



CHAPTER 2
INDUSTRIAL PROCESSES



2. INDUSTRIAL PROCESSES

2.1 Overview

Greenhouse gas emissions are produced from a variety of industrial activities which are not related to energy. The main emission sources are industrial production processes which chemically or physically transform materials. During these processes, many different greenhouse gases, including CO₂, CH₄, N₂O, and PFCs, can be released. Cement production is a notable example of an industrial process that releases a significant amount of CO₂. Different halocarbons (and SF₆) are also consumed in industrial processes or used as alternatives to ozone depleting substances (ODS) in various applications. Table 2-1 gives an overview of potential industrial emission sources of GHGs and ozone and aerosol precursors (NO_x, NMVOCs, CO and SO₂).

In some instances industrial process emissions are produced in combination with fuel combustion emissions and it may be difficult to decide whether a particular emission should be reported within the energy or industrial processes sector. Where the main purpose of the fuel combustion is to use the heat released, the resulting emissions are included as energy emissions, not industrial process emissions. There are, however, some chemical processes or stages of processes, which oxidise carbon as a feedstock and are exothermic. The reduction of iron in a blast furnace through the combustion of coke is an example. Invariably the heat released is used within the processes or for other energy needs of the producer. However, in this case, since the primary purpose of coke oxidation is to produce pig iron, the emissions are considered to be industrial.

In some cases not all fuel feedstock delivered to petrochemical plants is used for manufacture of other products. Some feedstock may in fact be used for energy purposes in the sense that it is combusted for the heat released. This may be included as energy in the national energy balance, but not necessarily. The separation of the feedstock and energy uses and the identification of any fuel by-products from the processes is a notoriously difficult area of energy statistics.

Where a country has difficulty in distinguishing whether an emission is energy- or industrial-based, compilers of industrial-process emissions statistics should liaise closely with their energy counterparts and compare their basic data for fuel use in the industrial processes to avoid double counting.

All emissions, including evaporative emissions, which occur in energy transformation activities are discussed in the Energy Chapter. Emissions from petrochemical processes are, however, covered in this chapter. Emissions of NMVOCs from use of solvents are discussed in the chapter "Solvents and other product use" even if they originate from an industrial process.

CO₂ from use of biological carbon as feedstock and fermentation processes should not be reported under "Industrial Processes" or any other sector of the *IPCC Guidelines* if they originate from sources of carbon that are from a closed cycle.

Non-combustion industrial processes resulting in N₂O emissions are recognised as important anthropogenic contributors to global N₂O emissions. It is estimated that this source category represents 10 to 50 per cent of anthropogenic N₂O emissions and 3 to 20 per cent of all global emissions of N₂O (IPCC, 1992). The main sources of industrial anthropogenic N₂O emissions are adipic acid and nitric acid production.

Hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF₆) are used as alternatives to ozone depleting substances being phased out under the Montreal Protocol. Current and expected applications of these compounds include refrigeration and air-conditioning, fire extinguishing, aerosols, solvents, and foam production. These chemicals are either emitted instantaneously or slowly being leaked out over time. Many of these compounds have high global warming potentials (GWPs) and long atmospheric lifetimes. Consumption of HFCs, and to some extent PFCs and SF₆, is expected to grow substantially in the next decades due to their importance as substitutes for ozone depleting substances.

HFCs, PFCs and SF₆ are also emitted from industrial processes, such as production of aluminium, magnesium and halocarbons (e.g., HCFC-22). In some countries PFC emissions from industrial processes could be an important contributor to national GHG emissions, due to high GWPs.

Much of the information on the greenhouse gases contained within this chapter is based on four key documents: "Anthropogenic Emissions of CO₂, CH₄ and N₂O in Norway", (Rypdal, 1993), "Greenhouse gas emissions in Norway", Norwegian Pollution Control Authority (1994), "Workbook for Industrial Emissions and Solvent Use", National Greenhouse Gas Inventory Committee, Australia (Workbook, Australia, 1995), and the previous version of the Industrial Processes Chapter in the *IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC, 1995). In addition, several experts, within and outside of the Industrial Processes Expert Group, have contributed to this chapter.



**TABLE 2-1
POTENTIAL EMISSIONS FROM INDUSTRIAL PROCESSES.**

Process	Greenhouse Gases						Ozone and Aerosol Precursors			
	CO ₂	CH ₄	N ₂ O	PFC	SF ₆	HFC	NO _x	NMVOC	CO	SO ₂
Mineral Products										
Cement production	x									x
Lime production	x									x
Limestone use	x									
Soda Ash prod. and use	x									
Asphalt roofing								x	x	
Road paving							x	x	x	x
Other	x	x					x	x	x	x
Chemical industry										
Ammonia	x						x	x	x	x
Nitric acid			x				x			
Adipic acid			x				x	x	x	
Urea			x							
Carbides	x	x						x	x	x
Caprolactam			x							
Petrochemicals		x	x			x		x		x
Metal Production										
Iron, steel and ferroalloys	x	x					x	x	x	x
Aluminium	x	x		x	x		x	x	x	x
Magnesium	x				x		x	x	x	x
Other metals	x	x			x		x	x	x	x
Other										
Pulp and paper							x	x	x	x
Food and drink production								x		
Production of halocarbons				x	x	x				
Use of halocarbons and SF ₆				x	x	x				
Other sources	x	x	x	x	x	x	x	x	x	x

The table does not necessarily cover all potential GHGs or industrial sources. A cross in the table does not imply that the emission estimations methodology is available in this report or that the emission of a given source and gas is significant.

2.2 General Methodology

2.2.1 Overview

The general methodology employed to estimate emissions associated with each industrial process involves the product of activity level data, e.g., amount of material produced or consumed, and an associated emission factor per unit of consumption/production according to the following method:

$$\text{TOTAL}_{ij} = A_j \times \text{EF}_{ij}$$

where:

- TOTAL_{ij} = process emission (tonnes) of gas i from industrial sector j
- A_j = amount of activity or production of process material in industrial sector j (tonnes/yr)
- EF_{ij} = emission factor associated with gas i per unit of activity in industrial sector j (tonne/tonne)

This general method represents the fundamental relationship to evaluate industrial process emissions. It should be noted, however, that a number of mathematical steps may be involved in reducing more complex mathematical formulae to the simplified form of the formula above. In cases where mathematical transformations are involved, justifications are presented.

Often process emissions from a certain industrial sector are caused by emissions from a few plants in each country. Therefore, measurement data are often available. Emission estimates should be based on such data if they exist instead of a more generalised methodology. Even if measurements are not available, calculations should preferably be based on plant-specific data.

2.2.2 Approaches to Avoid Double Counting of CO₂

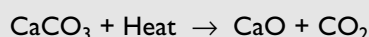
The IPCC Methodology for national GHG inventories requires an intentional double reporting of NMVOCs, methane and carbon monoxide, firstly in their individual inventories, and as CO₂ equivalent in the national CO₂ inventory. Whether an explicit addition to the CO₂ inventory is required depends on how the national CO₂ inventory has been calculated. Guidance on this point is contained under "Double Counting of Emissions" (See Overview) contained in each volume of the *IPCC Guidelines*.



2.3 Cement Production

2.3.1 Overview

Carbon dioxide emitted during the cement production process represents the most important source of non-energy industrial process of global carbon dioxide emissions. Cement production accounts for about 2.4 per cent of total global industrial and energy CO₂ emissions (Marland et al., 1989). Carbon dioxide is produced during the production of clinker and intermediate product from which cement is made. High temperatures in cement kilns chemically change raw materials into cement clinker (greyish-black pellets about the size of 12 mm-diameter marbles). Specifically, calcium carbonate (CaCO₃) from limestone, chalk or other calcium-rich materials is heated, forming lime (calcium oxide or CaO) and carbon dioxide in a process called calcination or calcining:



This lime combines with silica-containing materials, provided to the kiln as clays or shales, to form dicalcium or tricalcium silicates, two of the four major compounds in cement clinker (Griffin, 1987). The clinker is then removed from the kiln, cooled, and pulverised into an extremely fine grey powder. During this operation a small amount of gypsum is added to regulate the setting time of the cement. The finished product is called "Portland" cement¹.

It should be noted that when poured concrete is curing, some CO₂ is reabsorbed by the concrete from the atmosphere. This CO₂ reabsorption is, however, believed to be only a small fraction of the CO₂ emission resulting from cement production and is therefore usually ignored in emission calculations.

Most of the cement currently produced in the world is of Portland cement type, which contains 60 per cent to 67 per cent lime by weight. Other speciality cements are lower in lime, but are typically used in small quantities. Research is underway on cement formulations that have similar structural properties to Portland cement, but require less lime (Tresouthick and Mishulovich, 1990). Carbon dioxide emissions from cement production are essentially directly proportional to lime content, so production of cements lower in lime yield less CO₂.

Because CO₂ is emitted during clinker production (rather than cement production itself), emission estimates should be based on the lime content and production of *clinker*. Estimating emissions based on the lime content and production of *finished cement* ignores the consideration that some domestic cement may be made from imported clinker, or that some finished cement may use additional lime that is not accounted for in the cement calculations. Clinker statistics, however, may not be readily available in some countries. If this is the case, cement statistics can be used. The differences between the lime content and production of clinker and cement, *in most countries*, are not significant enough to affect the emission estimates.

¹ In some countries, e.g., Japan, an effort has been made to substitute blast furnace slag for lime. If this non-Portland type forms a significant quantity of cement production, it can reduce the average emission factor.

2.3.2 Emission Estimation Methodology for CO₂

Estimation of CO₂ emissions from cement production is accomplished by applying an emission factor, in tonnes of CO₂ released per tonne of clinker produced, to the annual clinker output.² The emission factor (EF) is the product of the fraction of lime used in the cement clinker and a constant reflecting the mass of CO₂ released per unit lime.

$$EF_{\text{clinker}} = \text{Fraction CaO} \times (44.01 \text{ g/mole CO}_2 / 56.08 \text{ g/mole CaO})$$

or

$$EF_{\text{clinker}} = \text{Fraction CaO} \times 0.785$$

There are two methods for calculating this emission factor. The first is to assume an average CaO fraction in clinker. Since clinker is mixed with gypsum, which contains no lime per unit, to make cement, clinker has a higher lime percentage than finished cement. The average clinker lime percentage has been estimated to be 64.6 per cent.³ This number when multiplied by the molecular weight ratio of CO₂/CaO (0.785) gives a clinker emission factor of 0.5071 tonnes of CO₂/tonne of clinker produced.

$$EF_{\text{clinker}} = 0.646 \times 0.785 = 0.5071$$

A second method is to assemble country or regional data on clinker production by type and clinker CaO content by type, then calculate a weighted average for cement lime content in the country. In most countries, the difference in the results of these two methods is likely to be small; any error in the lime content assumption is likely to be smaller than the uncertainty in clinker and cement production figures (Griffin, 1987).

If information on clinker production is not readily available, an emission factor in tonnes of CO₂ released per tonne of cement produced can be applied to annual cement production instead. This approach has been followed by Marland et al. (1989), who took the average CaO content of cement to be 63.5 per cent, yielding an emission factor of 0.4985 CO₂/cement (0.136 tonne CO₂ as C/tonne cement).

$$EF_{\text{cement}} = 0.635 \times 0.785 = 0.4985$$

Additional research indicates that "masonry cement", as opposed to "Portland cement", requires additional lime, over and above the lime used in its clinker. The following formula can be used to account for this activity:

² Note that the estimation of CO₂ from energy use during cement production is explained in the energy chapter; these emissions should be reported under Energy: Fuel Combustion activities.

