor approach to estimate 'use emissions' from sealed-pressure equipment, a term should be subtracted from the second equation to avoid double counting. See Table 8.1, Avoiding Double-Counting or Overlooking Emissions: Two Examples, for this term.

*Hybrid approach*: In countries where the disposal of equipment is well controlled and understood (i.e., where an efficient gas collection infrastructure is in place) and where emissions from use of sealed-pressure equipment are accounted for under 'use' above, the hybrid approach may be used, as follows:

**EQUATION 8.7B**
**EQUIPMENT DISPOSAL AND FINAL USE EMISSIONS - HYBRID**

$$\begin{aligned} \textit{Disposal and Final Use Emissions} &= \textit{Emissions from closed pressure equipment} \\ &+ \textit{Emissions from sealed pressure equipment } (\textit{EF}) \end{aligned}$$

Where:

*Disposal and final use emissions from closed-pressure equipment* = Nameplate capacity of retired closed-pressure equipment – $SF_6$ recovered from retired closed-pressure equipment, and

*Disposal emissions from sealed-pressure equipment* (*EF*) = [(Nameplate capacity of retired sealed-pressure systems) – (Nameplate capacity of retired sealed-pressure systems • Use emission factor • Lifetime of equipment)] • (1 – fraction of retiring equipment whose $SF_6$ is recovered • recovery efficiency)

As noted above, emissions estimated using the above approach should be periodically checked, e.g., by using a pure mass-balance approach and/or assessing recovery frequency and practices. Inventory compilers should pay particular attention to the fraction of retiring equipment whose $SF_6$ is recovered and to the fraction of the charge that is recovered when recovery is performed ('recovery efficiency'). Even in countries where it is the norm to recover $SF_6$ from retiring equipment, some venting may occur, and the venting of just a few percent of the $SF_6$ in retiring equipment will drive emission rates far above the minimum that is technically achievable and that would otherwise be a reasonable basis for an emission factor.

### *Emissions from $SF_6$ recycling and destruction*

Some $SF_6$ emissions occur after the chemical is recovered. These emissions include (1) emissions associated with recycling of $SF_6$, and (2) emissions associated with the destruction of $SF_6$. (Emissions associated with the shipment of $SF_6$ to off-site recyclers or destruction facilities are considered negligible.) Emissions from recycling of $SF_6$ are generally expected to be small — on the order of less than one percent of the total quantity fed into the recycling process. However, these emissions may be higher if state-of-the art handling equipment and practices are not used. In most cases, recycling is expected to occur on the site of the equipment manufacturer or user. In other cases, recycling may take place at a centralised recycling facility that is not associated with a chemical producer. Finally, recycling may take place on the premises of a chemical producer. Recycling emissions from chemical producers will be accounted for under chemical production (see Section 3.10 of this volume) and should not be included here.

Emissions associated with the destruction of $SF_6$ depend on the destruction efficiency of the process and the quantity of $SF_6$ fed into the process. Given the high stability and dissociation temperature of $SF_6$, the destruction efficiency may be as low as 90 percent. Thus, up to 10 percent of the $SF_6$ fed into the destruction process could be emitted. The quantity of gas fed into the destruction process is generally expected to be small compared to that recycled. However, this may vary from country to country.

It is *good practice* to develop country-specific emission factors for recycling and destruction that are based on full consideration of country-specific logistics and practices for $SF_6$ recycling and destruction.

Emissions from recycling of $SF_6$ may be estimated using the following equation:

**EQUATION 8.8**
**EMISSIONS FROM RECYCLING OF $SF_6$***

$$\text{Emissions from Recycling} = \text{Recycling emission factor} \bullet \text{Quantity } SF_6 \text{ fed into recycling process}$$

*Emissions from recycling that occurs at chemical production facilities should be excluded.

Emissions from destruction of $SF_6$ may be estimated using the following equation:

**EQUATION 8.9**
**EMISSIONS FROM DESTRUCTION OF $SF_6$**

$$\text{Emissions from Destruction} = \text{Destruction emission factor} \bullet \text{Quantity } SF_6 \text{ fed into destruction process}$$

**TABLE 8.1**
**AVOIDING DOUBLE-COUNTING OR OVERLOOKING EMISSIONS: TWO EXAMPLES**

| Example 1 – Double Counting | Example 2 – Omission |
|---|---|
| **Situation:** An emission-factor approach is used to estimate emissions from sealed-pressure equipment during use, and a mass-balance approach is used to estimate emissions during disposal of sealed-pressure equipment. | **Situation:** A mass-balance approach is used to estimate emissions during *use* of closed-pressure equipment, but an emission-factor approach is used to estimate emissions during *disposal* of closed-pressure. |
| **Potential problem:** Emissions during use may be double-counted because some of the $SF_6$ that is found to be missing when the equipment is disposed has already been counted as emitted during use. | **Potential problem:** Emissions that occur between the final servicing of the equipment and its disposal may be overlooked. These 'final use' emissions may account for a significant fraction of total use emissions, particularly if the equipment is refilled every 10 years or more. |
| **Solution:** Subtract lifetime use emissions (Nameplate capacity of retired sealed-pressure systems • Use emission factor • Lifetime of equipment) from emissions during disposal. | **Solution:** Use the mass-balance approach for both the use and disposal phases of the closed-pressure equipment life cycle. |

### A special case of the Tier 3 method: the utility-level, pure mass-balance approach

Countries that satisfy the *good practice* criteria for using the pure mass-balance approach beyond equipment manufacturing (i.e., countries where emissions during equipment installation, use, and disposal account for 3 percent or more of facility-level gas flows, where electrical equipment has been used for 10-20 years or more, and where emissions from sealed-pressure equipment are negligible), may, with little or no loss of accuracy, use a simplified version of the Tier 3 method to estimate emissions during equipment use. When summed together and reformulated in terms of facility-level gas flows, equations 8.5A, 8.6A, and 8.7A result in the following equation:

**EQUATION 8.10**
**UTILITY-LEVEL MASS-BALANCE APPROACH**

$$\text{User Emissions} = \text{Decrease in } SF_6 \text{ Inventory} + \text{Acquisitions of } SF_6 - \text{Disbursements of } SF_6 - \text{Net Increase in the Nameplate Capacity of Equipment}$$

Where:

*Decrease in $SF_6$ Inventory* = $SF_6$ stored in containers at the beginning of the year – $SF_6$ stored in containers at the end of the year

*Acquisitions of $SF_6$* = $SF_6$ purchased from chemical producers or distributors in bulk + $SF_6$ purchased from equipment manufacturers or distributors with or inside of equipment + $SF_6$ returned to site after off-site recycling

*Disbursements of $SF_6$* = $SF_6$ contained in equipment that is sold to other entities + $SF_6$ returned to suppliers + $SF_6$ sent off-site for recycling + $SF_6$ destroyed

*Net Increase in Nameplate Capacity of Equipment* = Nameplate Capacity of New Equipment – Nameplate Capacity of Retiring Equipment

Although the utility-level approach is less detailed than the full life cycle approach, it is simple, and for those countries whose national circumstances permit its use, it provides estimates that are closely related to actual gas loss.

### $SF_6$ EMISSIONS FROM MANUFACTURING OF ELECTRICAL COMPONENTS

Some electrical equipment components may contain 1 percent or less by weight of $SF_6$ in the insulating medium of the product. These components include but are not limited to medium voltage cast resin instrument transformers and high voltage bushings. In medium voltage (up to 52 kV) cast resin instrument transformers, $SF_6$ is used to fill up micro-cavities in the resin insulation to improve the dielectric quality and durability of the product. In High Voltage (above 52 kV) bushings, $SF_6$ is used as the blowing agent for the polyurethane resin in certain parts of the insulation system to improve the dielectric quality and durability of the product.

$SF_6$ emissions solely result from the casting/blowing process for the solid insulation of the product. All $SF_6$ used is assumed to be emitted at the manufacturing stage. To estimate emissions from this source, the pure mass-balance approach for equipment manufacturers (Equation 8.4A) may be used, setting the $SF_6$ contained in new equipment equal to zero.

Emission reduction measures focus on limiting losses/improving rate of recycling by suction devices and/or improved casting processes. $SF_6$ in this type of high voltage bushings may be replaced by another blowing agent in the future.

## 8.2.2.2 CHOICE OF EMISSION FACTORS

Because emission rates can vary not only from country to country but from facility to facility, inventory compilers using emission-factor based methods are encouraged to develop and use their own emission factors. Surveying a representative sample of equipment manufacturers and utilities within the country is an effective way to develop such factors. In general, it is *good practice* to document the evidence and reasoning supporting the selected emission factors, and to review these factors at least every 5 years.

Factors that influence emission rates include the design of the equipment (which varies depending on when and where the equipment was manufactured), $SF_6$-handling practices, availability of state-of-the-art handling equipment, $SF_6$ prices, and regulations (e.g., recovery requirements). Variation of any one of these can change emission rates over time or among countries.

## TIER 1 METHOD

Suggested default emission factors have been developed for some regions based on recent research. These factors are shown in Tables 8.2-8.4 below.

It is *good practice* to select default emission factors from countries and regions with equipment designs and $SF_6$-handling practices similar to those of the country whose emissions are being estimated. Because Japan and Europe supply most of the global demand for electrical equipment, equipment designs are likely to be similar to those of either Japan or Europe. With the exception of the factors for the U.S., regional default emission factors are those documented for 1995, i.e., before any special industry actions for emission reduction were implemented. In Japan in 1995, approximately 70 percent of the $SF_6$ used to test equipment during manufacture was recovered, and a similar percentage was recovered during equipment maintenance for equipment rated 110 kv or higher. (The 70 percent recovery fraction reflected recovery from an initial pressure of about 5 bars absolute to a final pressure of 1 to 1.5 bars absolute.) No gas was recovered from equipment rated lower than 110 kV (Maruyama *et al.*, 2000). In Europe in 1995, gas supply systems for equipment manufacture were usually decentralised, and filling tubes were not self-closing. Gas was recovered to approximately 0.05 bars absolute during manufacturing and maintenance (Ecofys, 2005).

**Table 8.2**
**Sealed pressure electrical equipment (MV Switchgear) containing $SF_6$:**
**default emission factors**

| **Phase**<br>**Region** | **Manufacturing**<br>**(Fraction $SF_6$ Consumption by Manufacturers)** | **Use (Includes leakage, major failures/arc faults and maintenance losses)**<br>**(Fraction per Year of Nameplate Capacity of All Equipment Installed)** | **Disposal**<br>**(Fraction Nameplate Capacity of Disposed Equipment)** | |
|---|---|---|---|---|
| | | | **Lifetime (years)** | **Fraction of charge remaining at retirement [b]** |
| Europe [a] | 0.07 | 0.002 | >35 | 0.93 |
| Japan [c] | 0.29 | 0.007 | Not reported | 0.95 |

[a] Source: 'Reductions of $SF_6$ Emissions from High and Medium Voltage Electrical Equipment in Europe,' Ecofys, June, 2005.

[b] This refers to the percentage of the original charge or nameplate capacity remaining in the equipment at end of life; it represents the fraction of the nameplate capacity potentially emitted before the equipment is recycled or disposed.

[c] Based on data reported by the Federation of Electric Power Companies (FEPC) and the Japan Electrical Manufacturers' Association (JEMA) (FEPC and JEMA, 2004). These organisations did not distinguish among equipment types in reporting average emission factors. The factors are therefore intended to be applied to all equipment types, including sealed pressure systems, closed pressure systems, and gas-insulated transformers.

Note: The emission factors above reflect the practices and technologies in place in 1995, i.e., before mitigation measures were implemented. References per footnotes a and c show how these developed further upon successive implementation of various voluntary measures later on. Another reference (Schwarz, 2006) relates state-of–the-art emission factors to mitigation measures in Germany.

**TABLE 8.3**
**CLOSED PRESSURE ELECTRICAL EQUIPMENT (HV SWITCHGEAR) CONTAINING $SF_6$:**
**DEFAULT EMISSION FACTORS**

| Phase / Region | Manufacturing (Fraction $SF_6$ Consumption by Manufacturers) | Use (Includes leakage, major failures/arc faults and maintenance losses) (Fraction per Year of Nameplate Capacity of All Equipment Installed) | Disposal (Fraction Nameplate Capacity of Disposed Equipment) | |
|---|---|---|---|---|
| | | | Lifetime (years) | Fraction of charge remaining at retirement [c] |
| Europe [a] | 0.085[b] | 0.026 | >35 | 0.95 |
| Japan [d] | 0.29 [b] | 0.007 | Not reported | 0.95 |
| U.S.[e] | [f] | 0.14 [g] | >35 | [h] |

[a] Source: 'Reductions of $SF_6$ Emissions from High and Medium Voltage Electrical Equipment in Europe,' Ecofys, June, 2005.

[b] Includes emissions from installation

[c] This refers to the percentage of the original charge or nameplate capacity remaining in the equipment at end of life; it represents the fraction of the nameplate capacity emitted before the equipment is recycled or disposed.

[d] Based on data eported by the Federation of Electric Power Companies (FEPC) and the Japan Electrical Manufacturers' Association (JEMA) (FEPC and JEMA, 2004). These organisations reported average emission factors that include emissions from all equipment types, including sealed pressure systems, closed pressure systems, and gas-insulated transformers.

[e] From the U.S. Inventory of Greenhouse Gases and Sinks, 1990-2002. (U.S. EPA, 2004). Value is from 1999, first year for which representative country-specific data were available.

[f] No country-specific value available.

[g] Includes emissions from installation.

[h] Disposal emissions are included in use emission factor in the US.

Note: The emission factors above reflect the practices and technologies in place in 1995, i.e., before mitigation measures were implemented. References per footnotes a and d show how these developed further upon successive implementation of various voluntary measures later on. Schwarz (2006) relates state-of–the-art emission factors to mitigation measures in Germany.

**TABLE 8.4**
**GAS INSULATED TRANSFORMERS CONTAINING $SF_6$: DEFAULT EMISSION FACTORS**

| Phase / Region | Manufacturing (Fraction $SF_6$ Consumption by Manufacturers) | Use (Includes leakage, major failures/arc faults and maintenance losses) (Fraction per Year of Nameplate Capacity of All Equipment Installed) | Disposal (Fraction Nameplate Capacity of Disposed Equipment) | |
|---|---|---|---|---|
| | | | Lifetime (years) | Fraction of charge remaining at retirement [a] |
| Japan [b] | 0.29 | 0.007 | Not reported | 0.95 |

[a] This refers to the percentage of the original charge or nameplate capacity remaining in the equipment at end of life; it represents the fraction of the nameplate capacity emitted before the equipment is recycled or disposed

[b] Based on data reported by the Federation of Electric Power Companies (FEPC) and the Japan Electrical Manufacturers' Association (JEMA) (FEPC and JEMA, 2004). These organisations did not distinguish among equipment types in reporting average emission factors. The factors are therefore intended to be applied to all equipment types, including sealed pressure systems, closed pressure systems, and gas-insulated transformers.

Note: The emission factors above reflect the practices and technologies in place in 1995, i.e., before mitigation measures were implemented. References per footnote b show how these developed further upon successive implementation of various voluntary measures later on. Schwarz (2006) relates state-of–the-art emission factors to mitigation measures in Germany.

### TIER 2 METHOD

Emission factors for the Tier 2 method are generally developed on the basis of data collected from representative manufacturers and utilities that track emissions by life cycle stage, essentially using the Tier 3, pure mass-balance method at their facilities for at least one year. (The disposal emission factor should also account for emissions that occur downstream of the utility site, as discussed below.) These emissions by life cycle stage are then divided by the corresponding $SF_6$ consumption or equipment capacity at that life cycle stage (i.e., $SF_6$ consumption for manufacturing emissions, total existing equipment capacity for use emissions, and retiring equipment capacity for final use and disposal emissions) to develop emission factors. For example, to develop an emission factor for manufacturing, total emissions from the survey of manufacturers are summed and then divided by the total $SF_6$ consumption of surveyed manufacturers. This emission factor can then be applied to the manufacturing sector as a whole, using national $SF_6$ consumption by manufacturers. A similar approach can be used to estimate and apply emission factors for equipment use.

The emission factor for disposal should fully account for three factors: (1) the recovery frequency (the fraction of equipment whose charge is recovered), (2) the recovery efficiency (the fraction of charge recovered when recovery is performed), and (3) the emissions from recycling and destruction of the recovered gas. The quantities in (1) and (2) will be automatically accounted for in emission factors based on use of the Tier 3 mass-balance method at representative utilities. However, the quantity in (3) reflects emissions that occur both on site and downstream of the utility/user. Thus, it must be accounted for separately. See the Tier 3 Method discussion below for guidance on estimating recycling and destruction emission factors.

The facility-level variant of the Tier 3 approach may also be used to develop emission factors, but these will be applied at a more aggregated level, i.e., to equipment manufacturing and use (where the latter includes installation, use, and disposal) rather than to each lifecycle stage.

#### TIER 3 METHOD

Because the Tier 3 method encourages the use of emission factors only when emission rates from processes are quite low (e.g., 3 percent of nameplate capacity per year or less) or when electrical equipment has only recently been introduced into a country, emission factors for this method may be difficult to measure directly using a mass-balance approach. To estimate Tier 3 emission factors, therefore, engineering studies may be used, identifying potential leak points and loss mechanisms and assigning probabilities and emission rates to these. Expected losses from service and maintenance should be factored into overall emission rates, as should losses from rare but catastrophic events that result in the loss of most of the equipment’s charge. Past experience with similar processes and designs should be considered. To ascertain and verify emission factors for use, surveys of equipment in the field may be carried out after several years of use, with the number of years determined by the expected leak rate and the limit of detection of the measuring equipment. Manufacturer statistics on equipment failure rates should be monitored to help ensure that catastrophic or gradual loss rates are not higher than expected. Disposal emissions are extremely sensitive to recovery frequencies (the fraction of equipment whose charge is recovered) and to recovery efficiencies (the fraction of charge recovered when recovery is performed, which, due to time considerations, may be lower than what is technically achievable). Thus, these should be monitored and documented carefully before establishing disposal emission factors.

Emission factors for recycling of recovered $SF_6$ may be based on professional judgement. Emission factors for destruction may be based on the rated destruction efficiency of the destruction technology, assuming that the technology is maintained and operated in a way that maintains its rated destruction efficiency.

### 8.2.2.3 CHOICE OF ACTIVITY DATA

The activity data necessary to carry out the various estimation methods may be gathered from chemical manufacturers, equipment manufacturers, equipment users, and equipment disposers and/or their industry associations in the country or the region. The best source(s) of data vary depending upon the method and national circumstances.

#### TIER 1 METHOD

***$SF_6$ consumption by equipment manufacturers:*** $SF_6$ consumption by equipment manufacturers can be estimated using information from the manufacturers on their purchases of $SF_6$, their returns of $SF_6$ to chemical producers, and changes in their inventory of $SF_6$ in containers. If information from equipment manufacturers is unavailable or incomplete, information from chemical producers and/or distributors on their sales to equipment manufacturers (less any returns) may be used.

***Nameplate capacity of new and retiring equipment*:** Nameplate capacity can be estimated using one or more of the following data sources: (1) information from equipment manufacturers/importers on the total nameplate capacity of the equipment they manufacture or import and export, (2) information from utilities on the total nameplate capacity of the equipment they install and retire each year, or (3) if information from (1) or (2) is not available, information from chemical manufacturers/importers on their sales of $SF_6$ to equipment manufacturers. The first two data sources are preferable to the third, because gas sales to equipment manufacturers will differ from the nameplate capacity of new equipment installed in the country, particularly if equipment imports or exports are significant. In estimating the nameplate capacities of new and retiring equipment, inventory compilers should include the nameplate capacity of imported equipment and exclude the nameplate capacity of exported equipment. (See Section 7.5, Refrigeration, Box 7.1, Accounting for Imports and Exports of Refrigerant and Equipment, for a full discussion of how to treat imports and exports in estimating these quantities. This guidance is directly applicable to this category.)

In the case of retiring equipment, capacity or sales information should be historical, starting in the year when the current year's retiring equipment was built. Typical values for the lifetime of electrical equipment range from 30 to 40 years. If information on the total nameplate capacity of retiring equipment is not available, it can be estimated from new nameplate capacity, using the estimated annual growth rate of equipment capacity. In estimating the growth rate, it is *good practice* to consider both the number of pieces of equipment sold each year and the average nameplate capacity of the equipment.[3]

The following equation can be used to estimate retiring nameplate capacity, if this information is not available directly:

**EQUATION 8.11**

**RETIRING NAMEPLATE CAPACITY**

$$\text{Retiring Nameplate Capacity} = \text{New Nameplate Capacity} / (1 + g)^{L}$$

Where:

L = equipment lifetime

g = rate of growth

According to a 2004 global survey, the average annual growth rate of $SF_6$ sales to equipment manufacturers between 1970 and 2000 was approximately 9 percent. (Smythe, 2004). In the absence of country-specific information, a default factor of 9 percent may be used.

***Total nameplate capacity of installed equipment*****:** The total nameplate capacity of equipment can be estimated using the same data sources as are used to estimate the nameplate capacity for new and retiring equipment. If data from equipment manufacturers is used, it should include data on sales over the full lifetime of the equipment (30 to 40 years).

### TIER 2 METHOD

Quantities can be estimated as for Tier 1 above.

### TIER 3 METHOD

To implement the Tier 3 method, information must be gathered at two levels. At the facility level, gas flows must be tracked correctly according to the Tier 3 method. At the national level, information from facilities (manufacturers, users, and disposers of equipment) must be collected, checked, summed, and if necessary, extrapolated to include estimates of emissions from facilities in the country that do not collect data. Guidance regarding the information to be tracked by facilities is provided in the descriptions of the Tier 3 method above. Gas consumption may be measured by weighing gas cylinders before and after filling or recovery operations or at the beginning and end of the year or by using flow meters (e.g., during equipment manufacturing). At the national level, trade associations for equipment manufacturers and utilities can be very helpful in disseminating knowledge to their members regarding the Tier 3 approach and in helping their members to track and report data consistently and transparently. Trade associations can also act as third parties to aggregate confidential or sensitive data so that it can be released (in aggregate) to the public. Where trade associations are not active, national inventory compilers can facilitate the collection of information at the facility level, as well as the reporting and verification of this information, by developing model emission tracking protocols or by adopting existing industry protocols that embody the Tier 3 approach. These protocols can then be distributed to the manufacturers, users, and disposers of electrical equipment. Electronic protocols such as spreadsheets further facilitate the tracking, documentation, and reporting of emissions and minimize opportunities for arithmetic error.

Because emission rates can vary from region to region and facility to facility, it is *good practice* to survey as many facilities as practical. In addition to manufacturers and utilities, countries should survey industrial sites and other non-utility sites if these contribute substantially to emissions from electrical equipment. If the number of facilities in a country is large (e.g., over 50), it may be difficult to achieve complete reporting. In these cases, countries may estimate emissions from non-reporting facilities by applying the Tier 2 method to these facilities

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[3] While the number of pieces of equipment sold each year has generally grown, the average nameplate capacity has generally declined.

or by using alternative activity data as described in Chapter 2 of Volume 1, Approaches to Data Collection. Sector-specific considerations in selecting and using alternative activity data are discussed below.

For sealed pressure equipment (which is widely dispersed among industrial users as well as utilities), manufacturers and distributors are likely to be the best source of complete information on national bank sizes and emission rates. To develop an accurate estimate, inventory compilers should survey manufacturers regarding their sales of equipment between the present and the time when currently retiring equipment was installed, or, if equipment has not yet begun to be retired, between the present and the time when the equipment was introduced into the country.

#### Sector-specific considerations in selecting and using alternative activity data for Tier 3

As discussed above, even when implementing a Tier 3 method it may not be possible to obtain data from all facilities. To obtain complete coverage of facilities, it is possible to use alternative activity data. For estimating emissions from non-reporting manufacturers, it may be possible to use the manufacturing capacity and/or collective market share (in terms of functional units) of the non-reporting manufacturers. For estimating emissions from non-reporting utilities, possible alternative data sets or drivers include (but are not limited to) the length of transmission lines, the combined length of transmission and distribution lines, or the number of substations of the non-reporting utilities. Transmission kilometres are likely to be a good predictor of emissions where most $SF_6$ is used in high voltage transmission equipment, as in the U.S. (A discussion of how transmission kilometres are used to estimate emissions in the U.S. can be found in Volume 1, Chapter 2, Approaches to Data Collection.) Where a high percentage of $SF_6$ is used in medium voltage distribution equipment or in gas-insulated substations, one of the other types of data may be appropriate.

Wherever alternative data sets are used, it is important to derive emission factors from a representative set of facilities to ensure that the resulting estimate of national $SF_6$ emissions is unbiased. Note that more than one factor may be appropriate, e.g., for different size utilities or for utilities in urban vs. rural locations. Because $SF_6$ use and emission patterns can change over time, it is *good practice* to update the analysis and emission factor(s) at least every five years. (For example, emission rates may change as compact and leak-tight equipment replaces larger, leakier equipment and as sealed pressure equipment grows in importance.) In some cases, countries may be able to make use of emission factors developed in countries with similar electrical grids. In these cases, it is *good practice* to document the similarities between the grids before applying the emission factor from the other country.

### 8.2.2.4 COMPLETENESS

Completeness for this source category requires accounting for emissions during the manufacture, use, and disposal of equipment, and during the recycling or destruction of $SF_6$ recovered from equipment. Where Tier 3 methods are used, completeness requires that all significant $SF_6$ users (manufacturers and utilities) be identified. When facility-level emissions data are not available from all of these users, emission estimates should be developed for them using one of the extrapolation methods described in Section 8.2.2.3, Choice of Activity Data.