³ Gregg Marland, ORNL, personal communication.



$$a \times (\text{All Cement Production}) \times \left(\frac{1-1/(1+b)}{1+b} \right) \times c \times 0.785$$

$$=$$

$$\text{tonnes CO}_2 \text{ from CaO added to masonry cement}$$

where:

- a = fraction of all cement produced that is masonry cement (e.g., 0.1-0.2)
- b = fraction of weight added to masonry cement by non-plasticiser additives such as lime, slag, and shale (e.g., 0.03, 0.05)
- c = fraction of weight of non-plasticiser additives that is lime (e.g., 0.6-0.8)

$$a \times (\text{All Cement Production}) = \text{masonry cement production}$$

$$\left(\frac{1-1/(1+b)}{1+b} \right) \times c = \text{fraction of lime in masonry cement not attributable to clinker}$$

$$\left(\frac{1-1/(1+b)}{1+b} \right) \times c \times 0.785 = \text{an emission factor of CO}_2 \text{ from masonry cement additives}$$

The recommended method for estimating CO₂ emissions from cement production is to multiply the most reliable figures available for tonnes of clinker produced by an emission factor of 0.5071 tonne CO₂/tonne clinker. Alternatively, cement production can be multiplied by an emission factor of 0.4985 tonne CO₂/tonne cement.

International cement production data are available from the United Nations (1988) and from the U.S. Bureau of Mines (1988). In some countries, national data may be available from appropriate government ministries. There is substantial overlap between the U.S. Bureau of Mines and the UN data sets, but the former is more complete. Published information is also available from the European Cement Association (CEMBUREAU, 1990).

2.3.3 Emissions Estimation Methodology for SO₂

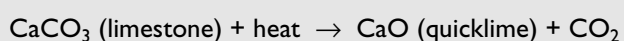
EMEP/CORINAIR has classified cement production as both an industrial combustion and an industrial process (SNAP codes 30311 and 40612, respectively). However, no description of emission factors for the non-combustion emissions are presented. A default methodology is, therefore, presented below.

SO₂ emissions will originate from sulphur in the fuel and in the clay raw material. Most (about 70-95 per cent) of the SO₂ generated in the process will be absorbed in the produced alkaline clinker (U.S. EPA 1995). The fuel emissions are counted as energy emissions while the SO₂ from the clay should be counted as non-combustion emissions. A non-combustion emission factor of 0.3 kg SO₂/tonne cement has been calculated from measurements in Norwegian plants (Rypdal 1995). This factor may vary from plant to plant as the sulphur content of raw materials and degree of absorption will vary. If no information on sulphur content and degree of absorption is available and there are no measurement data, a factor of 0.3 kg SO₂/tonne cement is suggested.

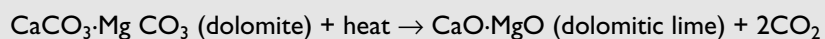
2.4 Lime Production

2.4.1 Overview

Calcined limestone (or quicklime) is formed by heating limestone to decompose the carbonates. This is usually done at high temperatures in a rotary kiln and the process releases carbon dioxide. 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 processed in this manner from the quarried limestone to produce quicklime in accordance with the following reaction:



Hydrated (slaked) lime is also produced, with additional hydration operations, at some facilities. Dolomitic limestone or magnesite may also be processed at high temperature to obtain dolomitic lime (and release CO_2) in accordance with the following reaction:



The production of lime involves a series of steps comparable to those used in the production of Portland cement clinker. These include quarrying the raw materials, crushing and sizing, calcining (i.e., high temperature heat processing $\sim 1100^\circ \text{C}$) the raw materials to produce lime, hydrating the lime to calcium hydroxide followed by miscellaneous transfer, storage and handling operations.

2.4.2 Emissions Estimation Methodology for CO_2

The mass of CO_2 produced per unit of lime manufactured may be estimated from the molecular weights and the lime content of products. On the basis of the calcination reaction, one mole of carbon dioxide is formed for each mole of quicklime produced from burning calcium carbonate. This was used to derive an emission factor based on the amount of quicklime produced (ORTECH, 1991), assuming complete dissociation of the carbonate rock and no reabsorption of CO_2 by lime in the kiln. In instances where dolomitic limestone is calcined, the emission factor was derived based on the lime: magnesia product (ORTECH, 1991). The emission factors are tabulated in Table 2-2.

For high calcium lime, CO_2 emissions are estimated according to:

$$\begin{aligned} \text{EF} &= 44.01 \text{ g/mole CO}_2 / 56.08 \text{ g/mole CaO} \\ &= 785 \text{ kg CO}_2 / \text{tonne high calcium lime} \end{aligned}$$



For dolomitic lime, CO₂ emissions are estimated according to:

$$\begin{aligned} \text{EF} &= 2 \times 44 \text{ g/mole CO}_2 / 96.39 \text{ g/mole CaO} \cdot \text{MgO} \\ &= 913 \text{ kg CO}_2 / \text{tonne dolomitic lime} \end{aligned}$$

The coefficient 2 relates to the stoichiometric ratio of CO₂ to CaO·MgO in the calcination process.

Both formulas assume pure lime, but in some cases the purity may range from 85 to 95 per cent (Workbook, Australia, 1995). In these cases, the formulas should be adjusted according to the lime purity.

Process	Component	Emission Factor	Reference
Lime Kiln-Calcite Feed	CO ₂	0.79 tonnes CO ₂ /tonnes quicklime produced	ORTECH, 1991
Lime Kiln-Dolomite Feed	CO ₂	0.91 tonnes CO ₂ /tonnes dolomitic lime	ORTECH, 1991

The consumption of lime may in cases result in the removal of CO₂ from the atmosphere. The use of hydrated lime (for water softening) for example, results in CO₂ reacting with lime to form calcium carbonate. Lime is also used as a CO₂ absorbent for atmospheric control in the storage of fruit. At this time, data is not available to reliably estimate the extent of atmospheric CO₂ removal from the use of lime.

2.4.3 Emissions Estimation Methodology for SO₂

Details for deriving emissions for this sector are not yet available. SO₂ should be considered. The non-combustion emissions will depend on the sulphur content and mineralogical form (pyrite or gypsum) of the stone feed, the quality of the lime produced and the type of kiln (U.S. EPA 1995). In this process, SO₂ emissions from combustion will usually exceed the non-combustion emissions (U.S. EPA 1995). Until more information becomes available, it is recommended that only emissions from fuel combustion (Energy Chapter) are considered.

2.5 Limestone and Dolomite Use

2.5.1 Overview

Limestone (CaCO₃) and dolomite (CaCO₃·MgCO₃) are basic raw materials having commercial applications in a number of industries including metallurgy (e.g., iron and steel), glass manufacture, agriculture, construction and environmental pollution control. In industrial applications involving the heating of limestone or dolomite at high temperatures, CO₂ is generated.

CO₂ from liming of soils should be reported in the Land-use Change and Forestry Chapter. Limestone and dolomite used in cement and lime production should be reported under that industry sector. Under this section are inventoried all other uses of limestone and dolomite which produce CO₂ emissions.

2.5.2 Emissions Estimation Methodology for CO₂

The mass of CO₂ emitted from the use of limestone and dolomite may be estimated from a consideration of consumption, purity of the raw materials and the stoichiometry of the chemical processes.

Emission factor, EF_{ls}, for limestone use:

$$\begin{aligned} EF_{ls} &= f \times [44.01 \text{ g/mole CO}_2] / [(100.09 \text{ g/mole CaCO}_3)] \\ &= (440 \times f) \text{ kg CO}_2 / \text{tonne limestone} \end{aligned}$$

where:

f is the fractional purity of limestone in CaCO₃ per tonne of total raw material weight (if unknown, the default factor for f is equal to 1).

Emission factor, EF_{ld}, for dolomite use:

$$\begin{aligned} EF_{ld} &= f \times [2 \times 44.01 \text{ g/mole CO}_2] / [(184.41 \text{ g/mole CaCO}_3 \cdot \text{MgCO}_3)] \\ &= (477 \times f) \text{ kg CO}_2 / \text{tonne dolomite} \end{aligned}$$

The total CO₂ emission from limestone and dolomite use in Gg/yr calculated as:

$$\begin{aligned} \text{Total}_{ld} &= \{(A_{ls} \times EF_{ls}) + (A_d \times EF_d)\} / 10^6 \\ &= \{(440 \times f \times A_{ls}) + (477 \times f \times A_d)\} / 10^6 \end{aligned}$$

where:

Total_{ld} is the process emission of CO₂ from limestone and dolomite use (Gg/yr)

A_{ls} is the consumption of limestone (tonnes/yr). Consumption is assumed to equal material mined (or dredged) plus material imported minus material exported. The consumption entering this calculation excludes limestone used for producing cement and lime, agriculture and processes where CO₂ is not generated.

A_d is the consumption of dolomite (tonnes/yr). Consumption is assumed to equal material mined plus material imported minus material exported. The consumption entering this calculation excludes limestone used for producing lime and magnesium, and processes where CO₂ is not generated.



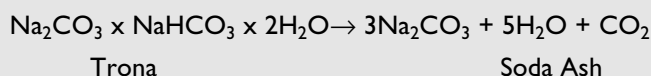
2.6 Soda Ash Production and Use

2.6.1 Overview

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 is emitted from the use of soda ash, and may be emitted during production, depending 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, sesquicarbonate and direct carbonation, are referred to as natural processes. The fourth, the Solvay process, is classified as a synthetic process.

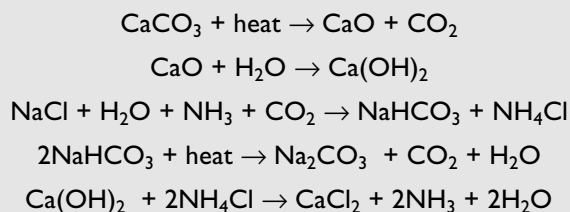
About 25 per cent of the world production is produced from natural sodium carbonate-bearing deposits referred to as natural processes. During the production process, trona (the principal ore from which natural soda ash is made) is calcined in a rotary kiln and chemically transformed into a crude soda 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:



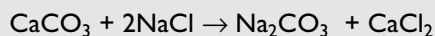
According to this reaction, it takes 10.27 tonnes of trona to produce 1 tonne of carbon dioxide. Hence, for natural soda ash production, emissions of carbon dioxide can be calculated by the following formula:

$$\text{EF} = 0.097 \text{ tonne CO}_2 / \text{tonne of Trona}$$

About 75 per cent of the world production is synthetic ash made from sodium chloride. In the Solvay process, sodium chloride brine, limestone, coke and ammonia are the raw materials 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 presented as follows:



The net overall reaction may be summarised as:



From the series of reactions presented above, CO₂ is generated in two pyrolysis processes. The CO₂ generated is captured, compressed and directed to Solvay precipitating towers for consumption in a mixture of brine (aqueous NaCl) and ammonia. Although CO₂ is generated as a by-product, the carbon dioxide is recovered and recycled for use in the carbonation stage and in theory the process is neutral, i.e., generation of CO₂ equals uptake.

In practice, however, CO₂ is emitted to the atmosphere during the production of soda ash because more CO₂ is produced than is stoichiometrically required. The excess CO₂ is produced by calcining limestone with metallurgical grade coke (approximately 7 per cent of limestone weight). In order to avoid double counting, CO₂ emissions associated with the use of coke in soda ash production should be accounted for separately and those emissions associated with the non-energy use of coke subtracted from the totals in the combustion section.

Carbon dioxide emissions are associated with the use of soda ash. Some of the major uses include glass manufacture, chemicals, soaps, detergents and flue gas desulphurisation. For each of these uses, it is assumed that for each mole of soda ash use, one mole of CO₂ is emitted (U.S. EPA, 1994b).

2.6.2 Emission Estimation Methodology for CO₂

Soda Ash Production

From stoichiometric considerations, the industrial process emission of CO₂ associated with the Solvay process is zero. The excess CO₂ emitted from soda ash production originates from coke oxidation (see the Energy Chapter for appropriate emission rate for coke combustion and use appropriate national statistics on coke use in soda ash production). For processes utilising trona, emissions can be calculated by the following formula:

$$\text{EF} = 0.097 \text{ tonne CO}_2 / \text{tonne of Trona}$$

During the production of soda ash in the Solvay process, calcium chloride is produced. In cases where calcium chloride is discharged to the sea, calcium chloride dissolves to form calcium and chloride ions. Calcium ions in turn take part in a number of chemical reactions, including the sequestering of carbonate ions to form calcium carbonate which represents a sink for CO₂. Available experimental data from Australia indicate that approximately 0.23 tonnes of CO₂ is sequestered from the ocean for each tonne of soda ash produced (Workbook, Australia, 1995).



Soda Ash Use

For each mole of soda ash use, one mole of CO₂ is emitted, so that the mass of CO₂ emitted from the use of soda ash may be estimated from a consideration of consumption data and the stoichiometry of the chemical process as follows:

$$\begin{aligned} \text{EF} &= 44.01 \text{ g/mole CO}_2 / 105.99 \text{ g/mole Na}_2\text{CO}_3 \\ &= 415 \text{ kg CO}_2/\text{tonne Na}_2\text{CO}_3 \end{aligned}$$

2.7 Production and Use of Miscellaneous Mineral Products

2.7.1 Asphalt Roofing Production

This is the production of saturated felt, roofing and siding shingles and roll roofing and sidings. Most of these products are used in roofing and other building applications. Emissions from these processes can be estimated from the national total mass of products. The emission factors in Table 2-3 given in the EMEP/CORINAIR Guidebook (SNAP 40610) are default factors.

	Emission Factor (Saturation with Spray)	Emission Factor (Saturation without Spray)
NM VOC	0.13 - 0.16	0.046 - 0.049
CO	NAV	0.0095
NAV = Not Available		

Asphalt blowing (SNAP 60310) 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. The blowing may take place in a refinery, an asphalt processing plant or an asphalt roofing plant. This activity leads to emissions of NM VOC. The emission factors in the EMEP/CORINAIR Guidebook range from 0.1 to 30 kg total organic compounds/tonne asphalt blown depending on the degree of control and it may be assumed that all the mass of asphalt used for non-paving use will be blown.

2.7.2 Road Paving with Asphalt

Asphalt road surfaces are composed of compacted aggregate and asphalt binder. Gases are emitted from the asphalt plant, the road surfacing operations and from the subsequent road surface. The emissions of NMVOC depend on the type of asphalt (slow, medium or rapid cure) and the amount of diluent. Emission factors given in Table 2-4 use the default assumptions given in the EMEP/CORINAIR Guidebook (SNAP 40611). The amount of diluent used is usually lower in warm countries than in the colder, and hence lower emission factors may be expected in warm countries.

	SO ₂	NO _x	CO	NMVOC
Asphalt Plant	0.12	0.084	0.035	0.023
Road Surface	NAV	NAV	NAV	320

If the tonnes of asphalt paved is not known but rather the area paved, a conversion factor of 100 kg asphalt/m² road surface may be used.

2.7.3 Production of Other Mineral Products

There may be several other mineral production processes emitting pollutants. These are probably not significant on a global scale, but may be significant on a national or local scale. There is generally little information about emissions from these processes.

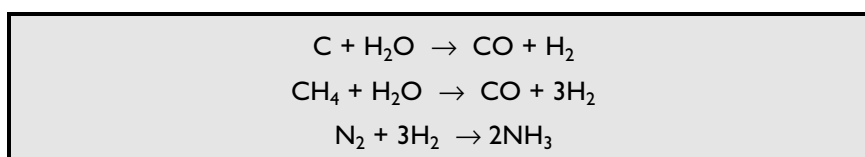
One emission source is the production of concrete pumice stone. As for cement production, SO₂ emissions will originate from the fuel use and sulphur in clay. About 45 per cent of the SO₂ generated in the process will be sequestered in the product. An emission factor of about 0.5kg SO₂/tonne product has been calculated from measurements in Norwegian plants (Rypdal 1995), and used where plant-specific data are not available.

NMVOCs may be emitted from manufacture of glass. An emission factor of 4.5 kg/tonne product has been derived from CASPER (1995).

2.8 Ammonia Production

2.8.1 Overview

In most instances, anhydrous ammonia is produced by catalytic steam reforming of natural gas (mostly CH₄) or other fossil fuels. As can be seen in the following reactions with methane as a feedstock, carbon dioxide is produced.





In general, the processes that affect CO₂ emissions in the production of ammonia 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 CO₂ to methane with nickel catalysts to purify the synthesis gas.

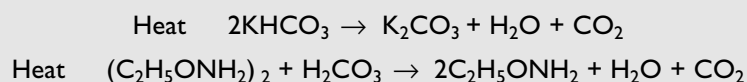
Natural gas is used as the feedstock in most plants, while other fuels (e.g., heavy oils) may be used with the partial oxidation process. In addition, plants may use by-product hydrogen, rather than natural gas, to produce ammonia (thereby eliminating the release of CO₂ from the synthesis process) (CFI, 1992). The production of ammonia represents a significant non-energy industrial source of CO₂ emissions.

2.8.2 Process Description

The primary release of CO₂ at plants using the natural gas catalytic steam reforming process occurs during regeneration of the CO₂ scrubbing solution with lesser emissions resulting from condensate stripping.

Carbon Dioxide Regenerator

After absorption of CO₂ 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 CO₂ from the bicarbonates according to the following reactions:



The stripping gas, containing CO₂ 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 CO₂ 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).

2.8.3 Emission Estimation Methodology for CO₂

Emissions of CO₂ will depend on the amount and composition of gas (or oil) used in the process. It is assumed that all carbon will be emitted to air. It is recommended that inventory contributions are compiled using point source methods due to the rather limited number of plants. Where greatest accuracy is desired, this will require direct contact with producers. Alternatively, total sector emissions may be determined on an area source basis using available emission factors and methods noted below.

The most accurate method of estimation will be:

$$\text{Emission (kt)} = \text{Consumption of gas (kt)} \times \text{carbon content} \times 44/12$$

If the gas consumption is not available, an alternative is to calculate the emissions from the ammonia production:

$$\text{Emission (kt)} = \text{Production of ammonia} \times \text{Emission factor}$$

In both cases, in order to avoid double counting, the quantities of oil or gas used must be subtracted from the quantity reported under energy and non-energy use in the Energy Chapter.

The CO₂ from ammonia production may be used for producing urea or dry ice. This carbon will only be stored for a short time. Therefore, no account should consequently be taken for intermediate binding of CO₂ in downstream manufacturing processes and products.

Emission Factor Information

If the emissions are calculated from the gas or oil consumption, the standard emission factors suggested in the energy chapter will be relevant. The carbon content of natural gas may vary, and it is recommended that this is determined for each plant.

Some emission factors related to the production of ammonia are shown in Table 2-5.

Country	Emission Factor ^{a,b} Tonne CO ₂ /tonne NH ₃ produced	Reference
Canada ^c	1.6	Jaques, 1992 Industrial Chemicals, 1980
Norway	1.5	Norsk Hydro, 1996

^a Reductions should be applied to account for any ammonia that is produced from by-product hydrogen.
^b Figure for Norway excludes gas used as a fuel. It is not clear if this is included in the Canadian figure. The figures are dependent on the carbon content in the feedstock.
^c Assumes 812 m³ gas/tonnes NH₃ and 0.525 kg carbon/m³ gas.

2.8.4 Emission Estimation Methodology for Ozone Precursors and SO₂

The production of ammonia is described in Section 2.8.1. However, emission methods have not yet been developed for the EMEP/CORINAIR Guidebook (SNAP 40403).

SO₂, NO_x, CO and NMVOC may be emitted in addition to CO₂. Default emission factors for uncontrolled emissions in Table 2-6 are taken from U.S. EPA 1995.



	SO ₂	TOC ^a	CO
Desulphurisation	0.03	3.6	6.9
Carbon dioxide regenerator	NE	0.5	1.0
Condensate steam stripper	NE	0.6	NE
Total	0.03	4.7	7.9

^a Total organic compounds
NE = negligible

There will usually be few ammonia plants in a country, and it is recommended that emissions from plant specific data be estimated.

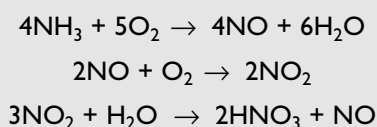
2.9 Nitric acid Production

2.9.1 Overview

The production of nitric acid (HNO₃) generates nitrous oxide (N₂O) as a by-product of the high temperature catalytic oxidation of ammonia (NH₃).

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.

Nitric acid production involves three distinct chemical reactions:



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 N₂O. Nitric oxide (NO), an intermediate in the production of nitric acid, is also documented to readily decompose to N₂O and nitrogen dioxide (NO₂) at high pressures for a temperature range of 30 to 50°C (Cotton and Wilkinson, 1988).

2.9.2 Emission Data of N₂O

Table 2-7 gives examples of emissions factors from nitric acid production plants, based on measurements. Emission rates depend upon technology and operating conditions.

	Emission Factor kg N ₂ O/tonne nitric acid	Reference
USA	2-9 ^a	Reimer et al., 1992
Norway: - modern, integrated plants	<2	Norsk Hydro, 1996
- atmospheric pressure plants	4-5	“
- medium pressure plants	6-7.5	”
Japan	2.2-5.7	Japan Environment Agency, 1995
<small>a. Emission factors up to 19 kg N₂O/tonne nitric acid have been reported for plants not equipped with non-selective catalytic reduction technology (NSCR) (Choe et al., 1993; Olivier, 1996; Oonk, 1996).</small>		

2.9.3 Emission Estimation Methodology for N₂O

There are usually only very few plants in each country producing nitric acid, so measured data on N₂O emissions are often available. These data also take into account the effect of any abatement technology installed at the specific plants. Emissions vary significantly from one plant to another, and if measured data are available, emission estimates should be based upon such data. Every effort should therefore be made to obtain measurement data.