In the manufacturing sector, this requires assessing emissions from:

- Manufacture of gas insulated switchgear (GIS), gas circuit breakers (GCB), high voltage gas-insulated lines (GIL), outdoor gas-insulated instrument transformers, reclosers, switches, and ring main units of both types (sealed and closed pressure systems, respectively up to and above 52 kV), and other equipment including but not limited to cast resin instrument transformers and certain types of bushings using $SF_6$ either as gas for the casting process or as a blowing agent;
- Manufacturers of gas-insulated power transformers (GIT);
- Minor $SF_6$ users, including equipment remakers and servicing companies;
- The $SF_6$ distribution chain from producers and distributors to manufacturing facilities.

In the utility and disposal sector, this requires accounting for all $SF_6$ losses associated with:

- New electrical equipment installations;
- Leakage, refill, maintenance, and equipment failures;
- Disposal of discarded electrical equipment;
- Recycling or destruction of $SF_6$ recovered from equipment (but recycling emissions from chemical producers should be counted under chemical production, which is covered in Section 3.10 of this volume).

It is *good practice* to identify and include industrial, military and small-utility applications if these are believed to contribute substantially to total emissions from the electrical equipment source category.

### 8.2.2.5 DEVELOPING A CONSISTENT TIME SERIES

When estimating emissions from equipment users over a time series, it is necessary to consider $SF_6$ emissions associated with the full set equipment at users' sites for the years of interest. Thus, when using approaches based on banks and emission-factors (e.g., the Tier 2 approach), countries will require information on the capacity and emission rate of equipment purchased and installed for 30 to 40 years preceding the years of interest.

In the user sector, if historical data are unavailable, *good practice* is to develop estimates using the top-down method, i.e., develop a model based on professional judgement by industry experts and inventory compilers and then calibrate as discussed below. Average leak rates for new equipment and the frequency of refill and routine maintenance all decreased from 1970 to 1995, and this trend has continued to the present. It is *not good practice* to apply current (post-2000) overall loss rates to historical years. Aggregate loss rates estimated from historical sales can be used in this case as well.

On the manufacturing side, if historical data for developing base year emissions for 1990/1995 are not available, the top-down method calibrated to more accurate estimates for current years may be applied. Since $SF_6$ handling practices of equipment manufacturers have changed substantially since 1995 (e.g., more gas is recovered), it is *not good practice* to apply current loss rates to historical estimates. Aggregate loss rates determined from global and regional sales and emission analyses may assist in providing an unbiased estimate for earlier years. It is *good practice* to recalculate emissions according to the guidance provided in Volume 1, Chapter 5, with all assumptions clearly documented.

## 8.2.3 Uncertainty assessment

When using the Tier 3 method, the resulting emissions estimates will have an accuracy of the order of ± 10 percent, and are likely to be more accurate than estimates developed using Tier 2 or Tier 1 methods.. If surveys are incomplete, the associated uncertainty will be greater. Particular sources of uncertainty may include:

- $SF_6$ exported by equipment manufacturers (either in equipment or separately in containers);
- $SF_6$ imported by foreign equipment manufacturers (either in equipment or in containers);
- $SF_6$ returned to foreign recycling facilities;
- Measurements of mass, density, and pressure (generally accurate to within one or two percent of the total quantity massed, but if emission rates are low, this may be a substantial percentage of those rates);
- Emission factors;
- Time lag between emissions and servicing;[4]
- Lifetime of the equipment;
- Regression error associated with any extrapolative approaches.

The estimated uncertainties in the default emission factors for the Tier 1 method are shown in Table 8.5, Uncertainties for Default Emission Factors for $SF_6$ Emissions from Electrical Equipment. These values are based on the variation observed in emission factors in Europe. If the factors in Tables 8.2-8.4 are applied outside the countries and/or regions in which they were developed, uncertainties will be greater.

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[4] See Chapter 1 of this volume for a discussion of this issue.

TABLE 8.5
UNCERTAINTIES FOR DEFAULT EMISSION FACTORS AND LIFETIME

| Phase / Equipment Type | Manufacturing | Use (Includes leakage, major failures/arc faults and maintenance losses) | Disposal | |
|---|---|---|---|---|
| | | | Lifetime (years) | Fraction of charge remaining at retirement |
| Sealed-Pressure[a] | ±20% | ±20% | -20%/+40% | [d] |
| Closed-Pressure[b] | ±30% | ±30% | -10%/+40% | [d] |
| Gas Insulated Transformers[c] | ±30% | ±30% | -10%/+40% | [d] |

[a] Estimated from 'Reductions of $SF_6$ Emissions from High and Medium Voltage Electrical Equipment in Europe,' Ecofys, June, 2005;no uncertainties available from Japan; not relevant for USA..

[b] Estimated from 'Reductions of $SF_6$ Emissions from High and Medium Voltage Electrical Equipment in Europe,' Ecofys, June, 2005; U.S. emission factors have higher uncertainty for manufacturing (±70%) and slightly lower uncertainty for use (±15%) (U.S. Inventory of Greenhouse Gases and Sinks (U.S. EPA, 2004)). No uncertainties available from Japan.

[c] Estimated by analogy with closed pressure systems; actual uncertainties may be somewhat higher. No uncertainties available from Japan.

[d] No uncertainties available on fraction of charge remaining at retirement.

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

### 8.2.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

Additional procedures specific to electrical equipment are outlined below:

**Comparison of emissions estimates using different approaches**

Inventory compilers should sum the facility-level data used as part of a bottom-up, Tier 3 method and cross-check the data against national level emissions calculated using country-level data (the Tier 2 method) and/or country-level data with the IPCC default emission factors (the Tier 1 method). The Tier 2 method may similarly be checked against the Tier 1 method. Countries may also compare their results to those derived using a country-level mass-balance approach, as described in Equations 7.3 and 7.9 of Chapter 7. If countries do not have manufacturing facilities, they may also compare their estimates against potential emissions estimated using national apparent consumption data.

**Review of facility-level emissions data**

In all instances where site-specific emissions data are obtained through surveys, inventory compilers should compare the emission rates between sites (adjusting for relative size or capacity) to identify significant outliers. They should investigate any outliers to determine if the differences can be explained or if there is an error in the reported emissions. As noted in Section 8.2.2.3, national inventory compilers can facilitate both the collection and verification of information at the facility level by distributing emission tracking protocols that embody the Tier 3 approach. Electronic protocols such as spreadsheets are particularly useful, as they minimize opportunities for arithmetic error. The calculations included in these protocols (whether electronic or not) can then be checked after they are submitted.

### Comparison of emission rates with those of other countries

Inventory compilers should compare effective emission factors (loss rates) with values reported by other countries in the region, or with defaults published in the scientific literature for equipment with a similar design and similar level of emissions control. Transparent reporting, as outlined above, is essential for making international comparisons.

## 8.2.4.2 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, Section 6.11. 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.

Some examples of specific documentation and reporting relevant to this source category ensuring transparency in reported emissions estimates are provided in Table 8.6, Good Practice Reporting Information for $SF_6$ Emissions from Electrical Equipment by tier.

Confidentiality issues may arise where there are limited numbers of manufacturers or utilities. In these cases, aggregated reporting for the total electrical equipment sector, or even total national $SF_6$ applications, may be necessary. National or regional associations of users and manufacturers may be willing to collect, check, and aggregate data, particularly when they have collected such data historically. They can then report the aggregated information to the inventory compiler, resolving the problem of confidentiality. If survey responses cannot be released as public information, third party review of survey data may be necessary to support data verification efforts.

TABLE 8.6
GOOD PRACTICE REPORTING INFORMATION FOR $SF_6$ EMISSIONS FROM ELECTRICAL EQUIPMENT BY TIER

| Data | Tier 3 | Tier 2 | Tier 1 |
|---|---|---|---|
| Annual, country-wide consumption of $SF_6$ by equipment manufacturers | | X | X |
| Nameplate capacity of new equipment | X | X | X |
| Nameplate capacity of existing equipment | X* | X | X |
| Nameplate capacity of retiring equipment | X | X | X |
| $SF_6$ destroyed | X | | |
| $SF_6$ in inventory at beginning of year | X | | |
| $SF_6$ in inventory at end of year | X | | |
| $SF_6$ purchased by facility | X | | |
| $SF_6$ sold or returned by facility | X | | |
| $SF_6$ sent off-site for recycling | X | | |
| $SF_6$ returned to site after recycling | X | | |
| $SF_6$ used to fill new equipment | X | | |
| $SF_6$ used to service equipment | X | | |
| $SF_6$ recovered from retiring equipment | X | | |
| Emission/recovery factors | X* | X | |
| Documentation for factors, if country-specific | X* | X | |

*Required for some variants of the methods.

# 8.3 USE OF $SF_6$ AND PFCs IN OTHER PRODUCTS

## 8.3.1 Introduction

This source category excludes the following source categories that are addressed elsewhere in the *2006 Guidelines*:

- Production of $SF_6$ and PFCs (Section 3.10);
- Production and use of electrical equipment (Section 8.2);
- Primary and secondary production of magnesium and aluminium (Chapter 4); and
- Semiconductor and flat panel display manufacturing (Chapter 6).

Identified remaining applications in this source category include:

- $SF_6$ and PFCs used in military applications, particularly $SF_6$ used in airborne radar systems, e.g., AWACS (Airborne Warning and Control System), and PFCs used as heat transfer fluids in high-powered electronic applications;
- $SF_6$ used in equipment in university and research particle accelerators;
- $SF_6$ used in equipment in industrial and medical particle accelerators;
- 'Adiabatic' applications utilising the low permeability through rubber of $SF_6$ and some PFCs, e.g., car tires and sport shoe soles;
- $SF_6$ used in sound-proof windows;
- PFCs used as heat transfer fluids in commercial and consumer applications;
- PFCs used in cosmetics and in medical applications;
- Other uses e.g. gas-air tracer in research and leak detectors.

## 8.3.2 Methodological issues

### 8.3.2.1 CHOICE OF METHOD

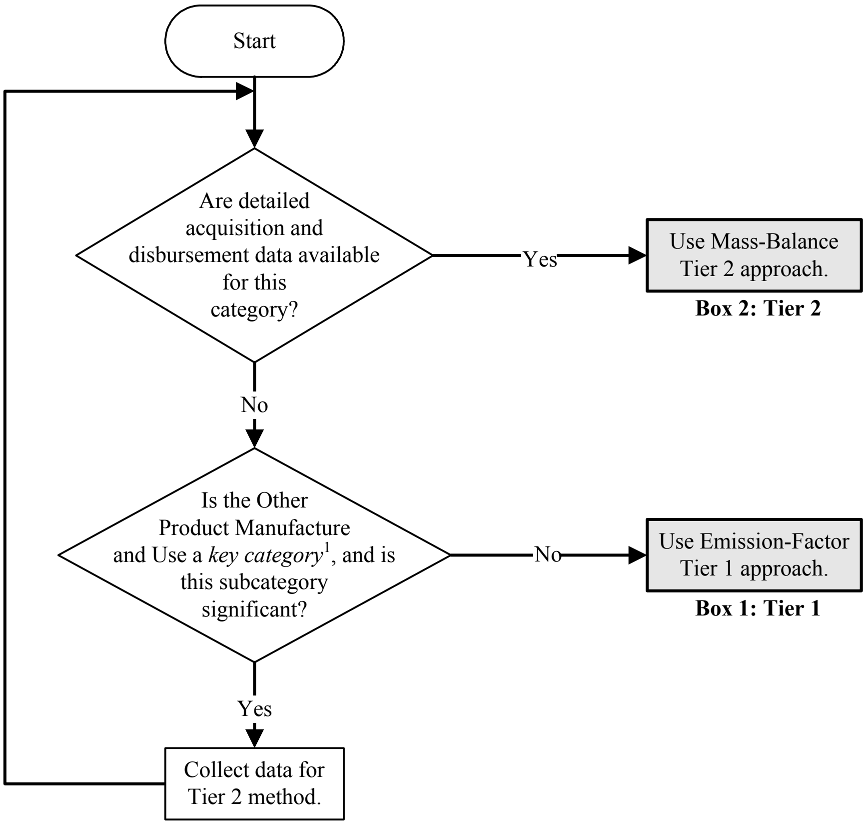
The *good practice* method is to use either consumption data from users of $SF_6$ or PFCs or top-down import, export and consumption data from national $SF_6$ producers and distributors, disaggregated by major type of $SF_6$ or PFC application. Acquiring this data will entail a survey of all producers and distributors of $SF_6$ and PFCs to identify total net $SF_6$ and PFC consumption. Once the data are obtained, the amount of $SF_6$ and PFC consumed by application in this source category should be estimated.

### MILITARY APPLICATIONS

### $SF_6$ EMISSIONS FROM OPERATION OF AWACS

$SF_6$ is used as an insulating medium in the radar systems of military reconnaissance planes of the Boeing E-3A type, commonly known as AWACS. The purpose of the $SF_6$ is to prevent electric flashovers in the hollow conductors of the antenna, in which high voltages of more than 135 kV prevail. When the plane ascends, $SF_6$ is automatically released from the system and into the atmosphere to maintain the appropriate pressure difference between the system and the outside air. When the plane descends, $SF_6$ is automatically charged into the system from an $SF_6$ container on board. Most emissions occur during the pressure-balancing process on ascent, but emissions from system leakage can also occur during other phases of flight or during time on the ground. Annual emissions per plane have been estimated to be 740 kg, while the charge of each system is approximately 13 kg.

**Figure 8.2 Decision tree for $SF_6$ from AWACS**



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 1 method – $SF_6$ emissions per plane

If a country does not have data on $SF_6$ consumption by its AWACS, it may use a per-plane emission factor to estimate emissions. An emission factor of 740 kg per plane per year is presented in Table 8.7 below; this figure is based on estimates of $SF_6$ emissions from NATO Boeing E-3As. Note that actual emissions per plane are strongly influenced by the average number of sorties (take-offs) per plane per year. More frequent sorties will raise the emission rate above 740 kg/plane; less frequent sorties will lower it. Leakage rates during flight or during time on the ground will also affect the emission rate.

**EQUATION 8.12**
**EMISSIONS FROM AWACS (DEFAULT EMISSION ACTOR)**

$$\text{User Emissions} = 740 \text{ kg} \bullet \text{Number of planes in AWACS fleet}$$

**TABLE 8.7**
**$SF_6$ EMISSIONS PER PLANE PER YEAR**

| Emissions per plane per year (kg $SF_6$) | Uncertainty |
|---|---|
| 740 kg | ±100 kg |
| Source: Schwarz (2005) | |

Table 8.8 includes information on national AWACS fleets world wide (Boeing, 2005); like other activity data, it may quickly go out of date. Countries are in the best position to know the numbers of planes in their AWACS fleets.

TABLE 8.8
NATIONAL AWACS FLEETS

| Country/ Organisation | USA | Japan | France | UK | Other NATO | Saudi Arabia | Total |
|---|---|---|---|---|---|---|---|
| No. AWACS | 33 | 4 | 4 | 7 | 17 | 5 | 70 |

Source: Boeing (2005)

### Tier 2 method – user mass-balance method

The most accurate method for estimating $SF_6$ emissions from AWACS is to track $SF_6$ consumption by the systems. To do so, the following equations, which are similar to the utility-level variant of the Tier 3 method for electrical equipment, may be used. Note that for AWACS, acquisitions and disbursements of $SF_6$ containers are likely to be considerably more important to the result than acquisitions and retirements of operating systems.

EQUATION 8.13
EMISSIONS FROM AWACS (USER MASS-BALANCE)

$$\text{User Emissions} = \text{Decrease in } SF_6 \text{ Inventory} + \text{Acquisitions of } SF_6 - \text{Disbursements of } SF_6 - \text{Net Increase in AWACS Fleet Charge}$$

Where:

*Decrease in $SF_6$ Inventory* = $SF_6$ stored in containers at the beginning of the year – $SF_6$ stored in containers at the end of the year

*Acquisitions of $SF_6$* = $SF_6$ purchased from chemical producers or distributors in bulk + $SF_6$ purchased from AWACS manufacturers or distributors with or inside of new planes + $SF_6$ returned to site after off-site recycling

*Disbursements of $SF_6$* = $SF_6$ contained in AWACS that are transferred to other entities + $SF_6$ returned to suppliers + $SF_6$ sent off-site for recycling + $SF_6$ destroyed

*Net Increase in AWACS Fleet Charge* = 13 kg • (New AWACS – Retiring AWACS)

## $SF_6$ AND PFC EMISSIONS FROM OTHER MILITARY APPLICATIONS

There is wide range of military applications using PFCs or $SF_6$.[5] Military electronics are believed to be an important and growing application of PFC heat transfer fluids, which are valued for their stability and dielectric properties. The fluids are used in ground and airborne radar (klystrons), avionics, missile guidance systems, ECM (Electronic Counter Measures), sonar, amphibious assault vehicles, other surveillance aircraft, lasers, SDI (Strategic Defense Initiative), and stealth aircraft. PFCs may also be used to cool electric motors, particularly in applications where noise reduction is valued, e.g., in ships and submarines. The specific PFCs used in these applications are believed to be similar to those identified as heat transfer fluids in electronics manufacturing in Chapter 6. Spray cooling, jet impingement cooling, and pool boiling appear to be the favoured systems for heat removal. In all of these cooling applications, the PFC is contained in a closed system, and neither replacement nor replenishment of the PFC liquid appears to be required. Thus, the greatest opportunities for emissions are the manufacture, maintenance, and, especially, the disposal of the equipment.

$SF_6$ is used in high-performance ground and airborne radar systems in their hollow conductors for transmission of high-frequency energy pulses at high voltages from the klystron. Another application of $SF_6$ is as an oxidant of lithium in Stored Chemical Energy Propulsion System (SCEPS), e.g., in naval torpedoes and in infrared decoys (Koch, 2004). Apparently, these applications of $SF_6$, like those of the PFC heat transfer fluids enumerated above, are generally more or less enclosed, but servicing and testing procedures may lead to emission. The use of $SF_6$ for the quieting of torpedo propellers has also been reported (NIST, 1997).

In addition, $SF_6$ may be emitted as a by-product of the processing of nuclear material for the production of fuel and nuclear warheads. $SF_6$ is known to be emitted from neutralising excess fluorine during the production of nuclear fuel for civilian applications (AREVA, 2005).

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[5] David Harris and James Hildebrandt, “Spray Cooling Electrical and Electronic Equipment,” *COTS Journal*, November 2003; C. Shepherd Burton, “Uses and Air Emissions of Liquid PFC Heat Transfer Fluids from the Electronics Sector,” Draft report prepared for Scott C. Bartos, U.S. Environmental Protection Agency.

Although it is believed that the total amounts of $SF_6$ and PFCs consumed and emitted in this sector may be significant, no data on quantities are publicly available so far. Therefore, inventory compilers should try to collect further information from the relevant authorities and, if possible, their suppliers. As noted above, the greatest opportunities for emissions from many of these applications appear to be the manufacture, maintenance, and disposal of the equipment. Thus, if inventory compilers can acquire information on emission rates during the manufacture, maintenance, and disposal of the equipment, along with the quantities of equipment manufactured, in use, and disposed, they can use the Tier 2 or Tier 3 method for electrical equipment to estimate emissions. For applications with different emissions profiles (e.g., prompt emissions), the appropriate equation from Section 8.2 may be used.

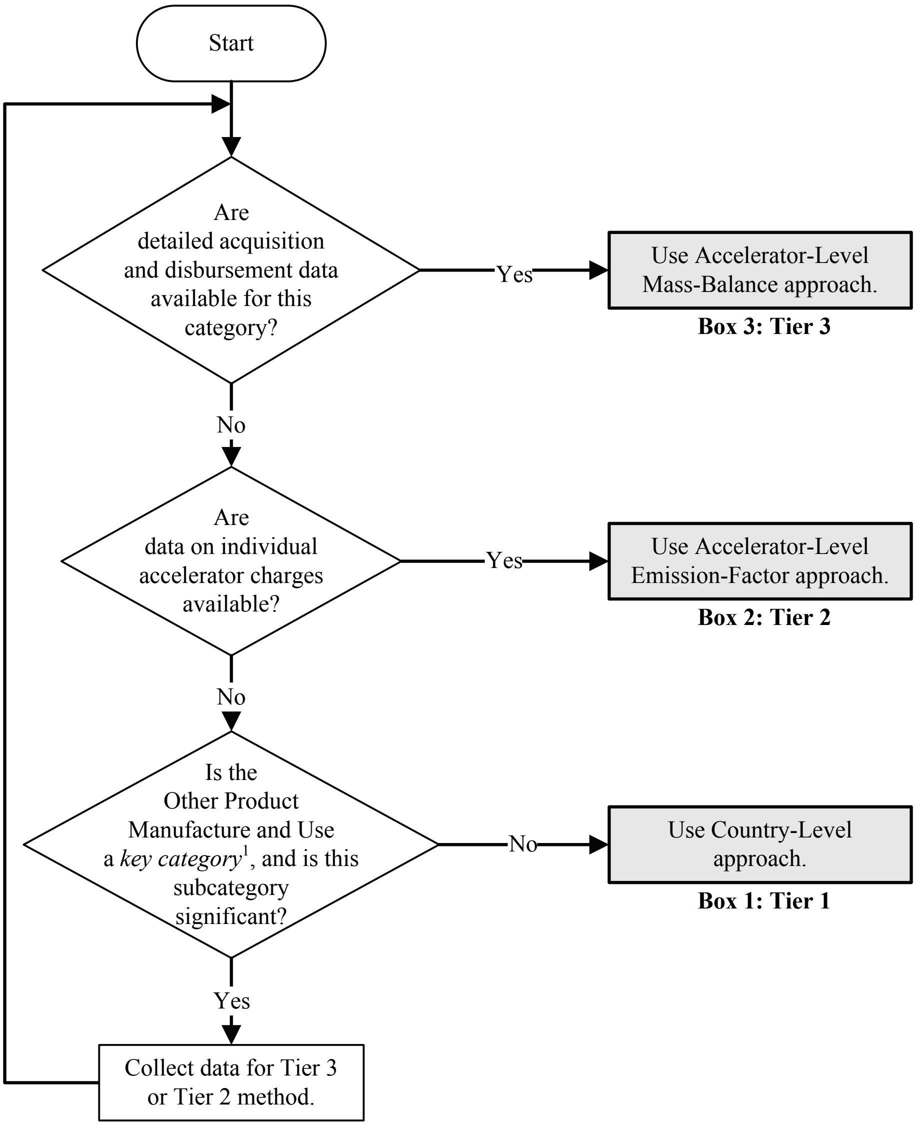
## $SF_6$ EMISSIONS FROM UNIVERSITY AND RESEARCH PARTICLE ACCELERATORS

$SF_6$ is used in university and research operated particle accelerators as an insulating gas. Typically, high voltage equipment is contained and operated within a vessel filled with $SF_6$ at a pressure exceeding atmospheric pressure. Charges range from five kilograms to over ten thousand kilograms, with typical charges falling between 500 and 3 000 kg. When the equipment requires maintenance, the $SF_6$ is transferred into storage tanks. $SF_6$ losses occur primarily during gas recovery and transfer, when pressure relief valves are actuated, and through slow leaks.

Based on two recent studies annual $SF_6$ losses range between 5 and 7 percent of vessel capacity per year and generally depend on the vessel opening frequency plus the efficiency of the recovery and transfer equipment. World banked capacity is roughly estimated to be 500 tonnes with annual $SF_6$ emissions of 35 tonnes.

Switzerland has developed a voluntary program to reduce $SF_6$ emissions from particle accelerators. Suggestions and techniques for reducing $SF_6$ emissions from these sources exist.

**Figure 8.3** **Decision tree for $SF_6$ from research accelerators**



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 1 method – country-level method

In cases where individual user accelerator charge data is unavailable, one extremely rough method involves determining the total number of university and research particle accelerators in the country and using several factors to determine the country-level annual emission rate as noted in Equation 8.14. For this Tier 1 method, the only data that requires collection is the total number of university and research particle accelerators in the given country.

**EQUATION 8.14**
**UNIVERSITY AND RESEARCH PARTICLE ACCELERATOR EMISSIONS (COUNTRY-LEVEL)**

Emissions = (Number of university and research particle accelerators in the country) • ($SF_6$ Use Factor) • ($SF_6$ Charge Factor, kg) • ($SF_6$ university and research particle accelerator Emission Factor)

Where:

*Number of university and research particle accelerators in the country* = The total number of university and research particle accelerators in the country. This rough method does not require countries to determine the number of accelerators that use $SF_6$. To determine if a country has a particle accelerator, go to http://www-elsa.physik.uni-bonn.de/Informationen/accelerator_list.html

*$SF_6$ Use Factor* = 0.33 Approximately one third of university and research particle accelerators use $SF_6$ as an insulator.

*$SF_6$ Charge Factor* = 2400 kg, $SF_6$, the average $SF_6$ charge in a university and research particle accelerator.

*$SF_6$ university and research particle accelerator Emission Factor* = 0.07, the average annual university and research particle accelerator emission rate as a fraction of the total charge.

### Tier 2 method – accelerator-level emission-factor approach

If data on the quantity of $SF_6$ contained within each university and research accelerator are available, a default emission factor of 7 percent may be multiplied by the total $SF_6$ charge contained in university and research accelerators in the country. The total country $SF_6$ emission rate from university and research accelerators is therefore calculated from Equation 8.15.

**EQUATION 8.15**
**UNIVERSITY AND RESEARCH PARTICLE ACCELERATOR EMISSIONS (ACCELERATOR-LEVEL EMISSION FACTOR)**

$$\text{Total Emissions} = SF_6 \text{ university and research particle accelerator Emission Factor} \bullet \sum \text{Individual Accelerator Charges}$$

Where:

*$SF_6$ university and research particle accelerator Emission Factor* = 0.07, the average annual university and research particle accelerator emission rate as a fraction of the total charge.

*Individual User Accelerator Charges* = $SF_6$ contained within each university and research accelerator.