However, if such data are not available, emissions should be calculated from production data of nitric acid within a country, and specific emission figures based on the actual technology, for which Table 2-7 can be consulted. When no measured data exist, specific emission factors at the upper end of the appropriate range should be chosen.

$$\text{N}_2\text{O-emissions} = \text{Production level} \times \text{Specific Emission Factor}$$

2.9.4 Emission Estimation Methodology for NO_x

Nitric acid is produced from the catalytic oxidation of ammonia. The process is described in Section 2.9.1 and in the EMEP/CORINAIR Guidebook (under SNAP 40402). In addition to the GHGs described in Section 2.9.1, there may be non-combustion emissions of NO_x.

Emissions are estimated from the amount of nitric acid produced. Factors range from 0.1- 1.0 NO_x/tonnes acid produced for the direct strong acid production process to 10-20 kg/tonnes acid produced for the low pressure process. 12.0 kg NO_x/tonnes nitric acid should be used where the process and technology details are not known.

There will usually be few nitric acid plants in a country, and it is recommended that emissions are calculated from plant specific data.

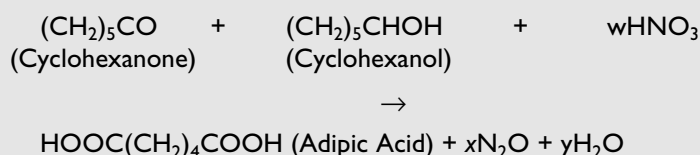


2.10 Adipic Acid Production

2.10.1 Overview

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.

Adipic acid is a dicarboxylic acid manufactured by a two-stage process. The first stage of manufacturing involves the oxidation of cyclohexane or cyclohexanone to form a cyclohexanone/cyclohexanol mixture. The mixture is then oxidised by nitric acid in the presence of a catalyst to form adipic acid. N_2O is generated as a by-product of the nitric acid oxidation stage:



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.

2.10.2 Emission Estimation Methodology for N_2O

Adipic acid production unavoidably produces N_2O as a by-product with an associated emission factor (for unabated emissions) of 300g N_2O /kg adipic acid produced (Thiemens and Trogler, 1991). Japanese emissions (measured at 264 g N_2O /kg adipic acid) are consistent with this value (Japan Environment Agency, 1995).

$$\begin{array}{c} N_2O \text{ emissions (kg)} = \text{Adipic Acid Production(tonnes)} \\ \times 300 \text{ kg } N_2O / \text{tonne Adipic Acid} \end{array}$$

Often, the abatement of N_2O results from the treatment of the off-gases⁴ in a reductive furnace. A number of adipic acid producers treat the off-gases with the aim of reducing NO_x emissions, but the treatment also destroys N_2O (Reimer et al., 1992).

There is a range of abatement efficiencies attainable with currently available technologies. Any reduction in N_2O emissions due to the installation of abatement systems should be assessed on a plant-specific basis where possible.

⁴ "Off-gases" are gases that are released from the process.

2.10.3 Emission Estimation Methodology for Ozone Precursors

The production of adipic acid is described in Section 2.10.1 and (under SNAP 40521) in the EMEP/CORINAIR Guidebook.

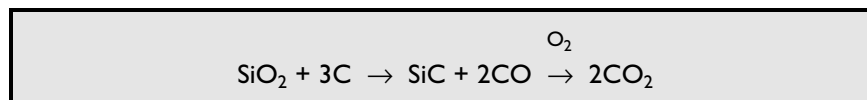
The EMEP/CORINAIR Guidebook indicates that there may be emissions of CO₂, NO and NO₂ in addition to N₂O, but does not propose emission factors at present. Furthermore, European reported emission data indicate that pollutants other than N₂O are not significant (CORINAIR-90). U.S. EPA emission factors are given in Table 2-8 (U.S. EPA 1995).

NO _x	CO	VOC
8.1	34.4	43.3

2.11 Carbide Production

2.11.1 CO₂ and CH₄ from Silicon Carbide Production

In the production of *silicon carbide*, CO₂ is released as a by-product from a reaction between quartz and carbon. Petrol coke is used as a carbon source. Silicon carbide is extremely hard and is widely used as an abrasive. The formula describing the reaction is given below but in practice it does not proceed in the stoichiometric proportions indicated.



Some carbon, about 35 per cent, is sequestered in the product.

Generally, the emissions from silicon carbide production can be calculated from a mass balance approach as:

$$\text{CO}_2 \text{ emissions (tonnes)} = A \times C (100-S) \times 3.67 \times 10^{-4}$$

where:

- A = consumption of coke in tonnes
- C = per cent carbon content in coke
- S = per cent carbon input sequestered in product



Typical default values for Norwegian plants for C (carbon content in coke) are 97 per cent and for S (sequestered carbon in product), 35 per cent. This implies a typical emission factor of 2.3 tonnes CO₂/tonne coke.

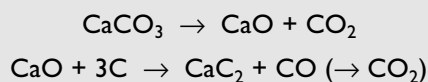
More carbon is actually needed in the process than calculated from a stoichiometric reaction. The suggested emission factors are calculated from coke input in Norwegian plants. The excess carbon is oxidised during the process, little is left as ash (Raanes, 1991).

The petrol coke used in this process may contain volatile compounds which will form methane. Some of this methane will escape to the atmosphere, particularly during the start up. Measurements at Norwegian plants suggest emission factors of 10.2 kg/tonne petrol coke or 11.6 kg/tonne carbide product.

2.11.2 CO₂ from Calcium Carbide Production

Calcium carbide is made by heating calcium carbonate and subsequently reducing CaO with carbon (e.g., petrol coke). Both steps lead to emissions of CO₂. Some carbon will be sequestered in the product. The most important application of calcium carbide is producing acetylene. Consequently, the sequestering will be for a short time only (less than a few years) and may be disregarded. On the other hand Ca(OH)₂ is produced as a by-product in the acetylene production. This Ca(OH)₂ will react with CO₂ to form CaCO₃. Hence, the CO₂ emitted from the limestone may be said to be recycled.

Production of CaC₂:



Use of carbide:



The CO gas will in most plants be utilised as energy. 1.8 tonnes CO₂/tonne calcium carbide will be released in the production process. In addition, 1.1 tonnes CO₂/tonne calcium carbide will be released when the carbide is used. The CO₂ emissions may be lowered by utilising the gas when producing dicyanodiamide from carbide (Olsen 1991).

Limestone contains about 98 per cent CaCO₃. 1750 kg limestone (or 950 kg CaO) and 640 kg reducing agent (including 20 kg carbon electrodes) are required to produce 1 tonne carbide.

Emissions may be calculated from the use of raw materials (limestone and coke) or from the production.

The emission factors in Table 2-9 are suggested in the latter case:

Limestone	760
Reduction	1090
Use of product	1100

The theoretical emission factor calculated from a stoichiometric reaction is 1.37 tonne CO₂/tonne carbide (for the carbonate and coke step). Excess carbon is however oxidised in the process. The suggested emission factors are 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.

Also note that the CaO (lime) might be produced at another plant than the carbide plant. In this case, the emissions from the CaO step should be reported as emissions from lime production (Section 2.4) and only the emissions from the reduction step and use of product should be reported as emissions from calcium carbide production.

2.11.3 Precursors and SO₂ from Carbide Production

Emission methods have not yet been developed for the EMEP/CORINAIR Guidebook. SO₂ is potentially emitted from the production processes due to sulphur in the raw coke material.

Silicon carbide: The emissions are most accurately calculated from the consumption of coke, the sulphur content of the coke, and the degree of control. In addition, CO is emitted due to incomplete oxidation of carbon coke. An emission factor of 0.4 tonne CO/tonne petrol coke has been determined for Norway (Rosland 1987), but this factor will be highly plant specific.

Calcium carbide: Nearly 100 per cent of the SO₂ potentially emitted will be sequestered in the product (Rypdal 1995, Rosland 1987). An emission factor of 1.5 kg SO₂/tonne coke is given in U.S. EPA 1995, but no experimental methods or assumptions are given. CO is generated in the process, but is usually oxidised in the process, used as a fuel or flared. This should be checked for the relevant plants.

2.12 Production of Other Chemicals

2.12.1 N₂O Emissions

Production of chemicals other than nitric acid and adipic acid may be sources of nitrous oxide, but more studies are needed to determine whether they represent a significant source of N₂O. Production of caprolactam, acrylonitrile, and catalytic cracking of oil, may be significant sources. Generally, suggested sources are related to either a process using a N-compound or a catalytic reduction step. Compared to emissions associated with



adipic acid and nitric acid production, the N₂O emissions from this source category will probably be small.

Caprolactam is a widely used chemical intermediate. Most of the 3 million tonnes produced per year is used in the production of nylon-6 (Fisher and Crescenti, 1994). Different methods are used for the manufacture of caprolactam. They are all based on catalytic oxidation of ammonia. In the Netherlands, caprolactam production was identified as a significant industrial source of N₂O (Kroeze, 1994).

In order to increase the yield of gasoline from oil, certain fractions from the oil are treated in a catcracker. Crude oil contains some nitrogen, and the nitrous oxide emissions from the cracking process may be significant. Depending on the regional market for light and medium-light oil products, catalytic cracking is more or less important in a specific region. A few studies on emissions from this source have been performed in the Netherlands but presently data are not available to suggest a methodology (Oonk, 1996).

Therefore, a general recommended method for estimation of N₂O emissions from these sources is not given here.

2.12.2 CH₄ Emissions

Although most methane sources from industrial processes individually are small, collectively they may be significant.

Chemical manufacturing processes, e.g., carbon black, ethylene, dichloroethylene, styrene and methanol, are potential sources of methane. However, sources other than those mentioned here may be of importance.

Few data on emissions are presently available. These are presented in Table 2-10:

TABLE 2-10 EMISSION FACTORS (G CH ₄ /KG PRODUCTION)		
	Emission factor (g CH ₄ /kg production)	Reference
Carbon black	11	Shareef et al., 1988, Stockton and Stelling 1987.
Ethylene	1	Shareef et al., 1988, Stockton and Stelling 1987.
Dichloroethylene	0.4	Shareef et al., 1988, Stockton and Stelling 1987.
Styrene	4	Shareef et al., 1988, Stockton and Stelling 1987.
Methanol	2	Shareef et al., 1988, Stockton and Stelling 1987.
Coke	0.5	Schade, 1980, Barnard, 1990.

2.12.3 Emissions of Ozone Precursors and SO₂

This section is concerned with emissions from small point sources. However, total emissions from these sources may be important. Only a simple methodology is suggested here. It should be noted that some of these sources may be individually very important in certain countries. In these cases a more detailed methodology should be used, based on plant specific data. The EMEP/CORINAIR Guidebook and the U.S. EPA guidelines should be consulted for advice on detailed methodologies and process descriptions.

A summary of default emission factors and ranges is given in Table 2-11. Ranges given for VOC emissions from many processes are quite large. Emission factors are likely to be quite process specific. For instance, polystyrene is manufactured in various grades by batch or continuous process. Higher emission factors are associated with the lower molecular weight of polystyrenes. The variation in emission factors from plants using the continuous process is quite large, depending upon the type of vacuum system employed (U.S. EPA 1995).

Evaporative emissions from petrochemical industries may be higher in warm than in temperate countries.



TABLE 2-11
EMISSION FACTORS FOR MISCELLANEOUS PRODUCTION PROCESSES IN CHEMICAL INDUSTRIES.
(KG/TONNE PRODUCT)

Source	SNAP	SO ₂	NO _x	NMVOC	CO
Acrylonitrile	40520	-	-	1 (0.4-100)	-
Acrylonitrile Butadiene Styrene (ABS) Resins	40515	-	-	27.2 (1.4-27.2)	-
Carbon black	40409	3.1	0.4	40 (5-90)	10 (5-14)
Ethylbenzene	40518	-	-	2 (0.1-2)	-
Ethylene and propylene	40501/40502	-	-	1.4	-
Formaldehyde	40517	-	-	5 (0-8)	-
Graphite	40411	-	-	NAV	-
Phthalic anhydride	40519	-	-	6.0 (1.3-6.0)	-
Polypropylene	40509	-	-	12 (0.35-12)	-
Polystyrene	40511	-	-	5.4 (0.2-5.4)	-
Polyethene - Low density	40506	-	-	3	-
Polyethene - Linear low density	-	-	-	2	-
Polyethene - High density	50507	-	-	6.4	-
Polyvinylchloride	40508	-	-	8.5 (0.14-8.5)	-
Styrene	40510	-	-	18 (0.25-18)	-
Styrene butadiene	40512-14	-	-	NAV	-
1,2, dichloroethane	40503	-	-	7.3 (0.2-7.3)	-
Sulphuric acid	40401	17.5 (1-25)	-	-	-
Titanium dioxide	40410	14.6 (0.9-14.6)	-	-	-
Urea	40408	NAV	NAV	NAV	NAV
Vinyl chloride ^a	40504				
1,2, dichloroethane	40505	-	-	2.2	-

Source: EMEP/CORINAIR guidebook, except the CASPER project (CASPER 1995).

^aThe emission factors should be used for the monomer and polymer separately even if they are produced at the same plant unless otherwise specified.

NAV = Not available.

Note: Ranges in brackets.

2.13 CO₂ Emissions from Metal Production

2.13.1 CO₂ from Metal Production - General Methodology

With a few exceptions, commercial production of metals from ores requires the use of carbon as a reducing agent. If the ore contains carbonate, CO₂ originating from the ore will also be emitted during production. On the other hand, carbon may also be sequestered in the metal.

The metal may be reduced by using coal, coke, prebaked anodes and coal electrodes. Wood chips and charcoal may also be used in some of the processes, but the resulting CO₂ emissions are not counted in Chapter 2 as net emissions. These net emissions of CO₂ should, however, be reported in the Land-Use Change and Forestry Chapter. Coke is produced from coal or refinery residuals (petrol coke). Prebaked anodes and electrodes are produced from coal. By-product fuel (coke oven gas and blast furnace gas) are produced in some of the processes. These fuels may be sold or used within the plant. They may or may not be included in the national energy balance. Care should consequently be taken not to double count emissions.

The following general formula may be used to estimate the emissions:

$$\text{Mass Reducing Agent} \times \text{Emission Factor} + (\text{Carbon ore} - \text{Carbon metal}) \times 3.67 = \text{Emission (tonnes CO}_2\text{)}$$

The first part of this formula (the amount of reducing agent used combined with an emission factor) will usually be most important and probably be sufficient for making a first estimate of the emissions.

The emission factors in Table 2-12 are suggested as default.

Reducing Agent	Emission Factor ^a
Coal ^b	2.5
Coke from coal ^b	3.1
Petrol coke	3.6
Prebaked anodes and coal electrodes	3.6
^a If better information on actual carbon content is not available nationally or cannot be calculated from data in the Energy Chapter. ^b Derived from data in the Energy Chapter	

In addition, CO₂ will be emitted from baking (prebaked anodes). In the aluminium industry about 5 per cent of the non-combustion CO₂ emissions using the prebaking technology will be from baking. No data is available for other metal industries using prebaked anodes.



2.13.2 Overview of Emissions of Ozone Precursors and SO₂ from Metal Production

Production of most metals may generate emissions of SO₂, CO, NO_x and NMVOC. Emissions of SO₂ originate from sulphur in the reducing agents and in the ores. The emissions will also depend on control technologies and the extent to which sulphur is sequestered in the products.

NO_x is produced primarily by the high temperature oxidation of nitrogen in air. In metal production, most NO_x emissions usually occur as a result of fuel combustion. However, high temperature metal production processes (such as roasting and reduction), which occur in the presence of air, will also produce nitrogen oxides. These NO_x emissions are in principle included in this section, but are often impossible to distinguish from the fuel NO_x.

CO is formed due to incomplete oxidation of the reducing carbon. This CO may in many plants be used as a fuel, and double counting of emissions already counted as energy must be avoided.

In addition, small amounts of NMVOCs may be emitted during parts of some of the processes, especially those involving coal.

2.13.3 Iron and Steel

2.13.3.1 Overview

Iron is produced through the reduction of iron oxide (ore) using metallurgical coke as the reducing agent in a blast furnace. Steel is then subsequently made from iron and scrap in other furnaces.

This sector includes two types of facilities. Large integrated primary iron and steel plants have coking, smelting and refining capacities to produce steel from raw coal and iron ore. Other, smaller plants produce iron and steel from coke generated off-site. The coke oven used at an integrated plant is identical to that used at off-site coking facilities. In the integrated plant, coke oven gases (COGs) are used both for oven under firing and combustion in the blast furnace and other parts of the process.

Common to all plants is a blast furnace, which reduces raw ore to molten pig iron by heating in the presence of carbon and oxygen. Coke, the source of carbon, has been estimated to be consumed at a rate of about 450 kg/tonne of hot metal (Rankin and Wright, 1992). "Flux" in the form of limestone (CaCO₃) or dolomite is also added to the furnace at a rate of about 250 kg/tonne of iron (U.S. EPA 1986).

Steel may be produced in a basic oxygen furnace (BOF), an electric arc furnace (EAF), an induction furnace or an open hearth furnace. The open hearth type is the oldest technology. Low carbon steel is produced in a BOF, where a mixture of pig iron and iron scrap is remelted in the presence of pure oxygen, which oxidises the dissolved carbon to carbon monoxide or carbon dioxide. Carbon and alloy steels are produced in an EAF, a refractory-lined pot which utilises electric heating through graphite electrodes which are consumed in the process. This type is charged with 100 per cent scrap iron.

2.13.3.2 Emission Estimation Methodology for CO₂

Process emissions of carbon dioxide in an iron and steel plant take place primarily as a result of coke oxidation. Additional emissions occur as the limestone flux gives off carbon dioxide during reduction of pig iron in the blast furnace, but this source is covered as emissions from limestone use (Section 2.5).

During steel production, CO₂ emissions also take place as a result of graphite electrode consumption in the EAF.

Pig iron (impure iron) contains about 4-4.5 per cent carbon by weight. In the conversion of pig iron to steel the carbon content is reduced to below 2 per cent by weight. The process takes place in a steel furnace which has been charged with pig iron, usually recycled iron or steel and alloying elements to improve material properties. As the carbon is removed from the pig iron, CO₂ and CO are evolved. The lost CO-carbon is eventually converted to carbon dioxide by combustion. This should not be considered as an energy emission, as it is inherently part of the iron reduction process. Care should be taken not to double count these emissions (when performing the energy balance).

The most accurate methodology is to calculate the emissions from the amount of reducing agent used as described in 2.13.1.

Parsons (1977) and ORTECH (1994) have studied the consumption of carbon at iron and steel production facilities. These results have been summarised by Environment Canada (1996). Emission factors per unit iron or steel produced are shown in Table 2-13.

Country	Description	Emission Factor	Reference
Canada ^a	Integrated facility ^b (coke plus iron and/or steel production).	1.6	Environment Canada (1996)

^a Includes CO₂ produced by coke and coke oven gas consumption. It does not include any form of conventional energy consumption. The emission factor applies to both iron or iron plus steel production, since uncertainty in the estimates overshadow the incremental difference in CO₂ emissions.

^b Environment Canada has reported an emission factor of approximately 1.5 tonnes CO₂/tonne iron or steel for a non-integrated facility. This is, however, a rather uncertain value.

Note: Figures exclude CO₂ from flux (CaCO₃) consumption.

2.13.3.3 Emission Estimation Methodology for Ozone Precursors and SO₂

Emissions from iron and steel may originate from various stages of the production process.

Iron production:

- Blast Furnace Charging: Primary iron production in smelters. No process emission factors are given in the EMEP/CORINAIR Guidebook (SNAP 40202). In the CASPER model (CASPER 1995) emission factors of NMVOC are given as 100 g/tonne product (range 20-200) and CO is given as 1330 g/tonne product (range 1180-20000).



Preliminary research from Environment Canada suggests that sulphur dioxide emissions from the blast furnace may be 1000-3000 g SO₂/tonne of iron produced.

- **Pig Iron Tapping:** This involves the removal of the molten pig iron from the smelter. While it does give rise to emissions of a range of heavy metals, according to the EMEP/CORINAIR Guidebook no appreciable emissions of the four gases occur. In the CASPER model (CASPER 1995) the following emission factors are given: SO₂: 30 g/tonne product, NO_x: 76 g/tonne product, CO: 112 g/tonne product and NMVOC: 20 g/tonne product.

Steel production:

- **Open Hearth Furnace:** Steel is produced in the open hearth furnace fired by gas or fuel oil. No data exist for process emission from open hearth furnaces.
- **Basic Oxygen Furnace Steel Plant:** Pure oxygen is blown into the furnace via a lance. Burning CO maintains exothermic conditions. Most CO emissions are therefore eliminated. The EMEP/CORINAIR Guidebook (SNAP 40206) provides no emission factors for the gases.
- **Electric Furnace Steel Plant:** This type of furnace is usually charged with 100 per cent scrap iron. Graphite electrodes conduct current through the metal to heat the charge. Emissions are dependent upon the quality of scrap metal and operating conditions. The EMEP/CORINAIR Guidebook (SNAP 40207) does not give any emission factors for the gases of interest.

Steel processing:

- **Rolling Mills:** Rolling mills use a range of different processes and emit differing amounts of pollutants according to the specific processes used. Most of the emissions from rolling mills are from the fuel used to heat the process. However cold-rolling will emit a range of gases in addition to the fuel combustion emissions. The emission factors expressed as the amount of steel cold rolled are taken from the EMEP/CORINAIR Guidebook (SNAP 40208) and are shown in Table 2-14. Note that SO₂, NO₂ and CO emission factors are only given for process smelter gas (as sometimes used for rolling pretreatment).

Pollutant	Emission Factor (default)	Emission Factor (Range)
SO ₂ ^a	45	30-60
NO _x ^a	40	20-50
CO ^a	1	0.3-1
NMVOC	30	20-30
^a from process smelter gas		

2.13.4 Ferroalloys

2.13.4.1 Overview

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. These alloys are used for deoxidising and altering the material properties of steel. Ferroalloy facilities manufacture concentrated compounds which are delivered to steel production plants to be incorporated in alloy steels. Ferroalloy production involves a metallurgical reduction process which results in significant carbon dioxide emissions.