### Tier 3 method –accelerator-level mass-balance method

$SF_6$ emissions from university and research facilities operating particle accelerators may be most accurately determined at the user level on an accelerator-by-accelerator basis. Emission calculations are estimated by tracking accelerator charge as well as $SF_6$ consumption and disposal. As detailed in Equation 8.16, the total emissions are equal to the sum of the individual users' emissions. Note, under this method, as the overall $SF_6$ emission rate from particle accelerators is small compared to other $SF_6$ uses, the associated $SF_6$ lost in manufacturing is considered negligible and is not included in the calculation.

**EQUATION 8.16**
**TOTAL RESEARCH ACCELERATOR EMISSIONS**

$$Total\ Emissions = \sum Individual\ Accelerator\ Emissions$$

Each particle accelerator's emissions can be calculated as follows:

**EQUATION 8.17**
**RESEARCH ACCELERATOR EMISSIONS (ACCELERATOR-LEVEL MASS-BALANCE)**

$$\text{Accelerator Emissions} = \text{Decrease in } SF_6 \text{ Inventory} + \text{Acquisitions of } SF_6 - \text{Disbursements of } SF_6 - \text{Net Increase in Accelerator Charge}$$

Where:

*Decrease in $SF_6$ Inventory* = $SF_6$ stored in containers at the beginning of the year – $SF_6$ stored in containers at the end of the year

*Acquisitions of $SF_6$* = $SF_6$ purchased from chemical producers or distributors in bulk + $SF_6$ purchased from accelerator manufacturers or distributors with or inside of new accelerator components + $SF_6$ returned to site after off-site recycling

*Disbursements of $SF_6$* = $SF_6$ contained in components transferred to other entities + $SF_6$ returned to suppliers + $SF_6$ sent off-site for recycling + $SF_6$ destroyed

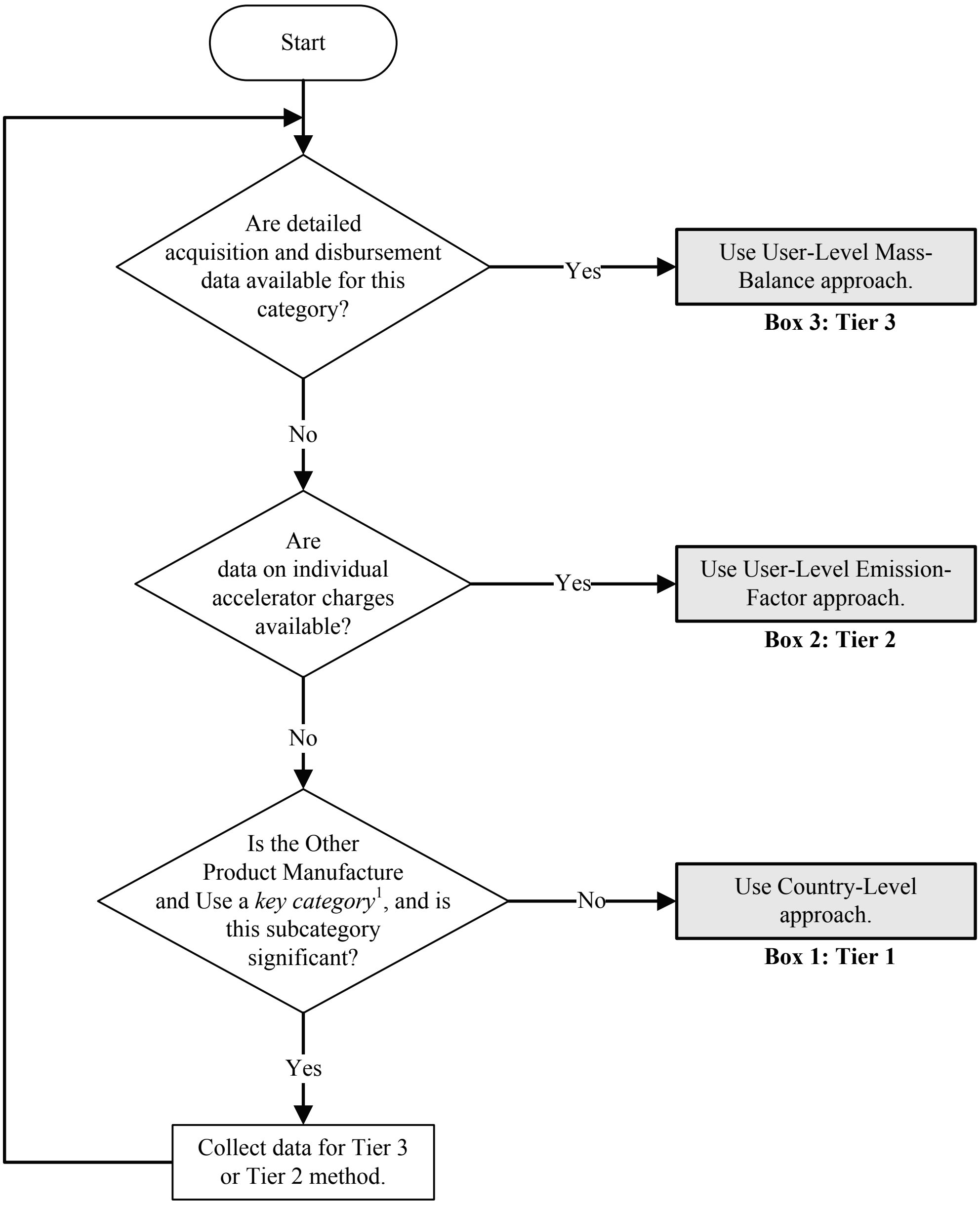
*Net Increase in Accelerator Charge* = $SF_6$ Charge of New Components – $SF_6$ Charge of Retiring Components

## $SF_6$ EMISSIONS FROM INDUSTRIAL AND MEDICAL PARTICLE ACCELERATORS

$SF_6$ is used as an insulating gas in two types of industrial particle accelerators (low and high voltage) and also in medical (cancer therapy) particle accelerators, as is the case for university and research particle accelerators. However, the emission and charge factors for industrial and medical particle accelerators are different from those of university and research accelerators, as discussed below.

Global banked capacity for industrial particle accelerators is roughly estimated to be 500 tonnes with annual $SF_6$ emissions of 35 tonnes. Global banked capacity for medical (radiotherapy) particle accelerators is roughly estimated to be less than 5 tonnes with annual $SF_6$ emissions of less than 5 tonnes. (Schwarz, 2005).

**Figure 8.4 Decision tree for industrial and medical particle accelerators**



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 1 method – country-level method

In cases where individual user accelerator charge data is unavailable, one extremely rough method involves determining the total number of particle accelerators by process description in the country and using factors to determine the country level annual emission rate as noted in Equation 8.18. For this Tier 1 method, the only data that requires collection is the total number of particle accelerators which contain $SF_6$ by process description in the given country.

**EQUATION 8.18**
**INDUSTRIAL/MEDICAL ACCELERATOR EMISSIONS (COUNTRY-LEVEL)**

Emissions = (Number of particle accelerators that use $SF_6$ by process description in the country) • ($SF_6$ Charge Factor, kg) • ($SF_6$ applicable particle accelerator Emission Factor)

Where:

*Number of particle accelerators by type in the country* = The total number of particle accelerators by type (industrial high voltage, industrial low voltage and radiotherapy) that use $SF_6$ in the country, 1, 2, etc. (Only count particle accelerators that use $SF_6$. This differs for the Tier 1 calculation for university and research particle accelerators)

*$SF_6$ Charge Factor* = The average $SF_6$ charge in a particle accelerator by process description as noted below.

*$SF_6$ particle accelerator Emission Factor* = The average annual $SF_6$ particle accelerator emission rate as a fraction of the total charge by process description.

**TABLE 8.9**
**AVERAGE $SF_6$ CHARGE IN A PARTICLE ACCELERATOR BY PROCESS DESCRIPTION**

| Process Description | $SF_6$ Charge Factor, kg |
|---|---|
| Industrial Particle Accelerators – high voltage (0.3-23 MV) | 1300 |
| Industrial Particle Accelerators –low voltage (<0.3 MV) | 115 |
| Medical (Radiotherapy) | 0.5[a] |

[a] This is the average of values ranging from 0.05 kg to over 0.8 kg, depending on model and manufacturer.

Source: Schwarz (2005)

### Tier 2 method – user-level emission-factor approach

If data on the quantity of $SF_6$ contained within each industry and medical accelerator are available, use the Tier 2 method for university and research facilities; however, multiply the emission factor for each process description provided below by the total, country-specific $SF_6$ charge for that process description.

**TABLE 8.10**
**EMISSION FACTOR FOR EACH PROCESS DESCRIPTION,**
**($SF_6$ EMISSIONS FROM INDUSTRIAL AND MEDICAL PARTICLE ACCELERATORS)**

| Process Description | Emission Factor, kg /kg $SF_6$ charge |
|---|---|
| Industrial Particle Accelerators – high voltage (0.3-23 MV) | 0.07 |
| Industrial Particle Accelerators – low voltage (<0.3 MV) | 0.013 |
| Medical (Radiotherapy) | 2.0[a] |

[a] This emission factor is the average of values ranging from 1 kg to 10 kg per kg charge, depending on model, manufacturer, and service intervals.

Source: Schwarz (2005)

### Tier 3 method – user-level mass-balance method

To calculate $SF_6$ emissions from industrial and medical particle accelerators, use the same Tier 3 method as the university and research facilities. The customer service organisations for manufacturers and distributors of the equipment are likely to have information on equipment stocks, imports, and exports, and on the quantities of $SF_6$ used to fill and refill the equipment.

## EMISSIONS FROM OTHER APPLICATIONS OF $SF_6$ AND PFCs

It is *good practice to* contact all gas producers/distributors to identify $SF_6$ and PFC users and to investigate the gas consumption of source categories other than those mentioned above. The key difference among the applications discussed below is the typical delay between the purchase of the $SF_6$ or PFC and the release of the chemical. In some cases (e.g., $SF_6$ used in sound-proof glazing, PFCs used as heat transfer fluids), the chemical is fairly well contained during the life of the equipment or product, and most emissions are associated with the manufacture and disposal of the product. In these cases, the delay between the purchase of the chemical and its final emission depends on the lifetime of the product, ranging from three years for tyres and sport-shoes to 25 years for sound-proof glazing. In other cases (e.g., use of $SF_6$ and PFCs as tracers or in medical applications), the chemical is fully emitted within a year of its purchase. If, as a result of an initial survey, applications with distinctive delayed emissions appear significant, then *good practice* is to use a source category-specific emission calculation, taking into account the delay in emissions.

### Adiabatic uses

Adiabatic uses of $SF_6$ and some PFCs exploit the low permeability of these gases through rubber. Historically, $SF_6$ has been the dominant gas in these applications; however, PFCs with similar molecular weights (such as $C_3F_8$) have recently been used as well. Applications with a delay period of 3 years include or car tyres, sport shoe soles and tennis balls (Schwarz *et al.*, 1996). For applications with emissions that are delayed by three years, the following formula can be used.

**EQUATION 8.19**
**ADIABATIC PROPERTY APPLICATIONS**

$$\text{Emissions in year } t = \text{Sales in year } (t-3)$$

### Sound-proof glazing

*Double-glazed sound-proof windows*: Approximately one-third of the total amount of $SF_6$ purchased is released during assembly (i.e., filling of the double glass window) (Schwarz/Leisewitz, 1999). For the stock of gas remaining inside the window (capacity), an annual leakage rate of 1 percent is assumed (including glass breakage). Thus, about 75 percent of initial stock remains at the end of its 25-year lifetime. The application of $SF_6$ in windows began in 1975, so disposal is only beginning to occur. Emissions from this source sub-category should be calculated using Equations 8.20 to 8.22:

**EQUATION 8.20**
**DOUBLE-GLAZED WINDOWS: ASSEMBLY**

$$\text{Assembly Emissions in year } t = 0.33 \bullet SF_6 \text{ purchased to fill windows assembled in year } t$$

**EQUATION 8.21**
**DOUBLE-GLAZED WINDOWS: USE**

$$\text{Leakage Emissions in year } t = 0.01 \bullet \text{Capacity of Existing Windows in year } t$$

**EQUATION 8.22**
**DOUBLE-GLAZED WINDOWS: DISPOSAL**

$$\text{Disposal Emissions in year } t = \text{Amount Left in Window at End of Lifetime in year } t \bullet (1 - \text{Recovery Factor})$$

Unless country-specific data are available, a default recovery factor value of zero should be assumed in Equation 8.22. If no specific information is available for these sub-source categories, *good practice* is to treat them as prompt emissions.

### PFCs used as heat transfer fluids in consumer and commercial applications

PFCs are used as heat transfer fluids in a number of high-power-density commercial and consumer electronic applications. Commercial applications include cooling for supercomputer, telecommunication, and airport radar systems, as well as drive units (rectifiers) on high-speed trains (Burton, 2006). These applications consume much smaller volumes of liquid PFCs than electronics manufacturing, but are believed to be significant among 'niche' applications. Consumer applications include cooling kits for desktop computers that are operated at high voltages to increase their processing speed. The specific PFCs used in these applications are believed to be similar to those identified as heat transfer fluids in electronics manufacturing in Chapter 6. In all of these applications, the liquid PFCs are used in closed modules, indicating that most emissions occur during the manufacture, maintenance, and disposal of the product or equipment. Thus, if inventory compilers can acquire information on emission rates during the manufacture, maintenance, and disposal of the equipment, along with the quantities of equipment manufactured, used, and disposed each year, they can use the Tier 2 or Tier 3 method for electrical equipment to estimate emissions. For applications with different emissions profiles (e.g., prompt emissions), the appropriate equation from Section 8.2 may be used.

### PFCs used in cosmetic and medical applications

PFCs with relatively large molecular weights (e.g., $C_{10}F_{18}$) are used in cosmetic and medical applications, exploiting their ability to carry oxygen to living tissue (May, 2006). Cosmetic applications include anti-wrinkle creams and are estimated to consume fairly small amounts. Current and potential medical applications include storage of pancreatic tissue for transplants (using the 'two-layer method'), eye surgery (to repair retinal tears), pneumonectomy (lung therapy and diagnosis), use as a contrast agent in ultrasonic and MRI examinations, blood extension, wound healing, and treatment of diseases of the middle ear. All but the first two medical applications involve only small quantities and/or are at the research stage. Storage of pancreatic tissue is a small but growing application. Emissions from medical uses are uncertain but are believed to be small.

In all of these applications, the PFC is believed to be emitted into the atmosphere within one year of its purchase. Thus, emissions from these sources can be estimated using Equation 8.23 for prompt emissions.

### Any other uses of $SF_6$ and PFCs

Other applications for $SF_6$ and PFCs that are not specifically addressed above include their use as tracers (in leak detection, indoor and outdoor tracking of air-masses, and oil recovery[6]) and use of $SF_6$ in the production of optical cables (for fluorodoping of glass fibres[7]). Often the gases or liquids are emitted within one year of purchase. In this case, *good practice* in calculating $SF_6$ and PFC emissions from these 'prompt' emissive applications is to use the following formula**:**

**EQUATION 8.23**
**PROMPT EMISSIONS**

$$\text{Emissions in year } t = (0.5 \bullet \text{Amount Sold in year } t) + (0.5 \bullet \text{Amount Sold in year } t-1)$$

This equation is similar to the equation for prompt ODS Substitute applications (e.g., aerosols and solvents) addressed in Chapter 7 of this volume. The equation covers more than one year because both sales and emissions are assumed to be continuous over the year; that is, chemical sold in the middle of year t-1 is not fully emitted until the middle of year t.

## 8.3.2.2 CHOICE OF EMISSION FACTORS

For 'other' source categories of $SF_6$ and PFCs that contribute substantially to a country's $SF_6$ and PFCs emissions, countries are encouraged to develop country-specific emission factors based on occasional surveys of representative subsets of sources. It is *good practice* to clearly document such emission factors. Default emission factors are provided above for AWACS, accelerators, prompt emissive applications and adiabatic applications, including windows.

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[6] D. Vlachogiannis *et al*. (2005). This paper indicated that some fraction of injected PFCs and $SF_6$ was destroyed during fuel combustion, but the magnitude of this fraction (compared to the fraction of injected chemical that escaped before combustion) was unclear.

[7] See further information on this application in Schwarz (2005).

### 8.3.2.3 CHOICE OF ACTIVITY DATA

The activity data for these sub-source categories should be consistent with the data used in the calculation of $SF_6$ emissions from other source categories (e.g., electrical equipment) to ensure that the estimate is complete and there is no double counting. For medical linear accelerators, the customer service organisations for manufacturers and distributors of the equipment are likely to have information on equipment stocks, imports, and exports, and on the quantities of $SF_6$ used to fill and refill the equipment. Guidance regarding possible sources of activity data for other sources is provided under the method for each source category.

### 8.3.2.4 COMPLETENESS

Data per application on import, export and consumption from national $SF_6$ and PFC producers and distributors will suffice, provided that (i) all $SF_6$ and PFC producers and distributors are identified, (ii) domestic consumers only purchase $SF_6$ and PFCs from national suppliers, and (iii) imports and exports in products (e.g., sport attributes) are negligible. It is *good practice* to check regularly for additional distributors to ensure that no gas is imported directly (in bulk) by end-users and that identified products containing $SF_6$ or PFCs are not imported in sizeable amounts.

Alternatively, if top-down data on chemical consumption is not available, countries may use information on the number of accelerators, AWACS, windows, etc. in use in the country, applying the emission factors that are supplied in the method for each source category.

### 8.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

For base year estimates, data may be needed for a few years prior to the base year; one year for prompt emissions and more years for delayed emission applications. It is *good practice* to calculate emissions using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, it is *good practice* to recalculate according to the guidance provided in Volume 1, Chapter 5.

## 8.3.3 Uncertainty assessment

If the survey of domestic sales per application by national gas producers and distributors is complete, then the accuracy of annual apparent consumption data will be high. The uncertainty in emissions estimates will be similarly small when the uses are all prompt emissions. In case of delayed emission applications, the uncertainties are:

- Default delay times in adiabatic property applications: 3±1 year;
- Defaults for soundproof windows: 50±10% filling emissions and 1±0.5% leakage/breach emissions.

If gas consumption data are not available, uncertainties regarding the numbers and usage of accelerators and AWACS, etc. become important.

- For accelerators, the total $SF_6$ charge and leak rate determine emissions and associated uncertainty
- For use of $SF_6$ in AWACS, the number of sorties per plane has a significant impact on emissions and uncertainty.

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

### 8.3.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

Additional procedures specific to other sources of $SF_6$ are outlined below:

#### Comparison of emissions estimates using different approaches

Inventory compilers should compare total national potential $SF_6$ and PFC emissions (minus the amount allocated to the source categories as per chapters 3.10, 4, 6 and 8.2) to the estimated $SF_6$ and PFC emissions from other uses. These adjusted potential national emissions can be used as an upper bound on emissions.

#### Activity data check

Inventory compilers should compare the activity data submitted by different producers and distributors, and, adjusting for relative size or capacity of the companies, identify significant outliers. Any outliers should be investigated to determine if the differences can be explained or if there is an error in the reported activity.

#### Comparison of emission rates with those of other countries

Inventory compilers should compare the emissions from other $SF_6$ and PFC end-uses included in the national inventory with information submitted by other similar countries. For each source, emissions per capita or per unit of GDP should be compared with the corresponding emission rates of other countries. If national figures appear to be relatively very high or very small, a justification should be provided.

### 8.3.4.2 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, Section 6.11. 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.

For transparency, it is *good practice* to report both actual and potential emissions from the source category 'other uses' separately from other $SF_6$ and PFC emissions. In addition, providing information on the specific applications that are included in this source category is useful for comparing (estimates of) national practices with other countries, regionally, or globally. In addition, the methods applied and references should be documented. For delayed emission sub-source categories, annual emissions, delay times and emission factors per type of sub-source category should be reported.

# 8.4 $N_2O$ FROM PRODUCT USES

## 8.4.1 Introduction

Evaporative emissions of nitrous oxide ($N_2O$) can arise from various types of product use, including:

- Medical applications (anaesthetic use, analgesic use and veterinary use);
- Use as a propellant in aerosol products, primarily in food industry (pressure-packaged whipped cream, etc);
- Oxidising agent and etchant used in semiconductor manufacturing;
- Oxidising agent used, with acetylene, in atomic absorption spectrometry;
- Production of sodium azide, which is used to inflate airbags;
- Fuel oxidant in auto racing; and
- Oxidising agent in blowtorches used by jewelers and others.

In general, medical applications and use as a propellant in aerosol products are likely to be larger sources than others. It is *good practice* to estimate and report $N_2O$ emissions from these sources. Inventory compilers are encouraged to estimate and report $N_2O$ emissions from the other sources as well, if data are available.

### MEDICAL APPLICATIONS

#### Anaesthetic use of $N_2O$

$N_2O$ for anaesthetic use is supplied in steel cylinders containing a minimum of 98 percent $N_2O$. $N_2O$ is used during anaesthesia for two reasons: a) as an anaesthetic and analgesic and as b) a carrier gas for volatile fluorinated hydrocarbon anaesthetics such as isoflurane, sevoflurane and desflurane. The anaesthetic effect of $N_2O$ is additive to that of the fluorinated hydrocarbon agents.

Not all anaesthetics require the use of $N_2O$, and the use of $N_2O$ is contra-indicated in a small number of medical situations. The carrier gas during anaesthesia may be either $N_2O$ and oxygen or a mixture of air and oxygen, in which case $N_2O$ is avoided.

Inhaled anaesthetic agents are increasingly administered via breathing systems which re-circulate the exhaled breath of the patient through a canister of carbon dioxide absorbent before directing the gases back to the patient. Using this method the flow of carrier gas can be reduced considerably after the first few minutes of anaesthesia when uptake by the patient is high. This technique is known as Low Flow Anaesthesia. Low Flow Anaesthesia has the advantage of reducing emissions as well as reducing cost.

Some anaesthetics may avoid both $N_2O$ and the fluorinated hydrocarbon agents completely by employing a technique in which an anaesthetic drug is continuously infused into a vein throughout the surgical procedure. This technique is known as Total Intravenous Anaesthesia.

#### Analgesic use of $N_2O$

Inhaled $N_2O$ is used to provide pain relief in certain situations. For example, it is supplied in steel cylinders containing pre-mixed $N_2O$ 50 percent and oxygen 50 percent as premixed nitrous oxide and oxygen mixtures in the UK. Premixed nitrous oxide and oxygen mixtures are used to provide pain relief in childbirth, and for painful procedures of short duration, e.g. for dressings to be changed in burns patients. Premixed nitrous oxide and oxygen mixtures are not used in countries with a very cold climate because the mixture can separate if the cylinders are stored below –6 degrees centigrade, with the consequent risk of administering pure nitrous oxide to patients with no oxygen.

#### Veterinary use of $N_2O$

$N_2O$ is also used during animal anaesthesia. Administration methods are similar to those used in human anaesthesia.

### USE AS A PROPELLANT IN AEROSOL PRODUCTS, PRIMARILY IN FOOD INDUSTRY

$N_2O$ is also used as a propellant in aerosol products primarily in food industry. Typical usage is to make whipped cream, where cartridges filled with $N_2O$ are used to blow the cream into foam.

# 8.4.2 Methodological issues

## 8.4.2.1 CHOICE OF METHOD

It is *good practice* to estimate $N_2O$ emissions from data of quantity of $N_2O$ supplied that are obtained from manufacturers and distributors of $N_2O$ products according to Equation 8.24 below. There will be a time delay between manufacture, delivery and use but this is probably small in the case of medical applications because hospitals normally receive frequent deliveries to avoid maintaining large stores. Therefore, it is reasonable to assume that the $N_2O$ products supplied will be used in one year. In the case of use as a propellant in aerosol products, there is no reliable data that prove there is a significant time delay between manufacture, delivery and use. Such being the case, it is considered practical to assume that the $N_2O$ products supplied will be used in one year. Equation 8.24 covers more than one year because both supply and use are assumed to be continuous over the year; that is, $N_2O$ supplied in the middle of year t–1 is not fully used and emitted until the middle of year t.

Different tiers could not be defined for this source category, because there is no other reliable estimation method. For example, in the case of medical applications, estimations from numbers of anaesthetics given, number of surgical beds or hours of anaesthesia could be considered but these methods are likely to be inaccurate. (See Section 8.4.2.3, Choice of Activity Data.)

**EQUATION 8.24**
**$N_2O$ EMISSIONS FROM OTHER PRODUCT USES**

$$E_{N2O}(t) = \sum_i \{ [0.5 \bullet A_i(t) + 0.5 \bullet A_i(t-1)] \bullet EF_i \}$$

Where:

$E_{N2O}(t)$ = emissions of $N_2O$ in year *t*, tonnes

$A_i$ (t) = total quantity of $N_2O$ supplied in year *t* in application type *i*, tonnes

$A_i$ (t-1) = total quantity of $N_2O$ supplied in year *t*-1 in application type *i*, tonnes

$EF_i$ = emission factor for application type *i*, fraction

## 8.4.2.2 CHOICE OF EMISSION FACTORS

### MEDICAL APPLICATIONS

It is assumed that none of the administered $N_2O$ is chemically changed by the body, and all is returned to the atmosphere. It is reasonable to assume an emission factor of 1.0.

### USE AS A PROPELLANT IN AEROSOL PRODUCTS, PRIMARILY IN FOOD INDUSTRY

For $N_2O$ used as a propellant in pressurized and aerosol food products, none of the $N_2O$ is reacted during the process and all of the $N_2O$ is emitted to the atmosphere resulting in an emissions factor of 1.0 for this source.

### OTHERS

For the other types of product use, it may not be appropriate to assume an emissions factor of 1.0. In case the inventory compilers estimate and report $N_2O$ emissions arising from product use other than medical applications and use as a propellant in aerosol products, they are encouraged to derive reasonable emission factors for that source from literature or measurements.