In ferroalloy production, raw ore, coke and slagging materials are smelted together under high temperature. A commonly used technology is the submerged-arc open-top electric furnace (EAF) (Environment Canada, 1983; Ontario Research Foundation, 1981). In the EAF, heating is accomplished by passing current through graphite electrodes suspended in a cup-shaped, refractory-lined steel shell. Carbon reduction of the metallic oxides occurs as both coke and graphite electrodes are consumed.

During ferroalloy smelting, the reduction reaction takes place at a high temperature. Carbon 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. For example, the following reaction occurs in the production of 50 per cent ferrosilicon (AWMA, 1993):



Primary emissions in covered arc furnaces consist almost entirely of CO as opposed to CO₂, due to the strong reducing environment (ORTECH, 1994). All CO is assumed, however, to be converted to CO₂ within days afterwards.

2.13.4.2 Emission Estimation Methodology for CO₂

The most accurate methodology is to calculate the emissions from the amount of reducing agent used as described in Section 2.13.1. Alternatively, the emissions may be calculated from the production volume. However, it is impossible to suggest default factors for this process. Ferroalloy production may more or less be based on biological carbon (wood and wood waste). To the extent that the biocarbon is replaced and that electricity is produced from e.g., hydro power, the production of ferroalloys may in principle be CO₂ free. However, in most countries a production based on biocarbon only will not be economical feasible. The suggested emission factors (Table 2.15) assume (if not otherwise specified) that all carbon is fossil and are derived from a material balance made by SINTEF (SINTEF 1991a) and Streibel (1974).



Type Ferroalloy	Emission Factor
Ferrosilicon - 50%Si	2-2.7
Ferrosilicon - 75%Si	3.9
Ferrosilicon - 90%Si	4.8-6.5
Silicon metal ^a	4.3
Ferromanganese	1.6
Silicon manganese	1.7
Ferrochromium	1.3
Ferrochromium-silicon	NAV

^a All producers probably use some biocarbon in order to obtain the desired product properties. 1.6 tonne bio-CO₂/tonne silicon may be considered as a minimum value and is *not* included in the emission factor in the table.
NAV = Not Available

2.13.4.3 Emission Estimation Methodology for Ozone Precursors and SO₂

SO₂, CO, NO_x and NMVOC are potentially emitted in the production process as described in Section 2.13.2.

Sulphur may be sequestered in the products. For ferromanganese and silicon manganese 98-99 per cent of the sulphur from ore and coke will be sequestered. Of the remaining ferroalloys, assume 5 per cent of the sulphur is sequestered (Rypdal 1995, Rosland 1987). In the CASPER model (CASPER 1995) a factor of 35 g/tonne product has been suggested for ferrosilicon.

NO_x will originate from production of ferrosilicon and silicon metal. A factor of 11.7 kg/tonne product has been determined (Rypdal 1995). However, this factor is highly uncertain, and there may also be emissions from the production of other ferroalloys. In the CASPER model (CASPER 1995) 0.05 kg/tonne has been suggested.

The emissions of NMVOC originate from coal or coke. The emissions are calculated from the consumption of coal and coke. An emission factor of 1.7 kg/tonne is suggested (Rypdal 1995).

The U.S. EPA has published uncontrolled CO emission factors for various ferroalloy products (U.S. EPA 1985). These vary with furnace type. Some of these factors are presented in Table 2-16.

TABLE 2-16 CO EMISSION FACTORS FOR FERROALLOY PRODUCTION (KG CO/TONNE METAL)		
Metal	Covered Furnace	Sealed Furnace
Ferrosilicon - 50%Si	1.09	NAV
Ferrosilicon - 75%Si	1.62	NAV
Silicon Manganese	NAV	0.84
Source: U.S. EPA reported by ORTECH (1994). NAV = not available.		

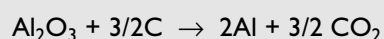
2.13.5 Aluminium

2.13.5.1 Overview

Primary aluminium is produced in two steps. First bauxite ore is ground, purified and calcined to produce alumina. Following this, the alumina is electrically reduced to aluminium by smelting in large pots.

During the reduction process, the aluminium smelting pot acts as the electrolysis cell. The pot itself, a shallow steel container, forms the cathode, while the anode consists of one or more carbon blocks suspended in it. In the pot, alumina (Al_2O_3), is dissolved in a fluoride bath consisting primarily of cryolite, Na_3AlF_6 . Passing electrolysis current through the cell also causes a heating effect through the resistance of the cell which maintains the electrolyte in a liquid state.

Molten aluminium is evolved while the anode is consumed in the reaction. However, the carbon functions as a fuel cell and as such substitutes electrical energy consumption. The aluminium forms at the cathode and gathers on the bottom of the pot. The favoured gaseous reaction product is CO_2 :



Most carbon dioxide is evolved from the reaction of the carbon anode with alumina, but some is formed as the anode reacts with other sources of oxygen (especially air). This occurs during cell operation and, in the case of prebaked electrodes, during anode production at the aluminium plant.

Three types of reduction cells are in use: prebaked anode, horizontal stud Söderberg anode and vertical stud Söderberg anode. Prebaked anodes have been preferred over Söderberg cells during the last 20 years because they are more productive and efficient with respect to electrical energy consumption and emit fewer organic compounds (U.S. EPA 1995).

2.13.5.2 Emission Estimation Methodology for CO_2

CO_2 emissions may be calculated from the amount of reducing agents used as described in Section 2.13.1. Alternatively, the emissions may be estimated from the production volume of primary metal and the specific consumption of carbon. Emissions factors for



CO₂ are suggested in Table 2-17 based on SINTEF 1991b and ORTECH 1994. The production and use of carbon anodes for aluminium smelting is a very well established process. Evidence suggests that there is little variation in CO₂ emissions from plants utilising similar technologies. It is very likely that use of the appropriate emission factor, along with the correct activity data, will produce accurate estimates.

Pollutant	Soderberg Process	Prebaked Anode Process
CO ₂	1.8	1.5

2.13.5.3 Emission Estimation Methodology for Ozone Precursors and SO₂

Emissions of carbon monoxide, nitrogen oxide and sulphur dioxide can be estimated from the amount of aluminium produced. Emissions may originate from the production process and baking of anodes. No distinction between the Soderberg and prebaked method is given in the EMEP/CORINAIR Guidebook (SNAP 40301). The suggested emission factors are shown in Table 2-18. No information is given about the degree of control.

Pollutant	Process	Emission Factor (Default)	Emission Factor (Range)
SO ₂	Electrolysis	14.2	10-17.5
	Anode baking	0.9	0.8-1.0
NO _x	Electrolysis	2.15	1.3-3.0
	Anode baking	NE	NE
CO	Electrolysis	135	27-680
	Anode baking	400	NAV

NE = negligible.
NAV = not available.

2.13.6 PFCs from Aluminium Production

2.13.6.1 Overview

Two PFCs, carbon tetrafluoride (CF₄) and carbon hexafluoride (C₂F₆), are known to be emitted from the process of primary aluminium smelting.

Aluminium is smelted in large pots by an electrolytic reduction process using carbon electrodes. The pot itself forms the cathode, while the anode consists of one or more carbon blocks. During production, alumina (Al₂O₃) is dissolved in a fluoride melt consisting primarily of cryolite, Na₃AlF₆. PFCs are formed during a phenomenon known as the Anode Effect (AE), when alumina levels are low. A forced reaction results when molten fluoride salts at high temperature combine with carbon at the anode to favour the formation of CF₄ and C₂F₆. This occurs because, during an AE, voltage rises to a level greater than that corresponding to the Gibbs energy of formation for these gases (Laval University, 1994).

When the melt becomes depleted of alumina (reduction to a level of 1.5-2.0 wt %), the AE occurs and the cell voltage rises from the normal value of 4-5 volts to 20-50 volts. This happens very suddenly and, in theory, is due to a sudden increase in electrical resistance across the anode-bath interface. As a result, the voltage rises to continue delivering current across the higher resistance. Competing reactions begin to occur to produce CO, CF₄ and C₂F₆ in addition to CO₂. It is believed that the carbon anode becomes completely covered by gas during the AE. The two reactions of interest at this point are:



The overall anode gas composition below the anode during an anode effect may be approximately 15 % wt CF₄, 20 wt % CO₂, 65 wt % CO and 1 wt % C₂F₆ (Thonstad, Oygard and Diep, 1994). AEs typically occur between 0.3 to 3 times daily on a given cell and last on the order of 2 to 20 minutes (Unisearch, 1994).

2.13.6.2 Emission Data

Measured Emission Data

In 1992, the Norwegian aluminium industry measured the emissions of PFCs from their smelters. The measurements in production cells were performed with a photoacoustic gas monitor (Norsk Hydro, 1996), (See Table 2-19). The results were different for prebaked lines (0.02 to 0.18 kg CF₄/tonne Al) and Söderberg lines (0.15 to 0.9 kg CF₄/tonne Al).



	Norway (Norsk Hydro, 1996)		Canada (Schiff, 1994)	
	CF ₄	C ₂ F ₆	CF ₄	C ₂ F ₆
Cell Technology	kg/tonne Al	kg/tonne Al	kg/tonne Al	kg/tonne Al
Side Worked Prebaked (SWPB)	NAV	NAV	1.19 ^a	0.067 ^a
Horizontal Stud Søderberg (HSS)	NAV	NAV	0.82 ^a	0.14 ^a
Vertical Stud Søderberg (VSS)	0.15-0.9	0.006-0.04	0.4 ^b	NAV
Centre Worked Prebaked (CWPB)	0.02-0.18	0.001-0.008	0.045-0.53 ^c	0.007-0.032 ^c

^a Based on samples from one plant.
^b Samples from one plant-value has been adjusted to compensate for error.
^c Based on sampling 5 plants.
NAV = Not Available.

In Australia, all aluminium smelters use pre-baked cell technology. Emission factors from the Australian aluminium industry are reported to be 0.53 kg CF₄/tonne Al, and 0.05 kg C₂F₆/tonne Al (Workbook, Australia, 1995).

A study of Canadian aluminium plants found CF₄ emission factors to be between 0.045 and 1.2 kg per tonne of aluminium produced (Unisearch, 1994). The emission factor for C₂F₆ was between 0.007 and 0.14 kg per tonne. The Canadian study further subdivided the Søderberg and Prebaked technologies into two separate categories (Table 2-19). This subdivision narrows the emission range for each category.

PFC emissions increase with frequency, intensity and duration of anode effects. The Norwegian study reported the frequency variation to be 0.03-0.24 AE per cell-day in Prebaked lines, and 1.0-2.76 AE per cell-day in Søderberg lines. Canadian data show AE frequency to vary between 0.2 and 2.6 per cell-day in all lines. Uncertainty in all measurements is relatively high (of the order of 50 per cent).

Estimated Emission Data

A preliminary U.S. EPA study suggested a range of 0.01 to 1.2 kg of CF₄ per tonne of aluminium produced by any technology (U.S. EPA, 1994a). This range is an average based on measured emissions from aluminium smelters in the United States, Canada and Norway. These values may underestimate emissions from other aluminium producing regions.

CICERO (1992) and, Khalil and Rasmussen (1985) have studied trends in atmospheric CF₄. The studies made projections based on the assumption that all atmospheric CF₄ originates from aluminium production. Though data are subject to large uncertainties, both papers lead to the conclusion that the average emission rate from aluminium smelting is around 1 kg per tonne metal.