### 8.4.2.3 CHOICE OF ACTIVITY DATA

#### MEDICAL APPLICATIONS

Total quantity of $N_2O$ supplied by application type should be obtained from manufacturers and distributors of $N_2O$ products. Alternatively, for medical applications, quantity of $N_2O$ usage may be obtained from the pharmacy department in individual hospitals that usually have records of the number and capacity of nitrous oxide cylinders purchased per annum.

The duration of hospital stay following a surgical procedure varies considerably from less than one day to several days or weeks. Estimates of the number of anaesthetics administered which are calculated from the surgical bed occupancy are likely to be inaccurate.

Because $N_2O$ is used in only a proportion of anaesthetics its use cannot be estimated reliably from the number of anaesthetics given.

The flow of $N_2O$ (L/min) delivered by the anaesthetic apparatus may be varied by the anaesthetist during the course of surgery, typically between zero and 6 L/min. Because of this considerable variability, estimates of consumption based on duration of anaesthesia are likely to be inaccurate.

The proportion of anaesthetics in which $N_2O$ is used varies between countries and between individual anaesthetists in a given country. Over the recent years there appears to be a general reduction in the proportion of anaesthetics which incorporate $N_2O$ but data are sparse.

#### USE AS A PROPELLANT IN AEROSOL PRODUCTS, PRIMARILY IN FOOD INDUSTRY

Total quantity of $N_2O$ supplied by application type should be obtained from manufacturers and distributors of $N_2O$ products.

### 8.4.2.4 COMPLETENESS

Data per application on import, export and consumption from national $N_2O$ manufacturers and distributors will suffice, provided that (i) all $N_2O$ manufacturers and distributors are identified, (ii) domestic consumers only purchase $N_2O$ from national suppliers, and (iii) imports and exports in products (e.g. sport attributes) are negligible. It is *good practice* to check regularly for additional distributors to ensure that no $N_2O$ is imported directly (in bulk) by end users and that identified products containing $N_2O$ are not imported in sizeable amounts.

### 8.4.2.5 DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to calculate emissions of $N_2O$ using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, it is *good practice* to recalculate according to the guidance provided in Volume 1, Chapter 5.

## 8.4.3 Uncertainty assessment

### 8.4.3.1 EMISSION FACTOR UNCERTAINTIES

In the published literature it is widely assumed that none of the $N_2O$ inhaled by a patient during anaesthesia is metabolised. $N_2O$ is taken up continuously from the lungs as dissolved $N_2O$ in blood. The portion which is not taken up is exhaled in the next breath. Uptake by the patient is high initially and falls progressively in a near-exponential fashion over time. It is reasonable to assume that all the administered $N_2O$ is eventually returned to the atmosphere and the emission factor is 1.0. This is a pragmatic assumption because there are no reliable data. Any error in the emission factor is likely to be extremely small in comparison with other uncertainties.

Also in the case of use as a propellant in aerosol products, $N_2O$ is not likely to be reacted during the process. Therefore, it is a pragmatic assumption that emission factor is 1.0, and any error in the emission factor is likely to be extremely small in comparison with other uncertainties.

In case the inventory compilers estimate and report $N_2O$ emissions arising from product use other than medical applications and use as a propellant in aerosol products, emission factor uncertainties may need to be carefully considered.

### 8.4.3.2 ACTIVITY DATA UNCERTAINTIES

The uncertainties in quantity of $N_2O$ supplied by application type obtained from manufacturers and distributors of $N_2O$ products may vary widely from country to country. If the uncertainty estimates are obtainable from the manufacturers and distributors, those estimates should be used. Otherwise, activity data uncertainties should be estimated by expert judgement.

## 8.4.4 Quality Assurance/Quality Control (QA/QC), 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. 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.

For transparency, providing information on the specific applications that are included in this source category is useful for comparing (estimates of) national practices with other countries, regionally, or globally. In addition, the methods applied and references should be documented.

It is *good practice* to conduct quality control checks and quality assurance procedures as outlined in Volume 1, Chapter 6. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

Additional procedures specific to this source category are outlined below:

#### Activity data check

Inventory compilers should compare the activity data submitted by different manufacturers and distributors of $N_2O$, and, adjusting for relative size or capacity of the companies, to identify significant outliers. Any outliers should be investigated to determine if the differences can be explained or if there is an error in the reported activity.

#### Comparison of emissions with other countries

Inventory compilers should compare the $N_2O$ emissions from types of product use included in the national inventory with information submitted by other similar countries. For each source, emissions per capita or per unit of GDP with other countries should be compared. If national figures appear to be relatively very high or very small, a justification should be provided.

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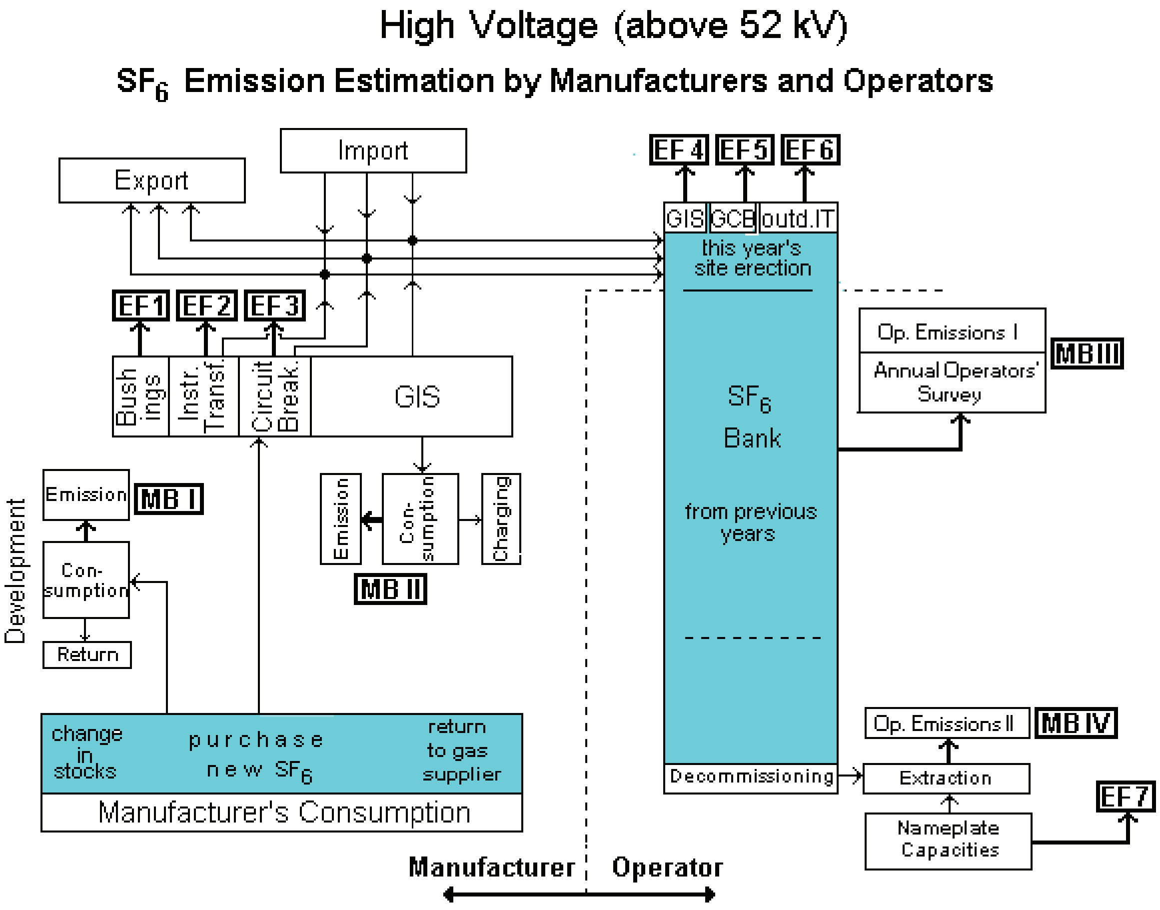
# Annex 8A Examples of Tier 3 national $SF_6$ inventory systems

Figures 8A.1 and 8A.2 illustrate the Tier 3 Hybrid approach as it is currently applied in Germany for closed pressure (high voltage) and sealed-pressure (medium voltage) equipment (Schwarz, 2006). In the diagram, ‘MB’ indicates processes or life cycle stages for which the mass-balance approach is used, while ‘EF’ indicates processes and life cycle stages for which emission factors are used. For example, in manufacturing, the mass-balance approach is used to estimate emissions from the filling of gas-insulated switchgear, while emission factors are used to estimate emissions from the filling of bushings, instrument transformers, and circuit breakers. In Germany, the latter processes have emission rates of 1 percent or less, making emissions difficult to measure using mass-balance methods. Note that this diagram is intended to be an example only; when implementing the Tier 3 approach, countries are encouraged to choose approaches and emission factors appropriate to their national circumstances.

**Figure 8A.1 Example of Tier 3 approach: Germany, High-Voltage equipment**

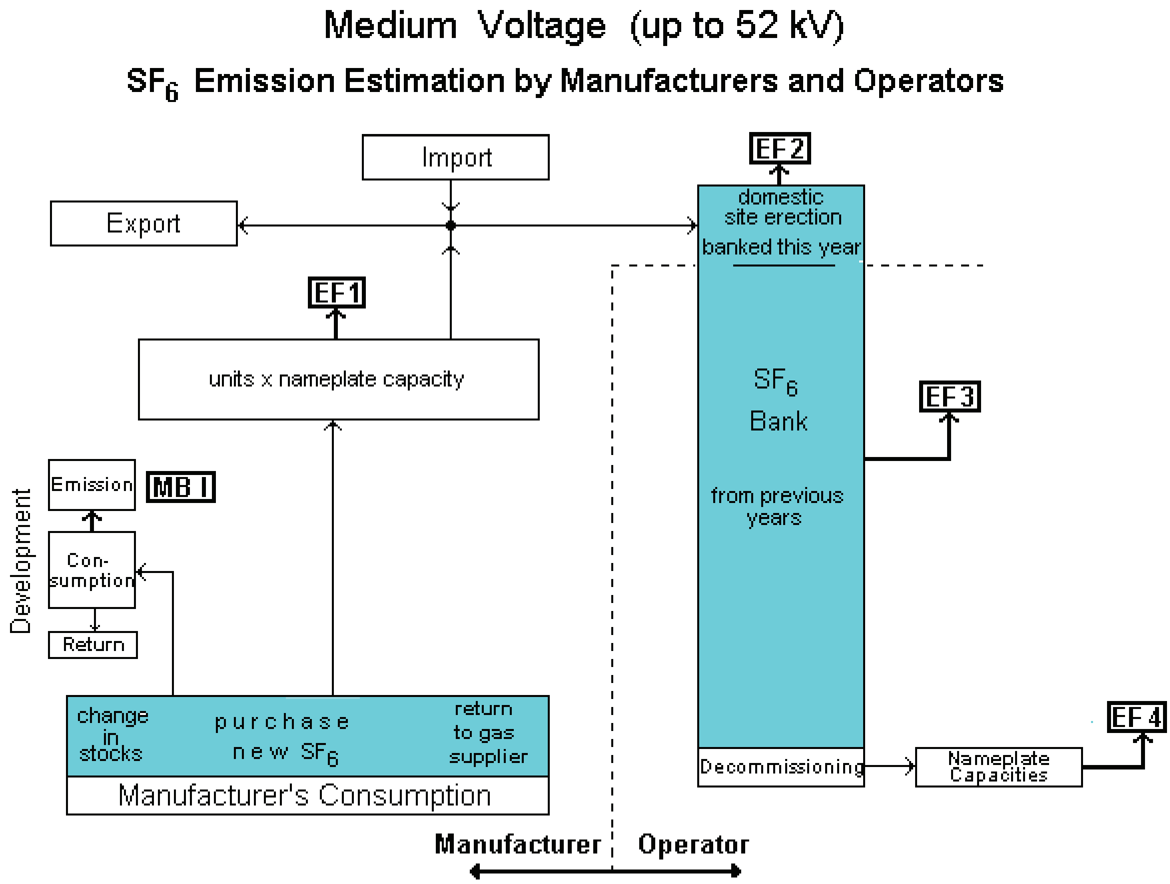


| Legend for Emissions Estimation in HV | | |
|---|---|---|
| **Mass Balance Approach** | | |
| **Symbol** | Equation | |
| **MB I** | Development Emissions = Consumption for Developing minus Return from Development Department | |
| **MB II** | GIS Charging Emissions = Consumption for Charging minus Charge (nameplate capacities); also applicable to Gas insulated Lines (GIL's) | |
| **MB III** | Operating Emissions I = Annually surveyed topping up by equipment operators | |
| **MB IV** | Operating Emissions II = Nameplate capacity of decommissioned equipment minus gas recovered from this equipment | |
| **Emission Factor (EF) Approach** | | |
| **Symbol** | **Kind of Emission Factor (EF)** | **Multiplied by** |
| **EF 1** | Factory Filling EF Bushings* | NC** of bushings filled in factory |
| **EF 2** | Factory Filling EF Outdoor Instrument Transformers (ITs) | NC of ITs filled in factory |
| **EF 3** | Factory Filling EF Gas Circuit Breakers (GCBs) | NC of GCBs filled in factory |
| **EF 4** | Site Erection EF GIS and GIL | NC of GIS and GIL filled on site |
| **EF 5** | Site Erection EF GCBs | NC of GCBs filled on site |
| **EF 6** | Site Erection EF Outdoor ITs | NC of Outdoor ITs filled on site |
| **EF 7** | Disposal EF | NC of decommissioned equipment |

* Bushings are treated as integral parts of GIS as of Site erection.

**NC = Total nameplate capacity of equipment undergoing a given process

**Figure 8A.2** **Example of Tier 3 approach: Germany, Medium-Voltage equipment**



| **Legend for Emissions Estimation in MV** | | |
|---|---|---|
| **Mass Balance Approach** | | |
| **Symbol** | Equation | |
| **MB I** | Development Emissions = Consumption for Developing minus Return from Development Department* | |
| **Emission Factor (EF) Approach** | | |
| **Symbol** | **Kind of Emission Factor (EF)** | **Multiplied by** |
| **EF 1** | Factory Filling EF | NC** filled in factory |
| **EF 2** | Site Erection EF | NC*** filled on site |
| **EF 3** | Operating EF | NC of operating equipment (total bank from this and previous years) |
| **EF 4** | Disposal EF | NC decommissioned |

* This mass balance approach also applies to manufacturing of Cast Resin Instrument Transformers (ITs).

**NC = Total nameplate capacity of equipment undergoing a given process.

*** In countries where MV equipment is already gas-filled in factories, site erection emissions are negligible.

# ANNEX 1

# WORKSHEETS

# Contents

Annex 1 Worksheets

2A Mineral Industry ........ A1.4
- 2A1 Cement Production ........ A1.4
- 2A2 Lime Production ........ A1.4
- 2A3 Glass Production ........ A1.5
- 2A4 Other Process Uses of Carbonates ........ A1.5

2B Chemical Industry ........ A1.6
- 2B1 Ammonia Production ........ A1.6
- 2B2 Nitric Acid Production ........ A1.6
- 2B3 Adipic Acid Production ........ A1.7
- 2B4 Caprolactam, Glyoxal and Glyoxylic Acid Production ........ A1.7
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- 2C2 Ferroalloys Production ........ A1.18
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- 2C4 Magnesium Production ........ A1.20
- 2C5 Lead Production ........ A1.21
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- 2D2 Paraffin Wax Use ........ A1.22

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- 2F2 Foam Blowing Agents ........ A1.26
- 2F3 Fire Protection ........ A1.27
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2F5 Solvents ........ A1.28
2F6 Other Applications ........ A1.28
2G Other Product Manufacture and Use ........ A1.29
2G1 Electrical Equipment ........ A1.29
2G2 $SF_6$ and PFCs from Other Product Uses ........ A1.31
2G3 $N_2O$ from Product Uses ........ A1.34

The worksheets in this annex are designed to enable users to perform at least the Tier 1 (and in some cases Tier 2) emission estimation for each category under IPPU Sector.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Mineral Industry - Cement Production** |
| **Category Code** | **2A1** |
| **Sheet** | **1 of 2** |

| | | | |
|---|---|---|---|
| Individual Type of Cement Produced[1] | A | B | C |
| | Mass of Individual Type of Cement Produced | Clinker Fraction in Cement | Mass of Clinker in the Individual Type of Cement Produced |
| | (tonne) | (fraction) | (tonne) |
| | | | $C = A * B$ |
| | | | |
| | | | |
| Total | | | |

1) Insert additional rows if more than two types of cement are produced.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Mineral Industry - Cement Production** |
| **Category Code** | **2A1** |
| **Sheet** | **2 of 2** |

| D | E | F | G | H | I |
|---|---|---|---|---|---|
| Imports for Consumption of Clinker | Exports of Clinker | Mass of Clinker Produced in the Country | Emission Factor for the Clinker in the Particular Cement | $CO_2$ Emissions | $CO_2$ Emissions |
| (tonne) | (tonne) | (tonne) | (tonne $CO_2$/ tonne clinker) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | $F = C – D + E$ | | $H = F * G$ | $I = H/10^3$ |
| | | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Mineral Industry - Lime Production** |
| **Category Code** | **2A2** |
| **Sheet** | **1 of 1** |

| | | | | |
|---|---|---|---|---|
| Type of Lime Produced[1, 2] | A | B | C | D |
| | Mass of Lime Produced | Emission Factor for Lime Production | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/ tonne lime) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | $C = A * B$ | $D = C/10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) Insert additional rows if more than two types of lime are produced.

2) When country-specific information on lime production by type is not available, apply the default emission factor to national level lime production data. (See Equation 2.8 in Chapter 2 of this volume.)

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Mineral Industry - Glass Production** | | | |
| **Category Code** | **2A3** | | | |
| **Sheet** | **1 of 1** | | | |
| | | | | |
| A | B | C | D | E |
| Total Glass Production | Emission Factor for Glass Production | Average Annual Cullet Ratio | $CO_2$ Emissions | $CO_2$ Emissions |
| (tonne) | (tonne $CO_2$/ tonne glass) | (fraction) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | D = A * B * (1 – C) | E = D/$10^3$ |
| | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Mineral Industry - Other Process Uses of Carbonates**[1)] | | | |
| **Category Code** | **2A4** | | | |
| **Sheet** | **1 of 1** | | | |
| | | | | |
| Type of Use | A | B | C | D |
| | Mass of Carbonate Consumed | Emission Factor for Carbonate Consumption[3), 4)] | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/ tonne carbonate) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = C/$10^3$ |
| Ceramics | | | | |
| Other Uses of Soda Ash | | | | |
| Non Metallurgical Magnesia Production | | | | |
| Other[2)] | | | | |

1) Limestone and other carbonate materials also are consumed in a variety of other industries not covered in Chapter 2 of Volume 3. Examples include carbonates used as fluxes and slagging agents in metals smelting and refining (e.g., iron and steel production and base metals such as copper), and as inputs to the chemical industry (e.g., fertiliser). The methods outlined here for estimating emissions from the use of carbonates are applicable to these other industries as well. It is *good practice* to allocate emissions from the use of limestone, dolomite and other carbonates to the industrial source category where they are emitted (e.g., iron and steel production).

2) This row should contain estimates of emissions that do not fit into any of the major sources presented in Table 2.7 in Chapter 2 of Volume 3. Insert additional rows, if necessary.

3) For the Tier 1 method, it is consistent with *good practice* for inventory compilers to assume that 85 percent of carbonates consumed are limestone and 15 percent of carbonates consumed are dolomite. For the Tier 1 method for soda ash use (Other Uses of Soda Ash), this default fraction (0.85:0.15) should not be applied, and the default value for sodium carbonate should be used. (For default emission factors for various carbonates, see Table 2.1 in Chapter 2 of Volume 3.

4) It is suggested that inventory compilers ensure that data on carbonates reflect pure carbonates and not carbonate rock. If data are only available on carbonate rock, a default purity of 95% can be assumed. For clays a default carbonate content of 10% can be assumed, if no other information is available.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Ammonia Production** |
| **Category Code** | **2B1** |
| **Sheet** | **1 of 2** |

| A | B | C | D | E |
|---|---|---|---|---|
| Amount of Ammonia Produced | Fuel Requirement for Ammonia Production | Carbon Content of Fuel | Carbon Oxidation Factor of Fuel | $CO_2$ Generated |
| (tonne) | (GJ/ tonne ammonia produced) | (kg C/GJ) | (fraction) | (kg $CO_2$) |
| | | | | E = (A * B * C * D) * 44/12 |
| | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Ammonia Production** |
| **Category Code** | **2B1** |
| **Sheet** | **2 of 2** |

| F | G | H | I |
|---|---|---|---|
| Amount of Urea Produced | $CO_2$ Recovered for Urea Production | $CO_2$ Emissions | $CO_2$ Emissions |
| (kg) | (kg $CO_2$) | (kg $CO_2$) | (Gg $CO_2$) |
| | G = F * 44/60 | H = E – G | $I = H/10^6$ |
| | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Nitric Acid Production** |
| **Category Code** | **2B2** |
| **Sheet** | **1 of 1** |

| A | B | C | D |
|---|---|---|---|
| Amount of Nitric Acid Production | Emission Factor | $N_2O$ Emissions | $N_2O$ Emissions |
| (tonne) | (kg $N_2O$/tonne nitric acid produced) | (kg) | (Gg) |
| | | C = A * B | $D = C/10^6$ |
| | | | |

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Chemical Industry - Adipic Acid Production** | | |
| **Category Code** | **2B3** | | |
| **Sheet** | **1 of 1** | | |
| | | | |
| A | B | C | D |
| Amount of Adipic Acid Production | Emission Factor | $N_2O$ Emissions | $N_2O$ Emissions |
| (tonne) | (kg $N_2O$/tonne adipic acid produced) | (kg) | (Gg) |
| | | C = A * B | D = C/$10^6$ |
| | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Caprolactam, Glyoxal and Glyoxylic Acid Production** | | | |
| **Category Code** | **2B4** | | | |
| **Sheet** | **1 of 1** | | | |
| | | | | |
| Chemical | A | B | C | D |
| | Amount of Chemical Production | Emission Factor | $N_2O$ Emissions | $N_2O$ Emissions |
| | (tonne) | (kg $N_2O$/tonne chemical produced) | (kg) | (Gg) |
| | | | C = A * B | D = C/$10^6$ |
| Caprolactam | | | | |
| Glyoxal | | | | |
| Glyoxylic Acid | | | | |
| Total | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Carbide Production** | | | |
| **Category Code** | **2B5** | | | |
| **Sheet** | **1 of 6 $CO_2$ Emissions (calculation based on raw material used)** | | | |
| | | | | |
| Type of Carbide Produced/ | A | B | C | D |
| | Raw Material (Petroleum Coke) Consumption | Emission Factor[1)] | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/tonne raw material used) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = C/$10^3$ |
| Silicon Carbide (SiC) | | | | |
| Calcium Carbide ($CaC_2$) | | | | |

1) The emission factor needs to be adjusted to account for the carbon contained in the product. See Section 3.6.2.1 of Volume 3.