The global emissions of PFCs to the atmosphere from all aluminium smelters was re-estimated for 1995 (Harnisch and Borchers, 1995), and reported to be closer to 1.4 kg CF₄/per tonne Al, and 0.2 kg C₂F₆/per tonne Al (Tabereaux, 1995). The distribution of four different cell technologies on a global scale is given in Table 2-20, together with estimated CF₄ emissions.

TABLE 2-20 ESTIMATED GLOBAL CF₄ EMISSIONS FROM SMELTERS WITH VARIOUS CELL TECHNOLOGIES		
Type of Cell Technology	Per Cent of World Production	kg CF ₄ /tonne Al
Modern Prebaked	20	0.05
HS Søderberg	11	1.0
“Older” Prebaked	40	1.75
VS Søderberg	29	2.0
Weighted average for all plants world-wide	100	1.40

Source: Tabereaux, 1995.

Calculation of Emission Data

Tabereaux (1995) has proposed a method for PFC emission calculation. He states that the generation of CF₄ in electrolysis cells follows Faraday's Law (i.e., the quantity of gas generated depends on the flow of electrical current in the cell). At 100 per cent efficiency, 13.68 g of CF₄ is formed for every kiloampere-minute (kA min) duration of the anode effect. For example, CF₄ emissions for an aluminium smelter having an average percentage (p) of 16 per cent CF₄ in pot gas during anode effects (AE), 91 per cent current efficiency (CE) for aluminium production, 0.5 anode effects per pot day (AEF), and anode effect duration (AED) of 2.5 minutes can be calculated from:

$\text{Kg CF}_4 / \text{tonne Al} = (\text{kg CF}_4/\text{kA min}) / (\text{kg Al/kA min}) \times (1000 \text{ kg/tonne}) \times (p/\text{CE}) \times \text{AEF} \times \text{AED}$
$= 13.68 / 8.05 \times (0.16 / 0.91) \times (0.5) \times (2.5)$
$= 0.373$

2.13.6.3 Emission Estimation Methodology for PFCs

Measurements

Since emissions of CF₄ and C₂F₆ vary so significantly from one aluminium smelter to the next, depending on cell type and AE parameters, the estimations will be highly uncertain unless actual emission measurements have been made. Every effort should be made to obtain such data.



Calculations

It is recognised that measurements are both expensive and time-consuming. It may, however, be much easier to make a limited survey of AE frequency and duration at smelters. In such cases, it is recommended that specific CF₄ emissions for anode effects longer than 2 minutes are calculated as follows:

$$\text{kg CF}_4/\text{tonne Al} = 1.698 \times (p / \text{CE}) \times \text{AEF} \times \text{AED}$$

p	=	average fraction of CF ₄ in the pot gas during anode effects
Prebaked: p	=	0.08 (8%)
Söderberg: p	=	0.04 (4%)
CE	=	current efficiency expressed as a fraction, rather than a percentage
AEF	=	number of anode effects per pot day
AED	=	anode effect duration in minutes

It is recommended that the default rate for C₂F₆ emissions be 1/10 that of CF₄.

Estimations

It is recommended that estimates are used only when no measured data exist. Specific emission factors should be chosen according to the type of technology used as shown in Tables 2-19 and 2-20 and applied to national primary aluminium production data for each technology. The following method may then be used to give an estimate of the annual CF₄ emissions from a smelter with a given cell technology.

$$\text{CF}_4 \text{ emission (kg)} = \text{EF}_{(\text{tech})} (\text{kg CF}_4/\text{tonne Al}) \times \text{pp}_{(\text{tech})} (\text{tonnes})$$

where:

EF _(tech)	=	emission factor by technology (from Table 2-20)
PP _(tech)	=	primary aluminium production by technology

2.13.7 Other Metal Production

2.13.7.1 Emissions of CO₂

This includes production of all non-ferrous metals except aluminium. The metals may be produced using carbon as reducing agents or by other methodologies.

Whether carbon is emitted or not depends on the production process. Some ores are not reduced with carbon. Hence, CO₂ emissions from these processes are low. The general methodology suggested, where emissions are calculated from the consumption of reducing agents and the carbon content of ores, is recommended. An overview of production processes is given in Table 2-21. Some metals may be produced from alternative production methods.

**TABLE 2-21
PRODUCTION PROCESSES FOR SOME METALS**

Metal	Main Ore(s)	Carbon Reduction	Electrolysis (without carbon)	Other (non-CO ₂)
Chromium^a	FeCr ₂ O ₄ , PbCrO ₄	x		
Copper	Cu ₂ S, CuFeS ₂ , Cu ₂ O,		x	x (SO ₂)
Gold	Element		x	x
Lead	PbS	x		x (SO ₂)
Magnesium	Carbonate	x	x	
Mercury	HgS			x (SO ₂)
Molybdenum	MoS ₂			x (SO ₂)
Nickel	NiS, NiO	x	x	x (SO ₂)
Platinum	Element, PtS			x
Silicon^b	SiO ₂ , Si-O-alkali	x		
Silver	Ag ₂ S, element			x
Tin	SnO ₂	x		
Titanium	TiO ₂ , FeTiO ₃	x ^c		
Tungsten	WO ₃			x
Uranium	U _x O _y			x
Zinc	ZnS, ZnCO ₃	x	x	x (SO ₂)

^a See also ferroalloy production
^b See also ferroalloy production and carbide production
^c Two step reduction process, involving first C + Cl₂, then Mg
 Note: The appearance of (SO₂) in the final column indicates that the production process is a major world-wide source of SO₂ emissions.

In the case of *magnesium* and other metals in a carbonate ore, the carbon emitted from the ore should be taken into account in addition to the coke reducing agent.

2.13.8 SF₆ Used in Aluminium and Magnesium Foundries

In the magnesium industry, SF₆ is used as a cover gas in foundries to prevent oxidation of molten magnesium. The Norwegian producer of magnesium has assessed whether SF₆ used as a cover gas reacts with other components in the furnaces. The results so far indicate that SF₆ is quite inert. For the time being it is therefore assumed that all SF₆ used as cover gas is emitted to the atmosphere. The consumption figures are therefore used as emission estimates.



In the aluminium industry SF₆ is used as a cover gas only for special foundry products. As SF₆ is assumed to be inert, SF₆ emissions should equal consumption:

$$\text{Emission of SF}_6 = \text{Consumption of SF}_6 \text{ in magnesium and aluminium foundries}$$

2.14 Pulp and Paper Industries

2.14.1 Overview

Pulp and paper production has three major processing steps: pulping, bleaching and paper production. The type of pulping and the amount of bleaching used depend on the nature of the feedstock and the desired quality of the end product. Kraft (sulphate) pulping is the most widely used pulping process and is typically used to produce strong paper products. The Kraft pulping process includes bleaching, chemical recovery and by-product recovery.

Sulphite pulping is another chemical pulping process. It produces a weaker paper than some other types of pulping, but the pulp is less coloured, making it more suitable for printing, often with little bleaching.

2.14.2 Simple Methodology for Ozone Precursors and SO₂

Simpler methodologies are presented in the EMEP/CORINAIR Guidebook for three paper pulping processes;

- Kraft (SNAP 40602),
- Acid sulphite (SNAP 40603)
- Neutral sulphite semi-chemical process (SNAP 40604).

Only data for the Kraft and Acid sulphite processes are available.

In the Kraft pulping process sodium sulphide and sodium hydroxide are used to chemically dissolve the lignin that binds the cellulose fibres. Emission factors are based on the production of air-dried pulp and are shown in Table 2-22 as suggested in the EMEP/CORINAIR Guidebook. The emissions of SO₂ may be lower in new mills than the older ones (U.S. EPA 1995).

TABLE 2-22 NON-COMBUSTION EMISSION FACTORS FOR PAPER AND PULP PRODUCTION - KRAFT PULPING (KG/TONNE DRIED PULP)		
Pollutant	Emission Factor (Default)	Emission Factor (Range)
SO ₂	7	0.005-10
NO _x	1.5	0.017-1.5
VOC ^a	3.7	0.1-4.9
CO ^b	5.6	NAV

^a Note, VOC is defined as the total gaseous non-methane organic compounds which include sulphur compounds.
^b Ref: U.S. EPA 1995.
 NAV = Not Available

The acid sulphite pulping process is similar to the Kraft process except that a sulphurous acid solution is used to dissolve the lignin in the wood. This solution is buffered by the use of bisulphide of sodium, magnesium, calcium or ammonium. SO₂ is considered to be the major pollutant. There are at least four types of processes: ammonium based (NH₃), calcium based (Ca), magnesium based (MgO) and sodium based (Na) (U.S. EPA, 1995). Emissions factors from U.S. EPA, 1995 are given in Table 2-23.

TABLE 2-23 NON COMBUSTION EMISSIONS FROM PAPER AND PULP PRODUCTION - ACID SULPHITE PULPING (KG/TONNE DRIED PULP)			
Pollutant	Type of Process	Emission Factor (Default)	Emission Factor (Range)
SO ₂	NH ₃ , Ca, MgO and Na	30	8-50

2.14.3 Detailed Methodology for Ozone Precursors and SO₂

The preferred methodology is to use continuous measurements data which may be available for SO₂ and NO_x. This is only feasible in modern plants where the number of measure points to be monitored is limited. Detailed emission factors related to the various processes are given in the EMEP/CORINAIR Guidebook.



2.15 Food and Drink

2.15.1 Alcoholic Beverages

NMVOCs are produced during the processing of cereals and fruits in preparation for the fermentation processes. The activity rate is the total annual production. The emission factors given in the EMEP/CORINAIR Guidebook (SNAP 40606-40608) are shown in Table 2-24.

Beverage	Emission Factor
Wine	0.08
Red wine	0.08
White wine	0.035
Beer	0.035
Spirits (unspecified)	15
Malt whiskey	15
Grain whiskey	7.5
Brandy	3.5

The emission factors and sources are derived for Europe; there may be different processes and emission factors in other parts of the world.

2.15.2 Bread Making and Other Food

The relevant precursor gas emitted during food production (SNAP 40605) is NMVOC. Emissions from processes not included are vegetable oil extraction (SNAP 60404), tobacco products and alcoholic beverages (see Section 2.15.1). Emissions are included from all processes in the food chain which occur after the slaughtering of animals or harvesting of crops.

Food production is divided into seven categories each with its own emission factor. The emission factors given in the EMEP/CORINAIR Guidebook are shown in Table 2-25.

The activity rate is the total annual production of food. The emission factors and sources are derived for Europe; there may be different processes and emission factors in other parts of the world.

TABLE 2-25 EMISSION FACTORS FOR BREAD AND OTHER FOOD PRODUCTION (KG/TONNE)	
Food Production Process	Emission Factor
Meat, fish and poultry	0.3
Sugar	10
Margarine and solid cooking fats	10
Cakes, biscuits and breakfast cereals	1
Bread	8
Animal Feed	1
Coffee roasting	0.55

2.16 Emissions Related to Production of Halocarbons and Sulphur Hexafluoride (HFCs, PFCs and SF₆)

2.16.1 By-product Emissions

Chemical by-products of industrial processes, substances which are different from the desired end-product, may be released into the atmosphere. It is well known that HFC-23 is produced along with HCFC-22 and it is estimated that the HFC-23 released from this source is currently equivalent to 4 per cent of the production of HCFC-22 (U.S. EPA, 1994b) assuming no abatement measures.