Note: Inventory compilers should use either this sheet (1 of 6) or the next sheet (2 of 6), not both.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Carbide Production** |
| **Category Code** | **2B5** |
| **Sheet** | **2 of 6 $CO_2$ Emissions (calculation based on carbide produced)** |

| Type of Carbide Produced | A | B | C | D |
|---|---|---|---|---|
| | Carbide Produced | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/tonne carbide produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = C/$10^3$ |
| Silicon Carbide (SiC) | | | | |
| Calcium Carbide ($CaC_2$) | | | | |
| Note: Inventory compilers should use either this sheet (2 of 6) or the previous sheet (1 of 6), not both. | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Carbide Production** |
| **Category Code** | **2B5** |
| **Sheet** | **3 of 6 $CO_2$ Emissions from Use of $CaC_2$ in Acetylene Production** |

| A | B | C | D |
|---|---|---|---|
| Calcium Carbide Used in Acetylene Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| (tonne) | (tonne $CO_2$/tonne carbide used) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | C = A * B | D = C/$10^3$ |
| | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Carbide Production** |
| **Category Code** | **2B5** |
| **Sheet** | **4 of 6 $CO_2$ Emission (Total)** |

| A | B | C | D |
|---|---|---|---|
| $CO_2$ Emissions from Silicon Carbide (SiC) Production | $CO_2$ Emissions from Calcium Carbide ($CaC_2$) Production | $CO_2$ Emissions from Use of $CaC_2$ in Acetylene Production | Total $CO_2$ Emissions |
| (Gg $CO_2$) | (Gg $CO_2$) | (Gg $CO_2$) | (Gg $CO_2$) |
| From D in Sheet 1 of 6 or D in Sheet 2 of 6 | From D in Sheet 1 of 6 or D in Sheet 2 of 6 | From D in Sheet 3 of 6 | D = A + B+ C |
| | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Carbide Production** |
| **Category Code** | **2B5** |
| **Sheet** | **5 of 6 $CH_4$ Emissions from Silicon Carbide (SiC) Production (calculation based on raw material used)** |

| A | B | C | D |
|---|---|---|---|
| Raw Material (Petroleum Coke) Consumption | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| (tonne) | (kg $CH_4$/tonne raw material used) | (kg) | (Gg) |
| | | C = A * B | D = $C/10^6$ |
| | | | |

Note: Inventory compilers should use either this sheet (5 of 6) or the next sheet (6 of 6), not both.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Carbide Production** |
| **Category Code** | **2B5** |
| **Sheet** | **6 of 6 $CH_4$ Emissions from Silicon Carbide (SiC) Production (calculation based on carbide produced)** |

| A | B | C | D |
|---|---|---|---|
| Carbide Produced | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| (tonne) | (kg $CH_4$/tonne carbide produced) | (kg) | (Gg) |
| | | C = A * B | D = $C/10^6$ |
| | | | |

Note: Inventory compilers should use either this sheet (6 of 6) or the previous sheet (5 of 6), not both.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Chemical Industry - Titanium Dioxide Production** |
| **Category Code** | **2B6** |
| **Sheet** | **1 of 1** |

| Type of production | A | B | C | D |
|---|---|---|---|---|
| | Amount of Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/tonne produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = $C/10^3$ |
| Titanium Slag | | | | |
| Synthetic Rutile | | | | |
| Rutile $TiO_2$ | | | | |
| Total | | | | |

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Chemical Industry - Soda Ash Production** | | |
| **Category Code** | **2B7** | | |
| **Sheet** | **1 of 2 Natural Soda Ash (calculation based on trona used)** | | |
| | | | |
| A | B | C | D |
| Amount of Trona Utilised | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| (tonne) | (tonne $CO_2$/tonne trona utilized) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | C = A * B | D = C/$10^3$ |
| | | | |
| Note: Inventory compilers should use either this sheet (1 of 2) or the next sheet (2 of 2), not both. | | | |

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Chemical Industry -Soda Ash Production** | | |
| **Category Code** | **2B7** | | |
| **Sheet** | **2 of 2 Natural Soda Ash (calculation based on production)** | | |
| | | | |
| A | B | C | D |
| Amount of Natural Soda Ash Produced | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| (tonne) | (tonne $CO_2$/tonne natural soda ash produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | C = A * B | D = C/$10^3$ |
| | | | |
| Note: Inventory compilers should use either this sheet (2 of 2) or the previous sheet (1 of 2), not both. | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **1 of 12 $CO_2$ Emissions from Methanol Production** | | | |
| | | | | |
| Type of Process/Type of Feedstock[1), 2)] | A | B | C | D |
| | Amount of Methanol Produced | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/tonne methanol produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = C/$10^3$ |
| Type of Process = [ ] (please specify) | | | | |
| Feedstock = [ ] (Please specify) | | | | |
| Type of Process = [ ] (please specify) | | | | |
| Feedstock = [ ] (Please specify) | | | | |
| Total | ▨ | ▨ | | |

1) For details of process types and feedstock types, see Table 3.12 in Chapter 3 of Volume 3. For the default process type and the default feedstock, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | |
| **Category Code** | **2B8** | | |
| **Sheet** | **2 of 12 $CH_4$ Emissions from Methanol Production** | | |
| | | | |
| A | B | C | D |
| Amount of Methanol Produced | Emission Factor | $CH_4$ Emission | $CH_4$ Emission |
| (tonne) | (kg $CH_4$/tonne methanol produced) | (kg) | (Gg) |
| | | C = A * B | D = C/$10^6$ |
| | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | | |
| **Category Code** | **2B8** | | | | |
| **Sheet** | **3 of 12 $CO_2$ Emissions from Ethylene Production** | | | | |
| | | | | | |
| Type of Feedstock[1), 2)] (please specify) | A | B | C | D | E |
| | Amount of Ethylene Produced | Emission Factor | Geographic Adjustment Factor[3)] | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne) | (tonne $CO_2$/tonne ethylene produced) | (%) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | | D = A * B * C/100 | E = D/$10^3$ |
| | | | | | |
| | | | | | |
| Total | | | | | |

1) For details of feedstock types, see Table 3.14 in Chapter 3 of Volume 3. For the default feedstock, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

3) For geographic adjustment factors, see Table 3.15 in Volume 3.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **4 of 12 $CH_4$ Emissions from Ethylene Production** | | | |
| | | | | |
| Type of Feedstock[1), 2)]<br>(please specify) | A | B | C | D |
| | Amount of Ethylene Produced | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| | (tonne) | (kg $CH_4$/tonne ethylene produced) | (kg) | (Gg) |
| | | | C = A * B | D = C/$10^6$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of feedstock types, see Table 3.14 in Chapter 3 of Volume 3. For the default feedstock, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **5 of 12 $CO_2$ Emissions from Ethylene Dichloride/Vinyl Chloride Monomer Production** | | | |
| | | | | |
| Type of Process1), 2) (please specify) | A | B | C | D |
| | Amount of Ethylene Dichloride (EDC) or Vinyl Chloride Monomer (VCM) Produced3) | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne EDC produced) or (tonne VCM produced) | (tonne $CO_2$/tonne EDC produced) or (tonne $CO_2$/tonne VCM produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = C/$10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.17 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

3) Inventory compilers should use either EDC production or VCM production (not both) as activity data.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **6 of 12 $CH_4$ Emissions from Ethylene Dichloride / Vinyl Chloride Monomer Production** | | | |
| | | | | |
| Type of Process1), 2) (please specify) | A | B | C | D |
| | Amount of Ethylene Dichloride (EDC) or Vinyl Chloride Monomer (VCM) Produced3) | Emission Factor | $CH_4$ Emission | $CH_4$ Emission |
| | (tonne EDC produced) or (tonne VCM produced) | (kg $CH_4$/tonne EDC produced) or (kg $CH_4$/tonne VCM produced) | (kg) | (Gg) |
| | | | C = A * B | D = C/$10^6$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Tables 3.11 and 3.19 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

3) Inventory compilers should use either EDC production or VCM production (not both) as activity data.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **7 of 12 $CO_2$ Emissions from Ethylene Oxide Production** | | | |
| Type of Process[1), 2)] (please specify) | A | B | C | D |
| | Amount of Ethylene Oxide Produced | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne ethylene oxide produced) | (tonne $CO_2$/tonne ethylene oxide produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | $D = C/10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.20 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **8 of 12 $CH_4$ Emissions from Ethylene Oxide Production** | | | |
| Type of Process[1), 2)] (please specify) | A | B | C | D |
| | Amount of Ethylene Oxide Produced | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| | (tonne ethylene oxide produced) | (kg $CH_4$/tonne ethylene oxide produced) | (kg) | (Gg) |
| | | | C = A * B | $D = C/10^6$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.21 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **9 of 12 $CO_2$ Emissions from Acrylonitrile Production** | | | |
| | | | | |
| Type of Process[1), 2)] (please specify) | A | B | C | D |
| | Amount of Acrylonitrile Produced | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne acrylonitrile produced) | (tonne $CO_2$/tonne acrylonitrile produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | $C = A * B$ | $D = C/10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.22 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **10 of 12 $CH_4$ Emissions from Acrylonitrile Production** | | | |
| | | | | |
| Type of Process[1), 2)] (please specify) | A | B | C | D |
| | Amount of Acrylonitrile Produced | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| | (tonne acrylonitrile produced) | (kg $CH_4$/tonne acrylonitrile produced) | (kg) | (Gg) |
| | | | $C = A * B$ | $D = C/10^6$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.22 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **11 of 12 $CO_2$ Emissions from Carbon Black Production** | | | |
| | | | | |
| Type of Process 1), 2) (please specify) | A | B | C | D |
| | Amount of Carbon Black Produced | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne carbon black produced) | (tonne $CO_2$/tonne carbon black produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | $C = A * B$ | $D = C/10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.23 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Petrochemical and Carbon Black Production** | | | |
| **Category Code** | **2B8** | | | |
| **Sheet** | **12 of 12 $CH_4$ Emissions from Carbon Black Production** | | | |
| | | | | |
| Type of Process 1), 2) (please specify) | A | B | C | D |
| | Amount of Carbon Black Produced (tonne carbon black produced) | Emission Factor (kg $CH_4$/tonne carbon black produced) | $CH_4$ Emissions (kg) | $CH_4$ Emissions (Gg) |
| | | | $C = A * B$ | $D = C/10^6$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 3.24 in Chapter 3 of Volume 3. For the default process type, see Table 3.11 in Chapter 3 of Volume 3.

2) Insert additional rows if necessary.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Chemical Industry - Fluorochemical Production** | | |
| **Category Code** | **2B9** | | |
| **Sheet** | **1 of 3 HFC-23 Emissions from HCFC-22 Production** | | |
| | | | |
| A | B | C | D |
| Amount of HCFC-22 Produced (kg) | Emission Factor (kg HFC-23/kg HCFC-22 produced) | HFC-23 Emissions (kg) | HFC-23 Emissions (Gg) |
| | | $C = A * B$ | $D = C/10^6$ |
| | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Fluorochemical Production** | | | |
| **Category Code** | **2B9** | | | |
| **Sheet** | **2 of 3 By-product Emissions from Production of Other Fluorinated Compounds** | | | |
| | | | | |
| Fluorinated Compound Emitted as By-product and Principal Fluorinated Compound Produced<br>(Please specify such as “xxx from yyy production”) 1) | A | B | C | D |
| | Amount of Principal Fluorinated Compound Produced | Byproduct Emission Factor 2) | Emissions | Emissions |
| | (kg) | (kg by-product gas emitted/kg F-compound produced) | (kg) | (Gg) |
| | | | C = A * B | $D = C/10^6$ |
| | | | | |
| | | | | |
| | | | | |

1) Insert additional rows if necessary.

2) For sources that are not *key categories*, fugitive and by-product emissions are considered the same and those emissions are calculated using the next sheet (3 of 3).

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Chemical Industry - Fluorochemical Production** | | | |
| **Category Code** | **2B9** | | | |
| **Sheet** | **3 of 3 Fugitive Emissions from Production of Other Fluorinated Compounds** | | | |
| | | | | |
| Fluorinated Compound Produced<br>(Please specify) 1) | A | B | C | D |
| | Amount of Fluorinated Compound Produced | Fugitive Emission Factor 2) | Emissions | Emissions |
| | (kg) | (kg fugitive gas emitted/kg F-compound produced) | (kg) | (Gg) |
| | | | C = A * B | $D = C/10^6$ |
| | | | | |
| | | | | |
| | | | | |

1) Insert additional rows if necessary.

2) For sources that are not *key categories*, fugitive and by-product emissions are considered the same. For Tier 1, in the absence of abatement measures, a default emission factor of 0.5 percent of production, not counting losses in transport and transfer of materials, is suggested for HFCs and PFCs,

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Iron and Steel Production** | | | |
| **Category Code** | **2C1** | | | |
| **Sheet** | **1 of 2 $CO_2$ Emissions** | | | |
| Type of Steelmaking Method, etc | A | B | C | D |
| | Amount of Steel or Iron Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne crude steel produced, pig iron, DRI, sinter or pellet) | (tonne $CO_2$/tonne production) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | D = $C/10^3$ |
| Basic Oxygen Furnace | | | | |
| Electric Arc Furnace | | | | |
| Open Hearth Furnace | | | | |
| Pig Iron Production (not converted into steel) | | | | |
| Direct Reduced Iron (DRI) Production | | | | |
| Sinter Production | | | | |
| Pellet Production | | | | |
| TOTAL | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Iron and Steel Production** | | | |
| **Category Code** | **2C1** | | | |
| **Sheet** | **2 of 2 $CH_4$ Emissions** | | | |
| Type of Production | A | B | C | D |
| | Amount of Production | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| | (tonne sinter, DRI or pig iron) | (kg $CH_4$/tonne production) | (kg) | (Gg) |
| | | | C = A * B | D = $C/10^6$ |
| Sinter Production | | | | |
| Direct Reduced Iron (DRI) Production | | | | |
| Pig Iron Production | | | | |
| TOTAL | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Ferroalloys Production** | | | |
| **Category Code** | **2C2** | | | |
| **Sheet** | **1 of 2 $CO_2$ Emissions** | | | |
| | | | | |
| Type of Ferroalloy[1), 2)]<br>(please specify) | A | B | C | D |
| | Amount of Ferroalloy Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne ferroalloy produced) | (tonne $CO_2$/tonne ferroalloy produced) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | C = A * B | $D = C/10^3$ |
| | | | | |
| | | | | |
| | | | | |
| Total | | | | |
| 1) For details of ferroalloy types, see Table 4.5 in Chapter 4 of Volume 3. | | | | |
| 2) Insert additional rows if necessary. | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Ferroalloys Production** | | | |
| **Category Code** | **2C2** | | | |
| **Sheet** | **2 of 2 $CH_4$ Emissions** | | | |
| | | | | |
| Type of Ferroalloy[1), 2)]<br>(please specify) | A | B | C | D |
| | Amount of Ferroalloy Production | Emission Factor | $CH_4$ Emissions | $CH_4$ Emissions |
| | (tonne ferroalloy produced) | (kg $CH_4$/tonne ferroalloy produced) | (kg) | (Gg) |
| | | | C = A * B | $D = C/10^6$ |
| | | | | |
| | | | | |
| | | | | |
| Total | | | | |
| 1) For details of ferroalloy types, see Table 4.7 in Chapter 4 of Volume 3. | | | | |
| 2) Insert additional rows if necessary. | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Aluminium Production** | | | |
| **Category Code** | **2C3** | | | |
| **Sheet** | **1 of 3 $CO_2$ Emissions** | | | |
| | | | | |
| Type of Technology | A | B | C | D |
| | Amount of Aluminium Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne aluminium produced) | (tonne $CO_2$/tonne aluminium produced) | (tonne) | (Gg) |
| | | | C = A * B | $D = C/10^3$ |
| Prebake | | | | |
| Soderberg | | | | |
| Total | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Aluminium Production** | | | |
| **Category Code** | **2C3** | | | |
| **Sheet** | **2 of 3 $CF_4$ Emissions** | | | |
| | | | | |
| Type of Technology | A | B | C | D |
| | Amount of Aluminium Production | Emission Factor | $CF_4$ Emissions | $CF_4$ Emissions |
| | (tonne aluminium produced) | (kg $CF_4$/tonne aluminium produced) | (kg) | (Gg) |
| | | | C = A * B | $D = C/10^6$ |
| CWPB | | | | |
| SWPB | | | | |
| VSS | | | | |
| HSS | | | | |
| Total | | | | |

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Aluminium Production** | | | |
| **Category Code** | **2C3** | | | |
| **Sheet** | **3 of 3 $C_2F_6$ Emissions** | | | |
| | | | | |
| Type of Technology | A | B | C | D |
| | Amount of Aluminium Production | Emission Factor | $C_2F_6$ Emissions | $C_2F_6$ Emissions |
| | (tonne aluminium produced) | (kg $C_2F_6$/tonne aluminium produced) | (kg) | (Gg) |
| | | | C = A * B | $D = C/10^6$ |
| CWPB | | | | |
| SWPB | | | | |
| VSS | | | | |
| HSS | | | | |
| Total | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Metal Industry - Magnesium Production** |
| **Category Code** | **2C4** |
| **Sheet** | **1 of 2 $CO_2$ Emissions from Primary Production** |

| Raw Material Source | A | B | C | D |
|---|---|---|---|---|
| | Amount of Primary Magnesium Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne primary magnesium produced) | (tonne $CO_2$/tonne primary magnesium produced) | (tonne) | (Gg) |
| | | | C = A * B | D = C/$10^3$ |
| Dolomite | | | | |
| Magnesite | | | | |
| Total | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Metal Industry - Magnesium Production** |
| **Category Code** | **2C4** |
| **Sheet** | **2 of 2 $SF_6$ Emissions from Magnesium Casting Processes** |

| A | B | C | D |
|---|---|---|---|
| Amount of Magnesium Casting | Emission Factor | $SF_6$ Emissions | $SF_6$ Emissions |
| (tonne magnesium casting) | (kg $SF_6$/tonne magnesium casting) | (kg) | (Gg) |
| | | C = A * B | D = C/$10^6$ |
| | | | |

Note: As regards HFC 134-a, FK 5-1-12 and their decomposition products (e.g., PFCs), no Tier 1 method is provided because the industrial experience in using these compounds (HFC 134-a and FK 5-1-12) for magnesium protection purposes is yet very limited. However, if the greenhouse gas emission from the use of magnesium cover gases is a national *key category*, it is *good practice*, for inventory preparation purposes, to collect direct measurements of these greenhouse gas emissions.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Metal Industry** | | | |
| **Category** | **Metal Industry - Lead Production** | | | |
| **Category Code** | **2C5** | | | |
| **Sheet** | **1 of 1** | | | |
| Source and Furnace Type$^{1), 2)}$<br>(please specify) | A | B | C | D |
| | Amount of Lead Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne lead produced) | (tonne $CO_2$/tonne lead produced) | (tonne) | (Gg) |
| | | | C = A * B | D = C/$10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of source and furnace types, see Table 4.21 in Chapter 4 of Volume 3.
2) Insert additional rows if necessary.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Metal Industry - Zinc Production** | | | |
| **Category Code** | **2C6** | | | |
| **Sheet** | **1 of 1** | | | |
| Type of Process$^{1), 2)}$<br>(please specify) | A | B | C | D |
| | Amount of Zinc Production | Emission Factor | $CO_2$ Emissions | $CO_2$ Emissions |
| | (tonne zinc produced) | (tonne $CO_2$/tonne zinc produced) | (tonne) | (Gg) |
| | | | C = A * B | D = C/$10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For details of process types, see Table 4.24 in Chapter 4 of Volume 3.
2) Insert additional rows if necessary.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Non-Energy Products from Fuels and Solvent Use - Lubricant Use** |
| **Category Code** | **2D1** |
| **Sheet** | **1 of 1** |

| A | B | C | D | E |
|---|---|---|---|---|
| Amount of Lubricant Consumed | Lubricant Carbon Content | Fraction Oxidized During Use (ODU factor) | $CO_2$ Emissions | $CO_2$ Emissions |
| (TJ) | (tonne-C/TJ) | (fraction) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | D = A * B * C * 44/12 | E = D/$10^3$ |
| | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Non-Energy Products from Fuels and Solvent Use – Paraffin Wax Use** |
| **Category Code** | **2D2** |
| **Sheet** | **1 of 1** |

| A | B | C | D | E |
|---|---|---|---|---|
| Amount of Paraffin Waxes Consumed | Paraffin Waxes Carbon Content | Fraction Oxidized During Use (ODU factor) | $CO_2$ Emissions | $CO_2$ Emissions |
| (TJ) | (tonne-C/TJ) | (fraction) | (tonne $CO_2$) | (Gg $CO_2$) |
| | | | D = A * B * C * 44/12 | E = D/$10^3$ |
| | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Electronics Industry - Integrated Circuit or Semiconductor** |
| **Category Code** | **2E1** |
| **Sheet** | **1 of 1** |

| Fluorinated Compounds (FCs) | A | B | C | D | E |
|---|---|---|---|---|---|
| | Fraction of Annual Plant Production Capacity Utilization1) | Annual Manufacturing Design Capacity1) | Tier 1 Default FC Emission Factor2) | $CO_2$ Equivalent Conversion Factor3) | FC Emissions4) |
| | (fraction) | (Gm$^2$ of silicon processed) | (kg FC/m$^2$ of silicon processed) | (tonne $CO_2$ /tonne FC) | (Gg $CO_2$ equivalent) |
| | | | | | $E = A * B * C * D * 10^3$ |
| $CF_4$ | | | 0.9 | | |
| $C_2F_6$ | | | 1 | | |
| $CHF_3$ | | | 0.04 | | |
| $C_3F_8$ | | | 0.05 | | |
| $NF_3$ | | | 0.04 | | |
| $SF_6$ | | | 0.2 | | |
| Total | | | | | |

1) The same value should be entered in each row.

2) In using Tier 1, inventory compilers should not modify, in any way, the set of the FCs assumed here. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods. Neither may inventory compilers change the values of any factors in this column.

3) Typically, global warming potential (100 year time horizon) identified in the IPCC Assessment Report can be used. These factors should be the same as those used for other sectors/categories to ensure that they are all internally consistent in the inventory.

4) The Tier 1 method, unlike the Tier 3 or 2 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce gas-specific emissions.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Electronics Industry - TFT Flat Panel Display** |
| **Category Code** | **2E2** |
| **Sheet** | **1 of 1** |

| Fluorinated Compounds (FCs) | A | B | C | D | E |
|---|---|---|---|---|---|
| | Fraction of Annual Plant Production Capacity Utilization1) | Annual Manufacturing Design Capacity1) | Tier 1 Default FC Emission Factor2) | CO$_2$ Equivalent Conversion Factor3) | FC Emissions4) |
| | (fraction) | (Gm$^2$ of glass processed) | (g FC/m$^2$ of glass processed) | (tonne CO$_2$ /tonne FC) | (Gg CO$_2$ equivalent) |
| | | | | | $E = A * B * C * D$ |
| CF$_4$ | | | 0.5 | | |
| NF$_3$ | | | 0.9 | | |
| SF$_6$ | | | 4 | | |
| Total | | | | | |

1) The same value should be entered in each row.

2) In using Tier 1, inventory compilers should not modify, in any way, the set of the FCs assumed here. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods. Neither may inventory compilers change the values of any factors in this column.

3) Typically, global warming potential (100 year time horizon) identified in the IPCC Assessment Report can be used. These factors should be the same as those used for other sectors/categories to ensure that they are all internally consistent in the inventory.

4) The Tier 1 method, unlike the Tier 3 or 2 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce gas-specific emissions.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Electronics Industry - Photovoltaics** |
| **Category Code** | **2E3** |
| **Sheet** | **1 of 2** |

| Fluorinated Compounds (FCs) | A | B | C |
|---|---|---|---|
| | Fraction of Annual Plant Production Capacity Utilization1) | Annual Manufacturing Design Capacity1) | Fraction of PV manufacture that uses fluorinated compounds |
| | (fraction) | (Mm$^2$ of substrate processed) | (fraction) |
| | | | |
| CF$_4$ | | | |
| C$_2$F$_6$ | | | |
| Total | | | |

1) The same value should be entered in each row.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Electronics Industry - Photovoltaics** |
| **Category Code** | **2E3** |
| **Sheet** | **2 of 2** |

| Fluorinated Compounds (FCs) | D | E | F |
|---|---|---|---|
| | Tier 1 Default FC Emission Factor1) | $CO_2$ Equivalent Conversion Factor2) | FC Emissions3) |
| | (g FC/m$^2$ of substrate processed) | (tonne $CO_2$ /tonne FC) | (Gg $CO_2$ equivalent) |
| | | | $F = A * B * C * D * E / 10^3$ |
| $CF_4$ | 5 | | |
| $C_2F_6$ | 0.2 | | |
| Total | | | |

1) In using Tier 1, inventory compilers should not modify, in any way, the set of the FCs assumed here. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods. Neither may inventory compilers change the values of any factors in this column.

2) Typically, global warming potential (100 year time horizon) identified in the IPCC Assessment Report can be used. These factors should be the same as those used for other sectors/categories to ensure that they are all internally consistent in the inventory.

3) The Tier 1 method, unlike the Tier 3 or 2 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce gas-specific emissions.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Electronics Industry - Heat Transfer Fluid** |
| **Category Code** | **2E4** |
| **Sheet** | **1 of 1** |

| Fluorinated Compounds (FCs) | A | B | C | D | E |
|---|---|---|---|---|---|
| | Fraction of Annual Plant Production Capacity Utilization | Annual Manufacturing Design Capacity | Tier 1 Default FC Emission Factor1) | $CO_2$ Equivalent Conversion Factor2) | FC Emissions3) |
| | (fraction) | (Gm$^2$ of silicon consumed) | (kg $C_6F_{14}$/m$^2$ of silicon consumed) | (tonne $CO_2$ /tonne $C_6F_{14}$) | (Gg $CO_2$ equivalent) |
| | | | | | $E = A * B * C * D * 10^3$ |
| $C_6F_{14}$ | | | 0.3 | | |

1) Tier 1 default emission factor assumes heat transfer fluids have the same GWP and $C_6F_{14}$ represents a suitable proxy. Inventory compilers should not change this value in using Tier 1 method.

2) Typically, global warming potential (100 year time horizon) identified in the IPCC Assessment Report can be used. These factors should be the same as those used for other sectors/categories to ensure that they are all internally consistent in the inventory.

3) The Tier 1 method, unlike the Tier 3 or 2 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce gas-specific emissions.

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Product Uses as Substitutes for Ozone Depleting Substances – Refrigeration and Air Conditioning** | | | |
| **Category Code** | **2F1** | | | |
| **Sheet** | **1 of 1** | | | |
| | | | | |
| HFCs/PFCs (please specify) | A | B | C | D |
| | Bank in Inventory Year[1] | Average Emission Factor from installed base | Agent in Retired Equipment in Inventory Year | Emissions in Inventory Year |
| | (tonne) | (%) | (tonne) | (tonne) |
| | | | | D = A * B/100 + C |
| HFC-23 | | | | |
| … | | | | |

1) In reality, it is necessary in the refrigeration and air conditioning application to deal with the development and tracking of banks. This means that an historical time series of country-specific or globally or regionally derived activity data is required dating back to the introduction of any new HFC or PFC. In order to do this, inventory compilers will need to implement spreadsheet calculations. A typical example, which is workable and inventory compilers could use, can be found in the *2006 Guidelines* CDROM. (V3_An1_Calculation_example_for_2F1.xls)

| | | | | |
|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | |
| **Category** | **Product Uses as Substitutes for Ozone Depleting Substances – Foam Blowing Agents** | | | |
| **Category Code** | **2F2** | | | |
| **Sheet** | **1 of 1** | | | |
| | | | | |
| HFCs/PFCs (please specify) | A | B | C | D |
| | Original Charge in Each of Previous Years[1] | Annual Losses Emission Factor | First Year Loss in Inventory Year[2] | Emissions in Inventory Year |
| | (tonne) | (%) | (tonne) | (tonne) |
| | | | | D = A * B/100 + C |
| HFC-245fa | | | | |
| … | | | | |

1) In reality, it is necessary in the foam application to deal with the historical time series of country-specific or globally or regionally derived activity data dating back to the introduction of any new HFC or PFC. In order to do this, inventory compilers will need to implement spreadsheet calculations. A typical example, which is workable and inventory compilers could use, can be found in the *2006 Guidelines* CDROM. (V3_An1_Calculation_example_for_2F2.xls)

2) For details on the first year loss emission factor, see Table 7.5 in Chapter 7 of this volume. In the case of open-cell foams, the first year loss emission factor is typically 100 %.

| | | | | | |
|---|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | | |
| **Category** | **Product Uses as Substitutes for Ozone Depleting Substances – Fire Protection** | | | | |
| **Category Code** | **2F3** | | | | |
| **Sheet** | **1 of 1** | | | | |
| HFCs/PFCs<br>(please specify) | A | B | C | D | E |
| | Bank in Inventory Year[1] | Average Emission Factor from installed base | Agent in Retired Equipment in Inventory Year | Rate of Recovery of the Agent in Retired Equipment | Emissions in Inventory Year |
| | (tonne) | (%) | (tonne) | (%) | (tonne) |
| | | | | | E = A * B/100 + C * (1 – D/100) |
| HFC-23 | | | | | |
| … | | | | | |

1) In reality, it is necessary in the fire protection application to deal with the development and tracking of banks. This means that an historical time series of country-specific or globally or regionally derived activity data is required dating back to the introduction of any new HFC or PFC. In order to do this, inventory compilers will need to implement spreadsheet calculations. A typical example, which is workable and inventory compilers could use, can be found in the *2006 Guidelines* CDROM. (V3_An1_Calculation_example_for_2F3.xls)

| | | | | | |
|---|---|---|---|---|---|
| **Sector** | | **Industrial Processes and Product Use** | | | |
| **Category** | | **Product Uses as Substitutes for Ozone Depleting Substances - Aerosols** | | | |
| **Category Code** | | **2F4** | | | |
| **Sheet** | | **1 of 1** | | | |
| A | | B | C | D | E |
| Quantity of HFCs/PFCs Contained in Aerosol Products Sold in Inventory Year | | Quantity of HFCs/PFCs Contained in Aerosol Products Sold in Prior Year | Emission Factor (Loss of Current Year's Use) | Emissions of HFCs/PFCs from Aerosol Products | Emissions of HFCs/PFCs from Aerosol Products |
| Chemical[1), 2)]<br>(please specify) | (tonne) | (tonne) | (fraction) | (tonne) | (Gg) |
| | | | | D = A * C + B * (1 – C) | E = D/$10^3$ |
| | | | | | |
| | | | | | |
| | | | | | |

1) For chemicals that are used for this application, see Table 7.1 in Chapter 7 of Volume 3.

2) Insert additional rows if necessary.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Product Uses as Substitutes for Ozone Depleting Substances - Solvents** |
| **Category Code** | **2F5** |
| **Sheet** | **1 of 1** |

| A | | B | C | D | E |
|---|---|---|---|---|---|
| Quantity of Solvents (HFCs/PFCs) Sold in Inventory Year | | Quantity of Solvents (HFCs/PFCs) Sold in Prior Year | Emission Factor (Loss of Current Year's Use) | Emission of HFCs/PFCs from Solvents | Emission of HFCs/PFCs from Solvents |
| Chemical 1), 2) (please specify) | (tonne) | (tonne) | (fraction) | (tonne) | (Gg) |
| | | | | D = A * C + B * (1 – C) | E = D/$10^3$ |
| | | | | | |
| | | | | | |
| | | | | | |

1) For chemicals that are used for this application, see Table 7.1 in Chapter 7 of Volume 3.

2) Insert additional rows if necessary.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Product Uses as Substitutes for Ozone Depleting Substances – Other Applications** |
| **Category Code** | **2F6** |
| **Sheet** | **1 of 1** |

| A | | B | C | D | E |
|---|---|---|---|---|---|
| Quantity of HFCs/PFCs Sold in Inventory Year | | Quantity of HFCs/PFCs Sold in Prior Year | Emission Factor (Loss of Current Year's Use) | Emission of HFCs/PFCs from Other Applications | Emission of HFCs/PFCs from Other Applications |
| Chemical 1), 2) (please specify) | (tonne) | (tonne) | (fraction) | (tonne) | (Gg) |
| | | | | D = A * C + B * (1 – C) | E = D/$10^3$ |
| | | | | | |
| | | | | | |
| | | | | | |

1) For chemicals that are used for this application, see Table 7.1 in Chapter 7 of Volume 3.

2) Insert additional rows if necessary.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - Electrical Equipment** | | |
| **Category Code** | **2G1** | | |
| **Sheet** | **1 of 5 Manufacturing Emissions of $SF_6$[1]** | | |
| Type of Equipment | A | B | C |
| | Total $SF_6$ Consumption by Equipment Manufacturers | Manufacturing Emission Factor[2] | Manufacturing Emissions |
| | (tonne $SF_6$) | (fraction) | (tonne $SF_6$) |
| | | | C = A * B |
| Sealed-Pressure | | | |
| Closed-Pressure | | | |
| Gas-Insulated Transformers | | | |
| Total | | | |

1) Emissions of PFCs can be estimated by the same calculation procedure.

2) Default emission factors depend on region for which emissions are being estimated. See Tables 8.2 through 8.4 in Chapter 8 of this volume.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - Electrical Equipment** | | |
| **Category Code** | **2G1** | | |
| **Sheet** | **2 of 5 Equipment Installation Emissions of $SF_6$[1]** | | |
| Type of Equipment | D | E | F |
| | Total Nameplate Capacity of New Equipment Filled on Site (not at the factory) | Installation Emission Factor[2] | Equipment Installation Emissions |
| | (tonne $SF_6$) | (fraction) | (tonne $SF_6$) |
| | | | F = D * E |
| Sealed-Pressure | | | |
| Closed-Pressure | | | |
| Gas-Insulated Transformers | | | |
| Total | | | |

1) Emissions of PFCs can be estimated by the same calculation procedure.

2) Default emission factors depend on region for which emissions are being estimated. See Tables 8.2 through 8.4 in Chapter 8 of this volume.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - Electrical Equipment** | | |
| **Category Code** | **2G1** | | |
| **Sheet** | **3 of 5 Equipment Use Emissions of $SF_6$[1)]** | | |
| | | | |
| Type of Equipment | G | H | I |
| | Total Nameplate Capacity of Installed Equipment | Use Emission Factor[2), 3)] | Equipment Use Emissions |
| | (tonne $SF_6$) | (fraction) | (tonne $SF_6$) |
| | | | I = G * H |
| Sealed-Pressure | | | |
| Closed-Pressure | | | |
| Gas-Insulated Transformers | | | |
| Total | | | |

1) Emissions of PFCs can be estimated by the same calculation procedure.

2) Default emission factors depend on region for which emissions are being estimated. See Tables 8.2 through 8.4 in Chapter 8 of this volume.

3) The 'use emission factor' includes emissions due to leakage, servicing, maintenance, and equipment failures.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - Electrical Equipment** | | |
| **Category Code** | **2G1** | | |
| **Sheet** | **4 of 5 Equipment Disposal Emissions of $SF_6$[1)]** | | |
| | | | |
| Type of Equipment | J | K | L |
| | Total Nameplate Capacity of Retiring Equipment | Fraction of $SF_6$ Remaining at Retirement[2)] | Equipment Disposal Emissions |
| | (tonne $SF_6$) | (fraction) | (tonne $SF_6$) |
| | | | L = J * K |
| Sealed-Pressure | | | |
| Closed-Pressure | | | |
| Gas-Insulated Transformers | | | |
| Total | | | |

1) Emissions of PFCs can be estimated by the same calculation procedure.

2) Default emission factors depend on region for which emissions are being estimated. See Tables 8.2 through 8.4 in Chapter 8 of this volume.

| | | |
|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | |
| **Category** | **Other Product Manufacture and Use - Electrical Equipment** | |
| **Category Code** | **2G1** | |
| **Sheet** | **5 of 5 Total Emissions of $SF_6$ 1)** | |
| Type of Equipment | M | N |
| | Total Emissions | Total Emissions |
| | (tonne $SF_6$) | (Gg $SF_6$) |
| | $M = C + F + I + L$ | $N = M/10^3$ |
| Sealed-Pressure | | |
| Closed-Pressure | | |
| Gas-Insulated Transformers | | |
| Total | | |

1) Emissions of PFCs can be estimated by the same calculation procedure.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** | | |
| **Category Code** | **2G2** | | |
| **Sheet** | **1 of 7 $SF_6$ Emissions from Military Applications (AWACS)** | | |
| A | B | C | D |
| National AWACS Fleet | Emission Factor | $SF_6$ Emissions | $SF_6$ Emissions |
| (number of AWACS) | (kg $SF_6$/plane) | (kg) | (Gg) |
| | | $C = A * B$ | $D = C/10^6$ |
| | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | | |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** | | | | |
| **Category Code** | **2G2** | | | | |
| **Sheet** | **2 of 7 $SF_6$ Emissions from University and Research Particle Accelerators** | | | | |
| A | B | C | D | E | F |
| Number of University and Research Particle Accelerators in the Country | $SF_6$ Use Factor | $SF_6$ Charge Factor | $SF_6$ Emission Factor | $SF_6$ Emissions | $SF_6$ Emissions |
| (number) | (fraction) | (kg $SF_6$/particle accelerator) | (fraction) | (kg) | (Gg) |
| | | | | $E = A * B * C * D$ | $F = E/10^6$ |
| | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | | | |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** | | | | |
| **Category Code** | **2G2** | | | | |
| **Sheet** | **3 of 7 $SF_6$ Emissions from Industrial and Medical Particle Accelerators** | | | | |
| Process Description | A | B | C | D | E |
| | Number of Particle Accelerators that use $SF_6$ by Process Description in the Country | $SF_6$ Charge Factor | $SF_6$ Emission Factor | $SF_6$ Emissions | $SF_6$ Emissions |
| | (number) | (kg $SF_6$/particle accelerator) | (fraction) | (kg) | (Gg) |
| | | | | D = A * B * C | E = D/$10^6$ |
| Industrial Accelerator (High Voltage: 0.3-23 MV) | | | | | |
| Industrial Accelerator (Low Voltage: <0.3 MV) | | | | | |
| Medical | | | | | |
| Total | | | | | |

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** | | |
| **Category Code** | **2G2** | | |
| **Sheet** | **4 of 7 $SF_6$ Emissions1) from Adiabatic Uses** | | |
| Type of Applications2), 3) (please specify) | A | B | C |
| | Sales into application in year t-3 | $SF_6$ Emissions in year t | $SF_6$ Emissions in year t |
| | (tonne) | (tonne) | (Gg) |
| | | B = A | C = B/$10^3$ |
| | | | |
| | | | |
| Total | | | |

1) Emissions of PFCs can be estimated by the same calculation procedure.

2) For example, car tires, sport shoe soles and tennis balls.

3) Insert additional rows, if necessary.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** |
| **Category Code** | **2G2** |
| **Sheet** | **5 of 7 $SF_6$ Emissions from Sound-Proof Glazing** |

| A | B | C | D | E | F |
|---|---|---|---|---|---|
| $SF_6$ Purchased to Fill Windows Assembled in Inventory Year | Assembly Emission Factor | Assembly Emissions | Capacity of Existing Windows in Inventory Year | Leakage Emission Factor | Leakage Emissions |
| (tonne $SF_6$) | (fraction) | (tonne $SF_6$) | (tonne $SF_6$) | (fraction) | (tonne $SF_6$) |
| | | C = A * B | | | F = D * E |
| | | | | | |

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** |
| **Category Code** | **2G2** |
| **Sheet** | **6 of 7 $SF_6$ Emissions from Sound-Proof Glazing** |

| G | H | I | J | K |
|---|---|---|---|---|
| Amount Left in Windows at End of Lifetime (Disposed of in Inventory Year) | Recovery Factor[1)] | Disposal Emissions | Total Emissions | Total Emissions |
| (tonne $SF_6$) | (fraction) | (tonne $SF_6$) | (tonne $SF_6$) | (Gg $SF_6$) |
| | | I = G * (1 – H) | J = C + F + I | $K = J/10^3$ |
| | | | | |

1) Recovery factor is assumed to be zero unless country-specific information is available.

| | |
|---|---|
| **Sector** | **Industrial Processes and Product Use** |
| **Category** | **Other Product Manufacture and Use - $SF_6$ and PFCs from Other Product Uses** |
| **Category Code** | **2G2** |
| **Sheet** | **7 of 7 Emissions of $SF_6$ and PFCs from Other Prompt Emissive Applications** |

| Type of Applications 1), 2)<br>(please specify) | A | B | C | D |
|---|---|---|---|---|
| | Sales into application in year t | Sales into application in year t-1 | Emissions in year t | Emissions in year t |
| | (tonne) | (tonne) | (tonne) | (Gg) |
| | | | C = 0.5 * (A + B) | $D = C/10^3$ |
| | | | | |
| | | | | |
| Total | | | | |

1) For example, tracers and use in production of optical cables.

2) Insert additional rows, if necessary.

| | | | |
|---|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | | |
| **Category** | **Other Product Manufacture and Use - $N_2O$ from Product Uses** | | |
| **Category Code** | **2G3** | | |
| **Sheet** | **1 of 2** | | |
| Type of Applications | A | B | C |
| | Quantity of $N_2O$ Supplied in this Application Type in Year t | Quantity of $N_2O$ Supplied in this Application Type in Year t-1 | Emission Factor |
| | (tonne) | (tonne) | (fraction) |
| | | | |
| Medical Applications | | | |
| Propellant in Aerosol Products | | | |
| Other (please specify) $^{1)}$ | | | |
| Total | | | |
| 1) Insert additional rows, if necessary. | | | |

| | | |
|---|---|---|
| **Sector** | **Industrial Processes and Product Use** | |
| **Category** | **Other Product Manufacture and Use - $N_2O$ from Product Uses** | |
| **Category Code** | **2G3** | |
| **Sheet** | **2 of 2** | |
| Type of Applications | D | E |
| | $N_2O$ Emission | $N_2O$ Emission |
| | (tonne) | (Gg) |
| | D = (0.5 * A + 0.5 * B) * C | $E = D/10^3$ |
| Medical Applications | | |
| Propellant in Aerosol Products | | |
| Other (please specify) $^{1)}$ | | |
| Total | | |
| 1) Insert additional rows, if necessary. | | |

# ANNEX 2

# POTENTIAL EMISSIONS (FORMERLY TIER 1 FOR CONSUMPTION OF HFCs, PFCs, AND $SF_6$)

## Authors

Paul Ashford (UK) and Jochen Harnisch (Germany)

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# ANNEX 2 POTENTIAL EMISSIONS (FORMERLY TIER 1 FOR CONSUMPTION OF HFCs, PFCs, AND $SF_6$)

## A2.1 BASIC METHOD TO CALCULATE POTENTIAL EMISSIONS

The following approach, formerly the Tier 1 approach for estimating 'potential' emissions related to the consumption of hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride ($SF_6$), is no longer recommended as a method for estimating HFCs, PFCs, or $SF_6$ emissions. This is because it is likely to grossly overestimate emissions from sources in which stock is growing quickly and emissions are delayed for decades, such as air conditioning and refrigeration equipment, foams, and electrical equipment. However, when considered along with estimates of actual emissions, the potential emissions approach can assist in validation of completeness of sources covered and as a QC check by comparing total domestic consumption as calculated in this 'potential emissions approach' per compound with the sum of all activity data of the various uses. It may also assist in monitoring the growth of banked greenhouse gases and thereby provide an indication of potential future environmental burdens. Thus, the method is included here for reference purposes e.g., to facilitate consistent time series.

Since net consumption of a chemical is equal to production plus imports minus exports, the calculation formula for the basic method (former Tier 1) is as follows:

**EQUATION A2.1**

$$Potential\ SF_6\ emissions\ from\ all\ uses = Production + (Imports - Exports) - Destruction$$

Production refers to production of new chemical. Reprocessing of recovered fluid should not be included. Imports and exports include bulk chemicals and may or may not include the quantity of chemical contained in products, such as refrigerators, air-conditioners, packaging materials, insulating foams, fire extinguishers, etc.

Although destruction of HFCs, PFCs, and $SF_6$ is currently not widely practised, and may be technically difficult in some cases, it should be included as a potential option to reduce emissions. By-product emissions during HFC, PFC, and $SF_6$ production and fugitive emissions related to production and distribution have to be calculated separately.

There are two versions that formerly had been labelled Tier 1 (a and b) depending upon whether HFCs, PFCs, and $SF_6$ in products are taken into account. In the former Tier 1a, chemicals contained in products are *not* considered. In the former Tier 1b, chemicals contained in products are considered. The reason for two versions is that it is expected that there may be difficulties in many countries with the availability of data regarding imports and exports of HFCs, PFCs, and $SF_6$ in products, at least in the short term. The former Tier 1b methodology is preferred if relevant data are available. As an alternative, alternative activity data can be used to take into account consumption (potential emissions) associated with the trade of products containing HFCs, PFCs, and $SF_6$.

If countries choose to develop potential emission estimates, they are encouraged to track individual HFCs, PFCs, and $SF_6$ separately. However, such tracking (particularly for imports and exports) is complicated by the fact that many of the commercial types of HFC/PFC refrigerants, blowing agents, solvents, etc. are mixtures of two or more HFCs and/or PFCs. It is important to note that the composition of fluids for similar purposes may vary according to individual formulas developed by the different chemical companies.

### *Former Tier 1a*

Quantities of HFCs, PFCs, and $SF_6$ contained in various products imported into or exported from a country may be difficult to estimate. In the former Tier 1a, only chemicals imported or exported in bulk are considered in the calculation of potential emissions, which is a similar approach presently used to report Ozone Depleting Substances (ODS) under the Montreal Protocol. The following definitions apply:

**EQUATION A2.2**

$$Imports = Imported\ HFC/PFC/SF_6\ in\ bulk$$

$$Exports = Exported\ HFC/PFC/SF_6\ in\ bulk$$

The application of the former Tier 1a may lead to underestimation or overestimation of potential emissions, depending on whether the majority of products containing HFCs, PFCs, and $SF_6$ is being imported or exported.

Data on production and exports of chemicals in bulk should be available from chemical companies. Information on imports of chemicals in bulk may be available from customs services. National environmental protection authorities may keep records of HFCs, PFCs, and $SF_6$ destroyed, if any.

Potential emission data for each individual chemical should be calculated according to the scheme in Table A2.1:

**TABLE A2.1**
**CALCULATION SCHEME FOR POTENTIAL EMISSIONS ACCORDING TO THE FORMER TIER 1a**

| |
|---|
| **REPORTING YEAR:** |
| **TYPE OF CHEMICAL (e.g., HFC-134a):** |
| Production of chemical<br>+ Import of chemical in bulk<br>– Export of chemical in bulk<br>– Destruction of chemical<br>= Sum (potential emission of chemical) |

Emissions related to production and distribution of HFCs, PFCs, and $SF_6$ have to be taken into account as described in Section 3.10, Fluorochemical Production.

### *Former Tier 1b*

The former Tier 1b is an extension of the former Tier 1a and includes HFCs, PFCs, and $SF_6$ contained in various products which are imported and exported. The following definitions then apply:

**EQUATION A2.3**

$$\begin{aligned}Imports &= Imported\ chemical\ in\ bulk\\ &\quad + quantity\ of\ chemical\ imported\ in\ HFC/PFC/SF_6\ containing\ products\\ Exports &= Exported\ chemical\ in\ bulk\\ &\quad + quantity\ of\ chemical\ exported\ in\ HFC/PFC/SF_6\ containing\ products\end{aligned}$$

Data on production and exports of HFCs, PFCs, and $SF_6$ in bulk should be available from the chemical companies to their national governments. Information on imports of bulk chemicals should be available from customs services, as well as, in theory, imports and exports of products and equipment containing HFCs, PFCs, and $SF_6$. However, in practice, tariff codes do not normally distinguish between those products and equipment containing HFCs, PFCs, and $SF_6$ and those which do not. Accordingly, the use of the alternative activity estimates for HFCs, PFCs, and $SF_6$ contained may be helpful. National environmental protection authorities may keep records of HFCs, PFCs, and $SF_6$ destroyed.

To calculate the potential emissions according to the former Tier 1b, the calculation scheme in Table A2.1 has to be extended to include the import and export of chemicals in products. Section A2.2 demonstrates a possible set-up, based on refrigeration equipment, foam products, fire extinguisher equipment, solvent and aerosols, for calculation of emissions from exports/imports and the results should be added to the emissions calculated using Table A2.1. In Section A2.2, HFC-xxx is used as an example to demonstrate the procedure, which in practice will have to be performed for each individual HFC, PFC and for $SF_6$.

# A2.2 ADDITIONAL CALCULATIONS FOR ESTIMATING POTENTIAL EMISSIONS ACCORDING TO THE FORMER TIER 1b

## REFRIGERATION

**EQUATION A2.4**

$$G_{HFC-xxx} = G(Unit\ i) \bullet n(Unit\ i) \bullet F_{HFC-xxx}(Unit\ i) + \cdots + G(Unit\ m) \bullet n(Unit\ m) \bullet F_{HFC-xxx}(Unit\ m)$$

Where:

$G_{HFC\text{-}xxx}$ = total import (export) of HFC-xxx in pre-charged refrigeration units[1]

G(Unit $i$) = refrigerant charge in a refrigeration unit of type $i$ ($i = i \rightarrow m$)

n(Unit $i$) = number of refrigeration units of type $i$ imported (exported)

$F_{HFC\text{-}xxx}$(Unit $i$) = fraction of component HFC-xxx[2] in the refrigerant (mixture) of a unit of type $i$

## FOAM PRODUCTS[3]

**EQUATION A2.5**

$$G_{HFC-xxx} = V(Foam\ i) \bullet J_{HFC-xxx}(Foam\ i) + \cdots + V(Foam\ m) \bullet J_{HFC-xxx}(Foam\ m)$$

Where:

$G_{HFC\text{-}xxx}$ = total import (export) of HFC-xxx in foams (flexible and rigid)

V(Foam $i$) = volume of foam of type $i$ imported (exported) ($i = i \rightarrow m$)

$J_{HFC\text{-}xxx}$(Foam $i$) = remaining amount of blowing agent HFC-xxx per volume unit of foam of type $i$

## FIRE EXTINGUISHERS (PRE-CHARGED)

**EQUATION A2.6**

$$G_{HFC-xxx} = G(Unit\ i) \bullet n(Unit\ i) \bullet F_{HFC-xxx}(Unit\ i) + \cdots + G(Unit\ m) \bullet n(Unit\ m) \bullet F_{HFC-xxx}(Unit\ m)$$

Where:

$G_{HFC\text{-}xxx}$ = total import (export) of HFC-xxx in pre-charged fire extinguishers

G(Unit $i$) = charge of fire extinguishing agent in a fire extinguishing unit of type $i$ ($i = i \rightarrow m$)

n(Unit $i$) = number of fire extinguishing units of type $i$ imported (exported)

$F_{HFC\text{-}xxx}$(Unit $i$) = fraction of component HFC-xxx[4] in the fire extinguishing agent of a unit of type $i$

---

[1] ‘Refrigeration units’ may be refrigerators, ice machines, AC window units, split-units, chillers etc.

[2] Many refrigeration units will contain HFC/PFC-mixtures. The fraction of each chemical (HFC-xxx) has to be considered.

[3] Include insulating and non-insulating foams in a variety of products, like refrigerators, insulation panels, prefabricated pipe section, PU formulated systems, etc.

[4] Many fire extinguishing units will contain HFC/PFC-mixtures. The fraction of each chemical (HFC-xxx) has to be considered.

## SOLVENTS

**EQUATION A2.7**

$$G_{HFC-xxx} = G(Solvent\ i) \bullet F_{HFC-xxx}(Solvent\ i) + \cdots + G(Solvent\ m) \bullet F_{HFC-xxx}(Solvent\ m)$$

Where:

$G_{HFC\text{-}xxx}$ = total import (export) of HFC-xxx in solvents

G(Solvent *i*) = quantity of solvent of type *i* imported (exported) ($i = i \rightarrow m$)

$F_{HFC\text{-}xxx}$(Solvent *i*) = fraction of component HFC-xxx[5] in solvent of type *i*

## AEROSOLS

**EQUATION A2.8**

$$G_{HFC-xxx} = G(Can\ i) \bullet n(Can\ i) + \cdots + G(Can\ m) \bullet n(Can\ m)$$

Where:

$G_{HFC\text{-}xxx}$ = total import (export) of HFC-xxx in aerosol cans

G(Can *i*) = charge of HFC-xxx propellant in an aerosol can of type *i* ($i = i \rightarrow m$)

n(Can *i*) = number of aerosol cans of type *i* imported (exported)

# References

IPCC (1997). Revised 1996 IPCC Guidelines for National Greenhouse Inventories. Houghton J.T., Meira Filho L.G., Lim B., Tréanton K., Mamaty I., Bonduki Y., Griggs D.J. Callander B.A. (Eds). Intergovernmental Panel on Climate Change (IPCC), IPCC/OECD/IEA, Paris, France.

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[5] Solvents will often not be pure HFCs or PFCs. The HFC/PFC fraction in the solvent composition (HFC-xxx) has to be considered.

# ANNEX 3

# IMPROVEMENTS SINCE 1996

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# ANNEX 3: IMPROVEMENTS SINCE 1996

This volume contains major changes and improvements to the section covering 'Industrial Processes' and 'Solvent and Other Product Use' in the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (*1996 IPCC Guidelines*). First, these *Guidelines* (*2006 IPCC Guidelines*) introduce practical guidance on allocation of carbon dioxide ($CO_2$) emissions released from combustion of fuel in the Energy Sector and Industrial Processes Sector, which was not clear in the *1996 IPCC Guidelines*. Second, these *Guidelines* are based on the principle that emissions should be reported in the industries where these emissions occur. Accordingly, there has been a shift in the categories in which some emissions are reported, particular those from the use of limestone, dolomite and other carbonates.

Other major changes and/or improvements listed below are associated to each Chapter of this volume.

## A3.1 MINERAL INDUSTRY EMISSIONS

There are three key changes to the Mineral Chapter in the *2006 IPCC Guidelines*, as compared to the earlier guidance documents. Firstly, a new input-based method has been introduced for all source categories that estimates emissions based on the quantity, type and composition of carbonate inputs to the production processes. For example, in addition to the Tier 2 method based on clinker output during cement production, an alternate method is elaborated based on estimating emissions from the carbonate input to the kiln.

Secondly, clear guidance has been developed to specify where emissions from the use of limestone, dolomite and other carbonates should be reported. As noted above, these *Guidelines* are based on the principle that emissions should be reported in the industries where they occur. For example, where limestone is used as a flux for iron and steel production, emissions from the use of the limestone should be reported under Iron and Steel Production. Only emissions from limestone and dolomite used in the mineral industry should be reported in the Mineral Industry Chapter. Inventory compilers are encouraged to assess carefully how this change may impact, in particular, emission estimates for the Mineral Industry, the Chemical Industry, and Metal Production.

In addition while earlier guidance highlighted only limestone and dolomite use, these *Guidelines* also outline methods for estimating emissions from use of other carbonates, including magnesia and sodium carbonate. These *Guidelines* also establish three approaches for estimating emissions from glass production. Acid-induced release of $CO_2$ from acidification of carbonate-containing materials (e.g., phosphate ores) is also considered, although specific estimation methods are not provided.

## A3.2 CHEMICAL INDUSTRY EMISSIONS

New sources of emissions have been introduced: nitrous oxide ($N_2O$) emissions from Production of Caprolactam, Glyoxal, and Glyoxylic acid, and $CO_2$ emissions from Titanium Dioxide Production. Soda Ash production was reallocated from Mineral Industry to Chemical Industry. In the Soda Ash Production section the methodology for synthetic (Solvay) soda ash production process, which was lacking in the *1996 IPCC Guidelines* and the *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (*GPG2000*), has been introduced.

$CO_2$ emission factors have been added for Petrochemical Production processes, including emission factors for methanol, ethylene, ethylene dichloride/vinyl chloride, ethylene oxide, acrylonitrile, and carbon black production. Methane emission factors have been updated for these petrochemical production processes. Styrene production is no longer included in the guidance document. A systematic description of Tier 1, 2 and 3 methodologies for all source categories is provided in the text.

The descriptions of emission-related processes have been enlarged giving more information about their chemistry and technology aspects.

More systematic guidance is also given to avoid double counting fuel products used as a feedstock or reductant (cross-cutting issue with Energy Sector). This issue is discussed in regard to ammonia production, carbide production, and titanium dioxide, and petrochemical production (Sections 3.2, 3.6, 3.7, and 3.9).

A discussion of utilisation of $CO_2$ in Urea Production is included in the section on Ammonia Production. Emissions from urea use that were previously accounted for in the Industrial Processes Sector have been reallocated according to the sectors where urea is used (Energy Sector and Agriculture, Forestry and Other Land Use (AFOLU) Sector) to take proper account of exports urea produced in ammonia plants. Emissions from other chemical products manufactured using $CO_2$ recovered in the ammonia production process are accounted together with emissions from ammonia production, as before.

The methodology for calculation of HFC-23 emissions from HCFC-22 production has incorporated the principal methods used within the industry, including continuous direct, proxy and in-process measurements in Tier 3 and efficiency-based material balance methods in Tier 2. In addition, explicit guidance has been added on fugitive and by-product emissions from the production of other fluorinated compounds including hydrofluorocarbons (HFCs), sulphur hexafluoride ($SF_6$) and uranium hexafluoride ($UF_6$).

# A3.3 METAL INDUSTRY EMISSIONS

The Metal Industry Section of *2006 IPCC Guidelines* incorporates a number of changes. Where carbon and carbon-containing materials, including carbonate containing minerals, are used in the metal production process for purposes other than the direct production of energy within the process, the $CO_2$ emissions are now counted within the metals guidance. For example, the $CO_2$ emissions from carbon-based electrodes for aluminium production are now included within the guidance for aluminium, and the $CO_2$ emissions from the use of limestone and dolomite used in iron and steel making are included within the guidance for iron and steel production.

The Metal Industry Section now includes guidance for estimating emissions of $CO_2$ and $CH_4$ from metallurgical (coal) coke production; however the $CO_2$ and $CH_4$ emissions from metallurgical coke production are to be reported under Energy Sector, not Industrial Processes and Product Use (IPPU) Sector. Emission factors for production of direct reduced iron (DRI), pellets, and sinter from iron ore and other iron-containing raw materials are now included under iron and steel production. Separate $CO_2$ emission factors are provided for blast furnace iron making and for steel making using the basic oxygen furnace (BOF), electric arc furnace (EAF) and open hearth furnace (OHF) processes.

$CO_2$ emissions from primary magnesium production based on dolomite and magnesite raw materials are also included in this section. In addition, new guidance has been developed and is available for calculation of $CO_2$ emissions resulting from production of zinc and lead. Separate $CO_2$ emission factors are provided for primary and secondary lead and zinc production processes. More comprehensive guidance is also included for ferroalloys production processes. Revised guidance is offered in the *2006 IPCC Guidelines* for magnesium for new gases reflecting efforts to replace sulphur hexafluoride as a cover gas. Finally, calculation factors have been updated to reflect the most recent experience for measured emission factors, typical compositions of process materials impacting calculations, and, in some instances new equations are included.

# A3.4 NON-ENERGY PRODUCTS FROM FUELS AND SOLVENT USE

Almost this entire source category, which is described in Chapter 5, is new within the IPPU Sector. The *1996 IPCC Guidelines* did cover emissions from asphalt and road paving, but in much less detail. The products covered here comprise: lubricants, paraffin waxes, bitumen/asphalt, and solvents.

Emissions from lubricants were previously covered under fuel combustion without any discrimination between emissions arising during lubricants use and any emissions from waste lubricants used for heat raising. The same is true for paraffin waxes. Asphalt emissions refer to production and use of asphalt for road paving, asphalt roofing and other applications. Asphalt emissions also include emissions from asphalt blowing. The subcategory '2D3 Solvent Use' refers to the subcategories 3A and 3B in the *1996 IPCC Guidelines*. Although asphalt and solvents are not significant sources of direct greenhouse gas emissions, they are included in this chapter to provide a description of them since they are sources of ozone precursors (non-methane volatile organic compounds (NMVOC), and in the case of asphalt also carbon monoxide (CO)). In particular, solvent use is a very substantial source of NMVOC.

# A3.5 ELECTRONICS INDUSTRY EMISSIONS

The *1996 IPCC Guidelines* and the *GPG2000*, described methods for estimating emissions from semiconductor manufacturing alone for seven fluorinated carbon compounds: $CF_4$, $C_2F_6$, $CHF_3$, $C_3F_8$, c-$C_4F_8$, $NF_3$ and $SF_6$. The *2006 IPCC Guidelines* expands that scope to include additional manufacturing sectors and more gases, updates the Tier 1 methodology and emission factors, and provides explicit estimates of uncertainties for emissions factors and activity data. The *2006 IPCC Guidelines* incorporates emissions from liquid crystal display (LCD) manufacturing, photovoltaic (PV) cell manufacturing and the use of heat transfer fluids in semiconductor manufacturing. In addition, the number of greenhouse gases in the *2006 IPCC Guidelines* has been expanded to include difluoromethane ($CH_2F_2$), octofluorocyclopentene ($C_5F_8$), hexafluorbutadiene ($C_4F_6$) and octafluorotetrahydrofuran ($C_4F_8O$); $F_2$ and $COF_2$ have also been added because, even though they are not greenhouse gases, $CF_4$ may be formed during their use. A new Tier 1 methodology is adopted that includes new default emissions factors and activity data for all sectors.

# A3.6 EMISSIONS OF FLUORINATED SUBSTITUTES FOR OZONE DEPLETING SUBSTANCES

The emissions in a number of the source categories (applications) covered by this chapter have been the subject of considerable study since the *1996 IPCC Guidelines* were written. This has been particularly the case for sectors with delayed emissions (e.g. refrigeration, foam and fire protection) where the earlier emission factor estimates proposed by Gamlen and others have been further developed to reflect the varying emission rates from a variety of sub-applications. Much of this was included in the *GPG2000*.

One of the consequences of this improved understanding has been recognition that the potential emissions approach used as Tier 1 in the *1996 IPCC Guidelines* is no longer appropriate. The potential emissions approach is still described in Annex 1 of this volume as a verification tool for completeness of sources and as a QC check of the sum of activity data per compound, which should be equal to the sum of apparent domestic consumption as calculated in the potential emissions approach. The Tier 1 approaches now proposed in these *Guidelines* are therefore actual emission estimation methods, although often based on default emission factors and with the potential to use global/regional activity databases where better information is not available. Chapter 7 of this volume contains examples of these new Tier 1 approaches and guidance on how to implement them. Simplified mass balance approaches have also been maintained in appropriate sectors, most typically where pressurised equipment is used and serviced (refrigeration & fire protection). Attention has also been addressed to the treatment of solvents contained in aerosols. Now emissions from all aerosol based products, irrespective of their purpose, will be reported within the aerosol application.

Activity information continues to be the biggest challenge in the ODS substitutes area, particularly at country-level, for two reasons. The first is that trade in products containing HFCs and/or perfluorocarbons (PFCs) can not easily be monitored and the second is that confidentiality of activity data for specific chemicals may need to be protected. Global/regional activity data from reputable sources may therefore provide significant help to some reporting countries and it is proposed that the IPCC Emission Factor Database (EFDB) act as the focal point for such data. However, while inclusion in the EFDB will provide a level of assurance that due process has been followed inventory compilers will remain responsible for assessing the appropriateness of such data for their purposes.

# A3.7 OTHER PRODUCT MANUFACTURE AND USE

The *1996 IPCC Guidelines* contained just two methods for estimating emissions of $SF_6$ from electrical equipment: (1) a potential approach that equated emissions to chemical consumption, and (2) a simple emission-factor-based approach that applied country-specific or global default emission factors to the quantities of $SF_6$ in operating and retiring equipment respectively. The *GPG2000* introduced three Tier 3 mass-balance methods and a more detailed Tier 2 emission-factor based approach that provided emission factors for each life cycle stage. In addition, the *GPG2000* provided regional default emission factors for the latter.

The *2006 IPCC Guidelines* simplify the *GPG2000* by (1) replacing two of the Tier 3 mass-balance methods with a single, flexible Tier 3 method that contains both mass-balance and emission-factor-based components. (2) moving the country-level mass-balance method to the QA/QC section, (3) moving the method for estimating potential emissions from the Methodological Choice discussion and into a separate section where it can be used for QA/QC, and (4) replacing the potential emissions approach with the default emission-factor-based approach, which has been moved from Tier 2 to Tier 1. These changes leave one Tier 3 method, one Tier 2 method, and one Tier 1 method. These *Guidelines* also update the regional emission factors provided in the *GPG2000*, providing values for additional types of equipment and for additional regions. Finally, these *Guidelines* incorporate new guidance on selecting and using alternative activity data when the preferred data are not available for all facilities. These updates incorporate the experience acquired over the past several years of reporting.

Specific methods for estimating emissions from research and industrial accelerators and from radar reconnaissance planes (e.g., AWACS) have been added to the 'Use of $SF_6$ and PFCs in Other Products' section. An indicative list of potential additional sources of $SF_6$ and PFCs has been added to guide the inventory preparer.

Also, Guidance on $N_2O$ emissions from product use such as medical application has been improved.

# A3.8 COMPLETENESS AND ALLOCATION OF $CO_2$ FROM NON-ENERGY USES OF FUELS

Two Quality Control (QC) approaches – a *$CO_2$ completeness check* and a *feedstock balance check* – have been introduced for checking the completeness of accounting $CO_2$ emissions from feedstock/reductant use of fossil fuels. Guidance is provided to facilitate the organisation and completion of this task: (a) checking that total reported bottom-up calculated $CO_2$ emissions from non-energy use sources (including uses as feedstock and reductant) at different subcategory levels are complete and consistent; and b) checking that feedstock/reductant requirements of processes included in the inventory are in balance with the non-energy use/feedstock supply as recorded in national energy statistics. Moreover, guidance is provided on documenting and reporting how these emissions are *allocated* in the inventory and how the completeness was checked (Section 1.4).

Section 1.3 provides an explanation of the principles which have guided the estimation and reporting of $CO_2$ emissions from the non-energy uses of fossil fuels, and describes the data issues related to the estimation methods.

# ANNEX 4

# GLOSSARY FOR INDUSTRIAL PROCESSES AND PRODUCT USE SECTOR

# ANNEX 4 GLOSSARY FOR INDUSTRIAL PROCESSES AND PRODUCT USE SECTOR

This annex provides definitions and abbreviations for terms used in this volume on Industrial Processes and Product Use (IPPU) Sector. This annex should be used in conjunction with the general 'Glossary' in Volume 1 of these Guidelines which provides definitions for terms used not only in this volume but also in the other volumes.

## Glossary

### ACETYLENE BLACK PROCESS

Thermal decomposition process to produce carbon black from acetylene.

### ADIPIC ACID (HEXANEDIOIC ACID)

A carboxylic acid primarily used in the chemical industry as an intermediate step in the production of nylon 6.6. It is commercially produced from cyclohexane by oxidation processes. The process of producing adipic acid produces nitrous oxide ($N_2O$) as a by-product.

### AMMOXIDATION

Process of conversion of olefin, paraffin, etc. to nitrile (R-CN) in the presence of ammonia ($NH_3$) and oxygen ($O_2$). A typical example is reaction of propylene ($C_3H_6$), ammonia and oxygen to produce acrylonitrile.

### ASPHALT

Asphalt is the mixed product of bitumen and aggregates (coarse or fine including sand), used for paving roads and pavements (i.e., sidewalks), also known as macadam, for roofing and industrial uses. Main asphalt types are: Hot Mix Asphalt (HMA), liquefied asphalt, cutback asphalt, slow-cure asphalts (synonym: road oil), emulsified asphalt and mastic asphalt. Cutbacks and emulsions are typically used as prime coats and tack coats; mastic asphalt for roofing. The mixture of aggregates (coarse or fine including sand) and hot bitumen when placed on the road, compacted and subsequently cooled, becomes the familiar asphalt. Aggregates make up approximately 90-96 percent of the asphalt mixture (asphalt binder makes up the other 4-10 percent). The term 'asphalt' in the USA is informally applied both to the bitumen (crude asphalt) that is a residue of the petroleum refining process and also to the 'asphalt binder' that is produced from bitumen and the 'asphaltic concrete' that is used for road paving and other applications.

### ASPHALT BINDER

Bitumen (crude asphalt) that has been prepared for use as a binder in Hot Mix Asphaltic Concrete and other paving applications. Asphalt binder is also sometimes referred to informally in the USA as 'asphalt cement'.

### ASPHALTIC CONCRETE

Asphaltic concrete consists of asphalt binder (bitumen, asphalt cement) and mineral aggregate mixed together, laid down in layers and compacted. Hot Mix Asphaltic Concrete (also referred to as Hot Mix Asphalt) is a combination of approximately 95 percent mineral aggregate bound together by asphalt binder that is heated prior to mixing. Asphaltic concrete is informally referred to in the USA as 'asphalt' or 'asphalt concrete'.

### BANK (FOR PURPOSES OF CHAPTERS 7 AND 8)

Banks are the total amount of substances contained in existing equipment, chemical stockpiles, foams and other products not yet released to the atmosphere. This terminology is traditionally used for substitutes for Ozone Depleting Substances and other fluorinated compounds.

### BASIC OXYGEN FURNACE (BOF)

Basic oxygen furnaces are the primary means of steel manufacture from pig iron and scrap steel. Oxygen is blown into the molten charge and oxidises the carbon present in the iron (about 4 percent) reducing it to the levels required for steel (about 0.5 percent). The carbon dioxide and carbon monoxide produced are carried away by the gas and dust collection system. The oxidation process heats the molten charge and helps melt the steel scrap added. Basic oxygen furnaces are also referred to as 'LD-converter' (or 'Linz-Donawitz converter') after the 'Linz-Donawitz' steelmaking process first developed in Austria.

### BITUMEN

Bitumen is a solid, semi-solid or viscous hydrocarbon with a colloidal structure, being brown to black in colour, occurring naturally or obtained as a residue in the distillation of crude oil, by vacuum distillation of oil residues from atmospheric distillation. It is a component of asphaltic concrete (typically 4 to 10 percent of the mixture) and serves to hold the aggregates (mineral matter that makes up the other part) together, generally used for construction of roads and for roofing material and in spray seal applications. Most (typically 80 to 90 percent) is used for paving of roads, typically 80 to 90 percent. Bitumen is usually stored at approximately 150°C to maintain it in a liquid form. In the USA bitumen is more commonly referred to as 'asphalt' or 'asphalt binder'.

### BLAST FURNACE

A furnace used in the iron and steel industry in which combustion is intensified by a blast of air, especially a furnace for smelting iron by blowing air through a hot mixture of ore, coke, and flux.

### BLOWN ASPHALT

Synonym for oxidised bitumen. Asphalt that has been treated by blowing hot air through it to produce physical properties required for the industrial use of the final product. Oxidised asphalts are typically used in roofing operations, pipe coating and hydraulic applications. Also known as 'air-blown asphalt' or 'air-refined asphalt'.

### BUSHING

A device that enables one or several electrical conductors to pass through a partition such as a wall or a tank and that insulates the conductors from it. The means of attachment (flange or fixing device) to the partition forms part of the bushing.

### CALCINATION

Chemical process in the manufacture of cement or lime in which the raw materials, primarily carbonates, are heated in kilns to produce a metallic oxide and carbon dioxide; e.g., $CaCO_3$ + heat = $CaO + CO_2$. More generally, calcination is a process of heat-induced driving off of structurally-bound volatiles other than water.

### CAPROLACTAM

Caprolactam ($NH(CH_2)_5CO$) is the monomer for nylon-6 fibres and plastics, with a substantial proportion of the fibre used in carpet manufacturing. Commercial processes for the manufacture of caprolactam are based on either toluene or benzene.

### CARBON BLACK FEEDSTOCK

A heavy aromatic oil that may be derived either as a by-product of the petroleum refining process or the metallurgical (coal) coke production process.

### CARBON MASS BALANCE CALCULATION (FOR PURPOSES OF SECTION 3.9)

A method of estimating total carbon emissions from a chemical process by identifying the mass flow rate and carbon content of each process stream flowing into the process and out of the process. The process streams to be considered include raw materials (i.e., feedstocks), supplemental fuels, primary products, secondary products, solid and liquid waste products, and exhaust gas streams (e.g., purge gas, off gas.)

### CARBONATES

Compounds containing the radical $CO_3^{-2}$. Upon calcination, the carbonate radical decomposes to evolve carbon dioxide ($CO_2$). Common carbonates consumed in the mineral industry include calcium carbonate ($CaCO_3$) or calcite; magnesium carbonate ($MgCO_3$) or magnesite; and calcium-magnesium carbonate ($CaMg(CO_3)_2$) or dolomite.

## CATALYST

A substance that accelerates the rate of a chemical reaction, but is not consumed as raw material and does not become a chemical product of the reaction.

## CATALYST SELECTIVITY

The percentage of the primary feedstock to the catalytic reaction process that is converted into the primary product of the process.

## CATALYTIC INCINERATION

Oxidation of organic compounds to $CO_2$ and $H_2O$ using a metal catalyst in a low temperature reaction. Catalytic incineration occurs at a lower temperature than thermal incineration.

## CATALYTIC OXIDATION

Generally referred to oxidation of feedstock (e.g., natural gas) to $CO_2$ and $H_2O$ using a catalyst.

## CEMENT KILN DUST (CKD)

Non-calcined to fully calcined dust produced in the kiln or pyroprocessing line. CKD may be partly or completely recycled to the kiln.

## CENTERLINE PROCESS

Centerline process refers to the nominal values of process variables that govern the performance specifications of commercial-ready manufacturing equipment. These are the nominal values for gas flows, chamber pressure, plasma power, etc. It is common for semiconductor device manufacturers to modify these conditions to optimize for particular requirements.

## CIRCUIT BREAKER

A mechanical switching device, capable of making, carrying and breaking current under normal circuit conditions and also making, carrying for a specified time and breaking current specified abnormal circuit conditions such as those of a short circuit.

## CLINKER

An intermediate product created at high temperature in a kiln during the manufacture of cement. In the kiln, calcium carbonate is calcined to lime (CaO) and carbon dioxide ($CO_2$). The CaO then reacts with silicon dioxide ($SiO_2$) and other oxides to form hydraulically reactive minerals (primarily calcium silicates) within semivitrified nodules called clinker. The clinker is then finely ground (typically with a small quantity of gypsum) to form cement. The $CO_2$ (both from calcination and from the combustion of kiln fuels) from clinker manufacture is normally released to the atmosphere as a waste product and is a significant global source of $CO_2$ emissions.

## CLOSED-PRESSURE SYSTEM

Electrical equipment that requires periodic refilling (topping up) with gas during its lifetime. This type of equipment generally contains between five and several hundred kilograms per functional unit. Transmission equipment normally falls into this category. In the latest IEC standards, the tightness of new closed pressure systems is specified by the relative leak rate of each compartment; standardized values for $SF_6$ are 0.5 percent and 1 percent per year. However, older closed pressure systems in the field may have significantly higher leak rates.

## COAL TAR

Liquid by-product formed from the distillation of bituminous coal to make coke. It is a viscous black liquid containing numerous organic compounds. Coal tar can be further distilled to give various aromatic compounds (distillates) and coal tar pitch (carbon pitch). Coal tar products are used as roofing, waterproofing, and insulating compounds and as raw materials for many dyes, drugs, and paints.

## COKE OVEN GAS

Obtained as a by-product of solid fuel carbonisation and gasification operations carried out by coke producers and iron and steel plants which are not connected with gasworks and municipal gas plants.

## COMBINED REFORMING

A combination of the conventional reforming process and catalytic oxidation reaction to produce methanol.

## CONVENTIONAL REFORMING

A combination of the steam reforming reaction to produce synthesis gas and the methanol-synthesis gas reaction to produce methanol.

## DESTRUCTION

In the case of a fluorinated greenhouse gas, ‘destruction’ means the process by which all or most of the compound is permanently transformed or decomposed into one or more stable substances which are not fluorinated greenhouse gases.

## DESTRUCTION OR REMOVAL EFFICIENCY (DRE)

Destruction or Removal Efficiency (DRE) means the efficiency, expressed as a decimal fraction (on a carbon or $CO_2$ equivalent basis), of a control device to destroy or remove all relevant contaminants. The DRE is equal to one minus the ratio of the amount of all relevant contaminants exiting the emission control device to the amount of all relevant contaminants entering the emission control device. Relevant contaminants mean any greenhouse gases covered by these Guidelines (see Volume 1, Chapter 8), including those formed during the destruction process.

## DIRECT CHLORINATION

Direct reaction of a compound to produce substituted chlorinated compounds, e.g., ethylene ($C_2H_4$) with chlorine ($Cl_2$) to produce ethylene dichloride.

## DIRECT REDUCED IRON

Also referred to as ‘sponge iron’; a metallic iron product obtained upon direct reduction of high grade iron ore pellets below the melting point of iron. The iron is reduced in the solid state without being converted into liquid form, as in a blast furnace.

## DISPOSAL EMISSIONS (FOR PURPOSES OF CHAPTER 8)

The emissions of fluorinated greenhouse gases that occur during the disposal or decommissioning of equipment. For the Tier 2 method (Equation 8.2), Disposal Emissions are defined to include emissions associated with the recovery of the gas, the recycling of the gas, and the destruction of the gas that is not recycled. For the Tier 3 method (Equations 8.7A and 8.7B), Disposal Emissions are defined to include emissions associated with the recovery of the gas. (Emissions associated with recycling and destruction are accounted for in separate Tier 3 equations.) Disposal emissions as defined for both Tiers are sensitive to the fraction of retiring equipment whose charge is recovered (Recovery Frequency) and to the fraction of the remaining charge that is recovered when recovery is performed (Recovery Efficiency).

## ELECTRIC ARC FURNACES (EAF)

The principal batch furnace type for the electric production of steel. The primary application of the EAF is for the remelting of steel scrap. However, EAFs can be charged with limited amounts of iron scrap, pig iron, and direct reduced iron. Heat is supplied from electricity that arcs from the graphite electrodes to the metal bath. The electrodes are usually made from graphite or from Soderberg (carbon) paste. EAFs are also used for other metallurgical applications, such as the production of ferroalloys and similar (silicon carbide).

## ELECTRICAL EQUIPMENT

Any item used for such purposes as generation, conversion, transmission, distribution or utilisation of electric energy, such as machines, transformers, apparatus, measuring instruments, protective devices and wiring systems. Most of the sulphur hexafluoride ($SF_6$) used in electrical equipment is used in gas-insulated switchgear and substations (GIS) and in gas circuit breakers (GCB), though some $SF_6$ is used in high voltage gas-insulated lines (GIL), outdoor gas-insulated instrument transformers and other equipment. In addition, perfluorocarbons (PFCs) are used in power transformers in some regions.

## ELECTRICAL EQUIPMENT FAILURE

A major or catastrophic failure of electrical equipment (in any function but gas containment itself) that results in the cracking or burning of one or more holes in a gas compartment and that therefore leads to the release of the charge in that compartment.

## EMISSION RATE

The emissions during a process, lifecycle stage, and/or defined period of time (usually a year), divided by the relevant activity data for that process or lifecycle stage, such as the total consumption of chemical for manufacturing or the Nameplate Capacity of the equipment for use. The preferred unit is percent per year.

## EQUIPMENT COUNT

An inventory of individual plant equipment (e.g., valves, flanges) that is used in implementing a leak detection program.

## ETHANE

A naturally occurring saturated hydrocarbon ($C_2H_6$) extracted from natural gas and refinery gas streams. It is mainly used in the production of ethylene by steam cracking.

## EXOTHERMIC

Chemical reaction where the energy content of the products is less than that of the reactants; heat is given out from the system.

## FACTORY FILLING EMISSIONS

Initial Charging Emissions that occur at the factory.

## FERROALLOY

Ferroalloy is the term used to describe concentrated alloys of iron and one or more metals such as silicon, manganese, chromium, molybdenum, vanadium and tungsten. Silicon metal production is usually included in the ferroalloy group because the silicon metal production process is similar to the ferrosilicon process. These alloys are used for deoxidising and altering the material properties of steel.

## FINAL USE EMISSIONS

The emissions that occur between the last refill of the equipment and its disposal. These may be a significant share of total emissions, particularly if the equipment has a low leak rate and is refilled infrequently.

## FLARE

Device to combust volatile organic compounds in exhaust gas streams without energy recovery.

## FLUORINATED COMPOUNDS (FCs)

Fluorinated compounds (FCs) is a term used in Chapter 6, ‘Electronics Industry Emissions’, to account for the broad range of high- and low (or zero)-GWP fluorinated gases and liquids used during electronics manufacturing. FCs include certain perfluorocarbons (PFCs), hydrofluorocarbons (HFCs) as well as sulphur hexafluoride ($SF_6$). Low (or zero)-GWP chemicals, such as $CH_2F_2$, $COF_2$ and $F_2$, are included when their use leads to the formation of high-GWP products such as $CF_4$.

## FURNACE BLACK

A type of carbon that is produced industrially in a furnace by incomplete combustion in an adjustable and controllable process that yields a wide variety of properties within the product (IUPAC).

## FURNACE BLACK PROCESS

Pyrolysis process to produce carbon black from carbon black feedstock and natural gas.

### GAS-INSULATED LINES

Metal-enclosed lines for electricity transmission and distribution in which the insulation is obtained, at least partly, by an insulating gas other than air at atmospheric pressure, with the external enclosure intended to be electrically grounded.

### HOT BRIQUETTED IRON

Direct reduced iron converted into briquettes, generally to facilitate the transportation of the material.

### HYBRID LIFE-CYCLE APPROACH

The Tier 3 method for estimating emissions from electrical equipment. This method estimates emissions by lifecycle stage using an emission-factor approach, a mass-balance approach, or a combination of the two, as appropriate given data availability and country- and process-specific circumstances.

### INCOMPLETE COMBUSTION.

Combustion of organic compounds in which the combustion results in less than 100 percent conversion of the organic compounds to $CO_2$ and $H_2O$. This may be due to a lack of oxygen or low temperature, preventing the complete chemical reaction. Carbon monoxide is produced as a by-product due to incomplete combustion.

### INITIAL CHARGING OR FILLING EMISSIONS

The emissions that occur during the initial filling of the equipment either in the factory or at the site where the equipment is to be used, as applicable.

### INSTALLATION EMISSIONS

Initial Charging Emissions that occur at the site where the equipment is to be used before the equipment is commissioned for operation.

### INSTRUMENT TRANSFORMER

A transformer intended to supply measuring instruments, meters, relays and other similar apparatus by converting the original system values for voltage and current into a replica suitable for data processing.

### LEAKAGE

The emissions from a piece or type of equipment during operation under normal operating conditions, excluding emissions from maintenance, service and electrical equipment failures.

### LEAK DETECTION PROGRAM

A program to directly measure emissions from fugitive emissions sources (e.g., valves, flanges) by measuring emissions from individual plant equipment.

### LEAK RATE

The Leakage from a piece or type of equipment over a given period of time, usually a year, divided by the Nameplate Capacity of the equipment. The preferred unit is percent per year.

### LIME KILN DUST (LKD)

Non-calcined to fully calcined dust produced in a lime kiln line. It is analogous to CKD, although LKD is only rarely recycled to the lime kiln. LKD can be used as a raw material in a cement kiln.

### LOSS RATE

Emission Rate.

### MANUFACTURING EMISSIONS

Emissions occurring on the premises and under the responsibility of the equipment manufacturer, including emissions from research and development, testing, and filling of equipment with operating or holding charges.

## MASS-BALANCE APPROACH (FOR PURPOSES OF CHAPTERS 7 AND 8)

A method for estimating emissions of fluorinated greenhouse gases from use in equipment that can be applied to individual units and to aggregates of units (for example by country, application or facility). In this approach, annual emissions are the difference between the quantity of gas consumed in the year and the quantity of gas used to fill the net increase in equipment capacity or to replace destroyed gas.

## METALLURGICAL COKE

Synonym for coke-oven coke. Coke, a high carbon fuel and/or reductant made by high temperature devolatilisation (carbonisation) of certain grades of bituminous coal, is a porous fuel with few impurities and high carbon content, mainly used in metallurgical processes such as in the blast furnace to make iron and in the manufacture of ferro-alloys, lead, and zinc. Semi-coke, the solid product obtained from carbonisation of coal at low temperature, is included with coke-oven coke and is used mainly as a domestic fuel. Not to be confused with petroleum coke.

## METERED DOSE INHALERS (MDIs) (MEDICAL AEROSOLS)

A method of dispensing inhaled pulmonary drugs.

## METHANOL

Also known as methyl alcohol, used especially as solvent, antifreeze, or denaturant. It is also used in the synthesis of other chemicals. Methanol produced from natural gas should be included with refinery feedstock figures.

## MINERAL PITCH

Residue of petroleum distillation. See ‘Asphalt’.

## NAMEPLATE CAPACITY

The full and proper charge of fluid/gas specified by the equipment manufacturer to achieve the equipment’s specified performance. The nameplate capacity is typically indicated on the equipment’s nameplate; it is not necessarily the actual charge, which may be influenced by leakage and other emissions. This definition is relevant to chapters 1, 6, 7 and 8 of this volume.

## NITRIC ACID

A strong acid used mainly as feedstock in fertiliser production and in the production of adipic acid. The production of nitric acid produces nitrous oxide ($N_2O$) as an unintended by-product.

## OLEFINS

Synonym for alkenes. Class of hydrocarbons with an open chain containing one or more double bonds. This group of hydrocarbons has the general formula $C_nH_{2n}$. Olefins are named after the corresponding paraffins by the addition of 'ene' or 'ylene' to the stem (e.g., polyethylene and polypropylene). The simplest olefin is ethylene, $C_2H_4$.

## OPEN HEARTH FURNACE

The open hearth furnace, also known as the reverberatory furnace, consists of a wide, saucer-shaped refractory-lined hearth with a low roof. Pig iron, limestone, and scrap are charged into the hearth and heated by overhead burners using preheated air, after which the furnace is charged with molten pig iron, which is further heated to produce steel. The burners are generally gas-fired.

## OXIDISED DURING USE FACTOR (ODU FACTOR)

A factor that represents the fraction of fossil fuel carbon that is oxidised during the use of non-energy products of fossil fuels.

## OXYCHLORINATION

Reaction of ethylene ($C_2H_4$) with hydrochloric acid (HCl) and oxygen ($O_2$) to produce ethylene dichloride and water ($H_2O$).

## OXYGEN STEEL FURNACE GAS

Obtained as a by-product of the production of steel in an oxygen furnace (or basic oxygen furnace): it is recovered on leaving the furnace. The gas is also known as converter gas or LD gas. Data should correspond to the quantity of gas used for the production of electricity or in cases where waste heat is recovered from the gas and sold to third parties. Quantities of this gas should be included with Blast Furnace Gas.

## OZONE-DEPLETING SUBSTANCES (ODS)

Substances known to deplete the stratospheric ozone layer. The ODSs controlled under the Montreal Protocol and its amendments are chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, methyl bromide ($CH_3Br$), carbon tetrachloride ($CCl_4$), methyl chloroform ($CH_3CCl_3$), hydrobromofluorocarbons (HBFCs), and bromochloromethane.

## PARAFFINS

Synonym for alkanes. The name paraffin often refers specifically to alkane molecules (isomers) having long straight chains. See also ‘Paraffin waxes’.

## PARAFFIN WAXES

Synonym for alkanes and paraffins. The name paraffin often refers specifically to alkane molecules (isomers) having long straight chains. These are saturated aliphatic hydrocarbons. These waxes are residues extracted when dewaxing lubricant oils. They have a crystalline structure which is more-or-less fine according to the grade. Their main characteristics are as follows: they are colourless, odourless and translucent, with a melting point above 45°C.

## PETROLEUM COKE (PETCOKE)

A shiny, black solid residue that is the final product of the condensation process in oil cracking and carbonisation in furnaces. It consists mainly of carbon (90 to 95 percent) and generally burns without leaving any ash. It is used mainly in metallurgical processes and as a fuel in cement manufacture. The term excludes those solid residues (metallurgical coke) obtained from carbonisation of coal. Sometimes one distinguishes between marketable coke or catalyst coke. Marketable coke is those grades of petroleum coke produced in delayed or fluid cokers that may be converted as relatively pure carbon. This ‘green’ coke may be sold as is or further purified by calcining. Catalyst coke is generated in many catalytic operations (e.g. catalytic cracking), where carbon is deposited on the catalyst, thus deactivating the catalyst. The catalyst is reactivated by burning off the carbon, which is used as a fuel in the refining process. This carbon or coke is not recoverable in a concentrated form.

## PITCH

Any of various dark heavy viscid substances obtained as a residue. Coal tar pitch is a component of the coal tar derived from metallurgical [coal] coke production in coke ovens, and is used in roofing, anode production, and other industrial applications. Mineral pitch is derived as a residue of petroleum distillation. The term ‘pitch’ is sometimes incorrectly used to describe bitumen or asphalt. Note that with respect to ‘coal tar’ the terms ‘coal tar’ and ‘coal tar pitch’ [carbon pitch] are not synonymous.

See: http://www.koppers.com/htm/PandS_Proc_Main.html

## PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION (PECVD)

Plasma enhanced chemical vapor deposition (PECVD) refers to chemical vapor deposition in which a radio frequency plasma is coupled to a low-pressure gaseous reaction mixture to facilitate the formation of the desired deposit (thin film) on a substrate located in the reaction chamber. Film formation occurs at lower temperatures with plasma versus without plasma. PECVD is used to deposit silicon dioxide, silicon nitride and silicon oxynitride films. During fabrication of a 16 Mbit DRAM device PECVD is used to deposit more than 20 layers. In addition to formation of volatile by-products, which are removed by gas flow through the reaction chamber, film deposition inexpediently forms on the reaction-chamber walls, which if not routinely cleaned will diminish process performance. Chamber cleaning is accomplished with FCs, using either an *in-situ* or a *remote* plasma cleaning step. Cleaning is accomplished by F-atoms (which are produced through plasma-induced dissociation of the FC) reacting with the inexpeediently deposited silicon to form the gas $SiF_4$, which is pumped from the chamber. Cleaning is complete when $SiF_4$ is no longer present in the chamber effluent.

## PLASMA ETCHING

Plasma etching refers to a method for the carefully controlled (isotropic or anisotropic) removal of material (typically silicon and aluminum) during the fabrication of very (or ultra) large scale integrated circuits. Either radio or microwave frequency radiation is coupled into a low pressure gas-mixture to ionise (plasma formation) and dissociate the gas molecules into more reactive constituents. The gas-mixture typically contains halogens such as fluorine (F), chlorine (Cl), bromine (Br) or iodine (I). Through photolithography and appropriate plasma chemistries, plasma-formed etchants directly and selectively transfer intricate patterns onto an underlying substrate. Isotropic etching is used to planarize metal layers of aluminum. To create a trench capacitor structure in a memory cell requires more than 20 different etching steps. Of the 400 or so process steps to fabricate a 16 MBit DRAM device, more than 50 are plasma etching steps (of course not all will use an FC).

## PLUME

The flow of pollutants from a process stack or vent into the atmosphere.

## POWER TRANSFORMER

A static piece of apparatus with two or more windings which, by electromagnetic induction, transforms a system of alternating voltage and current into another system of voltage and current usually of different values and at the same frequency for the purpose of transmitting electrical power.

## POZZOLANS

A siliceous material that in itself is not cementitious, but which develops hydraulic cement properties when it reacts with free lime (CaO) and water. Common examples of pozzolans include natural pozzolans (e.g., certain volcanic ashes or tuffs, certain diatomaceous earths, burned clays and shales) and synthetic pozzolans (e.g., silica fume, fly ash).

## PURGE GAS

A gas stream separated from a chemical process stream to remove impurities from the process, including volatile organic compounds, carbon monoxide, hydrogen, or other compounds. The purge gas may be burned for energy recovery or flared, or secondary products may be recovered from the purge gas.

## RECLOSERS

A self-controlled device for automatically interrupting and reclosing an alternating current circuit, with a predetermined sequence of opening and reclosing followed by resetting, hold-closed, or lock-out operation.

## RECOVERY

The collection and storage of fluorinated greenhouse gases from equipment and containers.

## RECOVERY AND DESTRUCTION EFFICIENCY (RDE)

This term is used primarily in the context of foams as a method of defining the overall efficiency of recovery and destruction of fluorinated gases as a percentage of the fluorinated gases that were in the foam or other product immediately prior to the commencement of the recovery process. Accordingly, this measure takes into consideration all losses associated with the recovery process as well as the destruction process and is thus distinguished from Destruction Efficiency (DE) and Destruction & Removal Efficiency (DRE) which are both limited to the activity of the destruction facility only. More information on the term is contained in the UNEP Task Force Report on Foam End-of-Life issues (2005).

## RECOVERY EFFICIENCY

The quantity of fluorinated greenhouse gas recovered from equipment divided by the quantity of fluorinated greenhouse gas remaining in the equipment at service or decommissioning (end of life).

## RECOVERY FREQUENCY

The fraction of equipment whose charge is recovered before the equipment is opened for service or is disposed of at end of life.

## REDUCTANT

Within the Guidelines the term relates to the use of carbon as reducing agent for the reduction of metal oxides to metals, e.g. iron and aluminium, in furnaces or electrolytic processes and to the use of carbon in the production of specific inorganic products, e.g., carbides and soda ash.

## REFRIGERANT (REFRIGERATION)

A heat transfer agent, usually a liquid, used in equipment such as refrigerators, freezers and air conditioners.

## RING MAIN UNIT

A term describing a standard piece of switchgear for secondary distribution purposes in medium voltage systems. A Ring Main Unit is typically composed of switches/Load break switches for switching power cable rings and of switches/load break switches in series with fuses for protection of distribution transformers (transformers from medium to low voltage).

## ROAD OIL

Any heavy petroleum oil, including residual asphaltic oil, that is used as a dust suppressant or surface treatment on roads and highways. It is generally produced in six grades from 0, the most liquid, to 5, the most viscous. Road oil was applied to gravel roads as a dust suppressant for many years. It was most commonly used in rural areas which often had a high proportion of unpaved roads and used oil markets (burning and re-refining) were located some distance away. The use of road oil for dust suppression has declined in recent years because of reductions in the proportion of unpaved roadways, the presence of highly toxic contaminants in used oils, competition from other used oil end uses (re-refining), and new environmental regulations. Synonym for slow-cure liquid asphalt.

## SEALED-FOR-LIFE EQUIPMENT

Sealed-Pressure Systems.

## SEALED-PRESSURE SYSTEM

Electrical equipment that does not require any refilling (topping up) with gas during its lifetime and which generally contains less than 5 kg of gas per functional unit. Distribution equipment normally falls into this category. To ensure that no refills are required during the approximately 40-year lifetime of the equipment, the Leak Rate for Sealed-Pressure Systems is generally less than 0.1 percent per year.

## SECONDARY PRODUCT

A saleable product that is produced by a chemical process in addition to the primary product produced by the process. For example, steam cracking for ethylene production produces ethylene as its primary product, but also produces saleable propylene, butadiene, and other secondary products.

## SHIFT REACTION

The reaction of carbon monoxide (CO) and steam ($H_2O$) to produce carbon dioxide ($CO_2$) and hydrogen ($H_2$)

## SITE ERECTION EMISSIONS

Installation Emissions.

## SLAG

A silicate byproduct or co-product of metal smelting; the largest source of slag is the iron and steel industry. Slag is formed through the interaction of slagging (and/or fluxing) agents (commonly silica plus limestone and/or dolomite and/or lime) and the metallic ores.

## SLAGGING AGENT

A material, such as limestone, dolomite, lime, and silica sand, which serves, through the formation of a slag, to strip impurities from ores, during the smelting of metallic ores. Slagging agents commonly perform a dual function as a flux.

## SLAKED LIME

Common name for calcium hydroxide (CaOH) that results from the hydration of high calcium or dolomitic lime.

## SODA ASH (SODIUM CARBONATE, $Na_2CO_3$)

Soda ash is a white crystalline solid that is used as a raw material in a large number of industries including glass manufacture, soap and detergents, pulp and paper production and water treatment. Four different processes may be used commercially to produce soda ash. Three of these processes, monohydrate, sodium sesquicarbonate (trona) and direct carbonation, are referred to as natural processes. The fourth, the Solvay process, is classified as a synthetic process.

## SOLVENT

The component of a solution that is present in the greatest amount. It is the substance in which the one or more substances – the so-called solutes – are dissolved forming a homogenous mixture. An example of a solid dissolving into a liquid, is salt or sugar dissolving in water; but also gases may dissolve into liquids, like carbon dioxide or oxygen in water, and liquids and gases into themselves. Fossil fuels used as solvent are notably white spirit and kerosene (paraffin oil). White spirit is used as an extraction solvent, as a cleaning solvent, as a degreasing solvent and as a solvent in aerosols, paints, wood preservatives, lacquers, varnishes and asphalt products. White spirit is used in paints, lacquers and varnishes; it is the most widely used solvent in the paint industry.

## STATE-OF THE ART HANDLING EQUIPMENT

Equipment that handles $SF_6$ at any stage of the equipment's life cycle in a manner that minimizes emissions of $SF_6$. Such equipment typically includes a compressor, a vacuum pump, filtering units, a storage container, an evaporator, hoses and connections, piping and junctions, control instruments and (self-closing) safety valves. Most important with regard to recovery emissions is the technical capability of the vacuum pump, which should be designed for evacuation down to 1 mbar. This capability, properly used, will keep handling losses below 2 percent of the equipment's nameplate capacity.

## STEAM CRACKING

The reaction of saturated hydrocarbons (e.g., ethane) with steam ($H_2O$) in a furnace to produce unsaturated hydrocarbons (e.g., ethylene.).

## STEAM REFORMING

The process of reaction of a hydrocarbon or alcohol fuel, such as natural gas or methanol, with steam to form hydrogen as a product. This is the commonly preferred method of bulk hydrogen generation. At high temperatures (700-1100 °C), steam reacts with methane ($CH_4$) to yield synthesis gas (carbon monoxide (CO) and hydrogen ($H_2$)).

## STOICHIOMETRIC RATIO

Stoichiometry refers to the quantitative relationship between reactants and products in a chemical reaction. In the Minerals industry, the stoichiometric ratio is used to determine the amount of carbon dioxide ($CO_2$) released per unit of carbonate input, and can be expressed as the molecular weight of $CO_2$ divided by the molecular weight of carbonate (e.g., 44.01g $CO_2$ / 100.09 g $CaCO_3$).

## SUPPLEMENTAL FUEL

Fuel provided to a chemical process, in addition to the primary feedstock to the process, to provide additional heat to the process.

## SWITCH

A mechanical switching device, capable of making, carrying, and breaking current under normal circuit conditions, i.e., carrying the nominal load current. A switch is also called a load break switch to distinguish it from a circuit breaker. Typically switches or load break switches are used also in combination with fuses in one or more poles in series in an composite unit such as ring main units for secondary distribution purposes.

## SWITCHGEAR

A general term covering switching devices and their combination with associated control, measuring, protective and regulating equipment, also assemblies of such devices and equipment with associated interconnections, accessories, enclosures and supporting structures, intended in principle for use in connection with generation, transmission, distribution and conversion of electric energy.

## SYNTHESIS GAS

A mixture of hydrogen and carbon monoxide, used to produce methanol and other chemicals.

## TAIL GAS

The exhaust gas from a chemical process.

## TAR

A viscous black liquid derived from the destructive distillation or pyrolysis of organic matter. Most tar is produced from coal as a by-product of metallurgical coke production in coke ovens, but it can also be produced from oil, peat or wood. See also ‘Coal tar’.

## THERMAL BLACK PROCESS

Thermal decomposition process to produce carbon black from carbon black feedstock and natural gas.

## THERMAL TREATMENT

Combustion of organic compounds to $CO_2$ and $H_2O$ using a flame in a high temperature reaction. Thermal treatment may occur with or without energy recovery.

## THIN-FILM TRANSISTOR (TFT)

Thin-film transistor (TFT) is the circuit element that enables frequent refreshing of flat panel displays, the circuit element that controls each pixel (or picture element) in the most common type of active matrix display. TFTs, which can be manufactured using both amorphous silicon technology on glass, plastic or thin-metal substrates and low-temperature polysilicon (LTPS) technology on glass or plastic substrates, are used in liquid crystal displays (LCDs) and increasingly in organic light emitting diode (OLED) and polymer organic light emitting diode (POLED) displays.

## TITANIUM DIOXIDE ($TIO_2$)

Titanium dioxide is the most important white pigment. The main use is in paint manufacture followed by paper, plastics, rubber, ceramics, fabrics, floor covering, printing ink, and other miscellaneous uses.

## USE EMISSIONS (FOR PURPOSES OF CHAPTER 8)

The emissions from a piece or type of equipment between its installation and disposal or between its installation and final refill, depending on the context. Use Emissions include emissions during operation, maintenance, and service of the equipment, as well as emissions associated with equipment failures. Use Emissions include and are generally significantly larger than Leakage, particularly when State-of the Art Handling Equipment is not used. In these Guidelines, Use Emissions associated with the Emission Factor Approach (Tiers 1, 2, and the Emission-Factor variant of Tier 3) include Final Use Emissions, while Use Emissions associated with the Mass-Balance Approach (the Mass-Balance variant of Tier 3) exclude Final Use Emissions.

## USE EMISSION RATE (FOR PURPOSES OF CHAPTER 8)

The Use Emissions over a given period of time, usually a year, divided by the Nameplate Capacity of the equipment. The Use Emission Rate includes emissions during operation, maintenance, and service of the equipment, as well as emissions associated with equipment failures. In general, the Use Emission Rate is significantly higher than the Leak Rate. In these Guidelines, the Use Emission Rate associated with the Emission Factor Approach (Tiers 1, 2, and the Emission-Factor variant of Tier 3) includes Final Use Emissions.

## VENTING

Controlled release of natural gas and waste gas/vapour streams.

### WHITE SPIRIT

Refined distillate intermediates with a distillation in the naphtha/kerosene range between 135°C to 200°C. In contrast, industrial spirits (specific boiling point, SBP) are light oils distilling between 30°C and 200°C. There are 7 or 8 grades of industrial spirit, depending on the position of the cut in the distillation range. The grades are defined according to the temperature difference between the 5 percent volume and 90 percent volume distillation points (which is not more than 60°C). White spirit is an industrial spirit with a flash point above 30°C.

# Abbreviation

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| AGO | Australian Greenhouse Gas Office |
| APME | Association of Plastics Manufacturers Europe |
| AWACS | Airborne Warning and Control System |
| BAT | Best Available Techniques |
| BFC | Blast Furnace Gas |
| BOF | Basic Oxygen Furnace (steelmaking) |
| BREF | Best Available Techniques Reference Documents (under European Integrated Pollution Prevention and Control Bureau.) http://eippcb.jrc.es/pages/FActivities.htm |
| C4 + | By-product hydrocarbons containing more four or more carbon atoms (e.g., butanes, pentanes, hexanes, heptanes) |
| $CaCO_3$ | Calcium carbonate |
| CaO | High calcium lime |
| $Ca(OH)_2$ | Slaked high-calcium lime |
| $Ca(OH)_2$• $Mg(OH)_2$ | Slaked dolomitic lime |
| CaO·MgO | Dolomitic lime |
| CKD | Cement Kiln Dust |
| CIGRE | International Council on Large Electric Systems |
| COG | Coke Oven Gas |
| DOE | United States Department of Energy |
| DRE | Destruction or Removal Efficiency |
| DRI | Direct Reduced Iron |
| EAF | Electric Arc Furnace (steelmaking) |
| EDC | Ethylene Dichloride |
| EG | Ethylene Glycol |
| EO | Ethylene Oxide |
| FEPC | The (Japanese) Federation of Electric Power Companies |
| FGD | Flue Gas Desulphurisation |
| FgH-ISI | Fraunhofer-Institut für Systemtechnik und Innovationsforschung |
| GCB | Gas Circuit Breakers |
| GIL | Gas Insulated Lines |
| GIS | Gas Insulated Switchgear and Substations |
| GIT | Gas Insulated power Transformers |
| HBI | Hot Briquetted Iron |
| HMA | Hot Mix Asphalt |
| HV (Switchgear) | High Voltage (Switchgear) for rated operating voltages above 52 000 Volts |
| IEC | International Electro-technical Commission |
| ITs | Instrument Transformers |
| JEMA | The Japan Electrical Manufacturer's Association |
| LKD | Lime Kiln Dust |

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|---|---|
| LVOC | Large Volume Organic Chemical |
| LVIC | Large Volume Inorganic Chemical |
| $MgCO_3$ | Magnesium carbonate |
| MV (Switchgear) | Medium Voltage (Switchgear) for rated operating voltages above 1 000 Volts and up to 52 000 Volts |
| OHF | Open Hearth Furnace (steelmaking) |
| PC | Portland cement |
| PECVD | Plasma Enhanced Chemical Vapor Deposition |
| RDE | Recovery and Destruction Efficiency |
| TFT | Thin-Film Transistor |
| VCM | Vinyl Chloride Monomer |