In the Tier 1 methodology (Section 2.17.3), this factor, or a similar number derived for the particular country's circumstances, can be used to estimate national emissions of HFC-23 from the total national HCFC-22 production (for both potentially dispersive and feedstock end-uses). Problems with collecting specific component data can be circumvented by providing a single number for total emissions of HFC-23.

$$\text{By-product Emissions (tonnes)} = \text{By-product Factor (tonnes/tonne)} \\ \times \text{Total HCFC-22 Production (tonnes)}$$

For the Tier 2 methodology (Section 2.17.4), a potentially more accurate estimate is the sum of factory specific emissions determined using standard methods to estimate the composition and flowrate of gas streams vented to atmosphere. In this case:

$$\text{By-product Emissions} = \sum_i \sum_j \int_t f_{ij} C_{ij}$$



where:

the sum over all i plants, over all j streams in each plant of the emitted flows f and concentrations c is integrated over time (t).

Other by-product emissions of HFCs, PFCs and other greenhouse gases from chemical production processes should be identified and treated in the same way.

2.16.2 Fugitive Emissions

Fugitive emissions of a chemical occur during the production and distribution of a chemical. In this chapter, fugitive emissions associated with use are not addressed specifically, being counted in the emissions related to consumption (see Section 2.17). In the case of fluorocarbon processes, fugitive emissions have been estimated to be approximately 0.5 per cent of the total production of each compound (UNEP, 1994).

In the Tier 1 methodology, this factor, or a similar number derived for the particular country's circumstances, can be used to estimate national fugitive emissions of individual HFCs and PFCs associated with national production. Problems with collecting specific component data can be circumvented by providing a single number for total emissions of each HFC and PFC.

$$\text{Fugitive Emissions (tonnes)} = \text{Fugitive Release Factor (tonnes/tonne)} \\ \times \text{Individual HFC or PFC Production (tonnes)}$$

For a Tier 2 methodology, a potentially more accurate estimate is the sum of factory specific emissions determined using standard methods to estimate the composition and flowrate of gas streams vented to atmosphere. In this case:

$$\text{Fugitive Emissions} = \sum_i \sum_j \int_t f_{ij} C_{ij}$$

where:

the sum over all i plants, over all j streams in each plant of the emitted flows f and concentrations c integrated over time (t).

2.17 Emissions Related to Consumption of Halocarbons and Sulphur Hexafluoride (HFCs, PFCs, and SF₆)

2.17.1 Overview

Partially fluorinated hydrocarbons (HFCs), perfluorinated hydrocarbons (PFCs), and sulphur hexafluoride (SF₆) 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 (Kroeze, 1995; U.S. EPA, 1992b):

- refrigeration and air conditioning
- fire suppression and explosion protection
- aerosols
- solvent cleaning
- foam blowing
- other applications⁵

Primary uses of SF₆ include:

- gas insulated switch gear and circuit breakers
- fire suppression and explosion protection
- other applications⁶

Partially and fully fluorinated hydrocarbons (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 ozone depleting substances (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-22⁷ production. HFC-134a entered production in 1991 and a variety of other HFCs are now being produced (Enquete Commission, 1994).

PFCs are chemicals containing only carbon and fluorine. PFCs have been produced commercially for 30 years, primarily for use as cooling/heating agents in specialised market segments and in vapour phase reflow soldering and electronic safety testing (Kroeze, 1995). Like HFC emissions, PFC emissions result from two sources; emissions from commercial use of PFCs and emissions as by-products of industrial processes. PFCs are anthropogenic compounds; no natural sources have been found, though a small, but as yet unidentified, natural source of one PFC is suspected (Abrahamson, 1992).

SF₆ is a particularly potent GHG with a 100-year GWP of 23,900 and an estimated lifetime of about 3200 years (IPCC, 1996)(Table 2-26).

The chemicals (HFCs, PFCs, SF₆) are of concern, however, because they have high global warming potentials and long atmospheric residence times.

Table 2-26 gives an overview over the most important HFCs and PFCs (U.S. EPA, 1992b; UNEP, 1994; Kroeze, 1995), including application area and GWP relative to CO₂ (100 year integration time). The various HFCs and PFCs have very different strengths as GHGs. PFCs have particularly high GWPs. The consumption pattern with respect to the individual gases must be known, therefore, or estimated with reasonable accuracy, to achieve useful estimates for the contribution to global warming from emission of these groups of chemicals.

⁵ HFCs and PFCs may be used in sterilisation equipment, for tobacco expansion applications, and as solvents in the manufacture of adhesives, coating and inks.

⁶ SF₆ may be used as an insulating medium, tracer, in leak detectors, and in various electronic applications. Aluminium and magnesium foundries are also major users of SF₆, but the emissions associated with these industries are covered in Section 2.13.8

⁷ HCFCs - hydrochlorofluorocarbons.



As CFCs, halons, carbon tetrachloride, methyl chloroform, and, ultimately, HCFCs are phased out, HFCs are likely to be widely used as replacements. PFCs may be used to a limited extent. Even though up to 75 per cent of current application of CFC may be covered by different technologies in the future (McFarland and Kaye, 1992), HFC use is expected to grow substantially.

NF₃ is another gas which is likely to contribute to global warming. It may be used for chip etching (Cook, 1995) but is not included here.

TABLE 2-26
POTENTIAL APPLICATION AREAS AND GLOBAL WARMING POTENTIALS (GWPs) FOR HFCs, PFCs, AND SF₆

Chemical	GWP ^a	Refrigeration and Air Conditioning	Fire Suppression and Explosion Protection	Aerosols	Solvent Cleaning	Foam Blowing	Other Applications ^b
HFC-23	11700	x	x				
HFC-32	650	x					
HFC-125	2800	x	x	x		x	x
HFC-134a	1300	x	x	x		x	x
HFC-143a	3800	x				x	
HFC-152a	140	x		x		x	
HFC-227ea	2900	x	x	x			x
HFC-236fa	6300	x				x	
HFC-245ca	560	x				x	
HFC-356						x	
HFC-43-10					x		
PFC-116	9200	x					
PFC-218	7000	x					
PFC-410	7000		x				
PFC-614			x		x		
Other PFCs ^c					x		
SF ₆ ^d	23900		x				x

^a 100 year time horizon (IPCC, 1996).
^b Other applications include sterilisation equipment, tobacco expansion applications, and as solvents in the manufacture of adhesive coatings and inks (Kroeze, 1995; U.S. EPA, 1992b).
^c E.g., PFC-512, PFC-612, PFC-716, PFC-819.
^d Gas insulated switchgear and circuit breakers.

2.17.2 General Methodology

Emissions from industrial processes can be estimated in two ways; as potential emissions, Tier 1, (a and b), and as actual emissions, Tier 2.

Potential emissions of a certain chemical are equal to the amount of virgin chemical consumed in the country minus the amount of chemical recovered for destruction or export in the year of consideration. All chemicals consumed will eventually be emitted to the atmosphere over time if not destroyed⁸, and in the long term (e.g., 50 yrs), potential emissions will equal actual emissions.

However, the method does not take into account accumulation or possible release⁹ of chemical in various products and equipment, which means over the short term (e.g., 10-15 yrs) estimates may become very inaccurate. Since accumulation is thought to be the dominant process at the present time, potential emission calculations will strongly over estimate emissions.

The error is minimised when enough time has passed for HFC/PFC-containing equipment and products to begin to be retired. 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.

Actual emission estimates take into account the time lag between consumption and emission, which may be considerable in some application areas, e.g., closed cell foams, refrigeration and fire extinguishing equipment. Time lag results from the fact that a chemical is placed in new products and then slowly leaks out over time. A household refrigerator, for example, emits only small amounts of refrigerant through leakage and emissions during servicing throughout its lifetime and most of its charge is not released until its disposal, many years after production.

The amount of a chemical escaping to the atmosphere in a given year will only be similar to the quantity consumed in a static situation with respect to chemical usage pattern, market development, system or product design and tightness, servicing and recovery practices, etc. This is very different from the current situation. Since countries are only beginning to use and produce the chemicals, only a small fraction of products with HFCs/PFCs are being stored in the market.

Until a more stationary situation is established, which may take 15-20 years for industrialised countries and an additional 10 years for developing countries, the time lag between consumption and emission has to be taken into account to achieve reasonably correct estimates for annual emissions.

Hence, actual emissions estimates are the most accurate with respect to emissions in individual years, provided that the necessary information is available for their calculation. If essential data are not available, the potential emission calculations provide a more simple approach for reasonable emission estimates.

The following procedures described for HFCs/PFCs are applicable for SF₆ as well.

⁸ The destruction of fluorocarbons could 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).

⁹ If non-halocarbon technology takes over market shares.



2.17.3 Tier I: Basic Method

2.17.3.1 Overview

Potential emission calculations are regarded as the basic methodology for HFC and PFC emission estimates, which any country should apply. However, if relevant information is available, it is recommended that emissions are reported according to the Tier 2 methodology in Section 2.17.4.

Since net consumption of a chemical equals production plus imports minus exports, the calculation formula for the basic method (Tier I) is as follows:

$$\text{Potential Emissions} = \text{Production} + \text{Imports} - \text{Exports} - \text{Destruction}$$

Although destruction of HFCs and PFCs is currently not practised, and may be technically difficult (U.S. EPA, 1995), it should be included as a future option to reduce emissions. By-product emissions during HFC/PFC production and fugitive emissions related to production and distribution have to be calculated separately, as described in Section 2.16.

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.

There are two versions of Tier I (a and b) depending upon whether HFCs/PFCs in products are taken into account. In Tier Ia, chemicals contained in products are *not* considered. In Tier Ib, 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 in products, at least in the short term. The Tier Ib methodology is preferred if relevant data are available.

Irrespective of the Tier I methodology chosen, emissions with respect to individual HFCs and PFCs have to be reported. Information on the practical use of the various commercial types of HFC/PFC refrigerants, blowing agents, solvents, etc. will be required. Many of these products are mixtures of two to four HFCs/PFCs, and the composition of fluids for similar purposes may vary according to individual formulas developed by the different chemical companies.

2.17.3.2 Tier Ia

Quantities of HFCs/PFCs contained in various products imported into or exported from a country may be difficult to estimate. In Tier Ia, 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:

$$\begin{aligned} \text{Imports} &= \text{Imported HFC/PFC in bulk} \\ \text{Exports} &= \text{Exported HFC/PFC in bulk} \end{aligned}$$

The application of Tier 1a may lead to underestimation or overestimation of potential emissions, depending on whether the majority of HFC/PFC containing products 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 destroyed, if any.

Potential emission data for each individual chemical should be calculated according to the scheme in Table 2-27:

Reporting year:	
Type of chemical (e.g., HFC-134a):	
Production of chemical	tonnes
+ Import of chemical in bulk	tonnes
- Export of chemical in bulk	tonnes
- Destruction of chemical	tonnes
= Sum (potential emission of chemical)	tonnes

Emissions related to production and distribution of HFCs/PFCs have to be taken into account as described in Section 2.16.2.

2.17.3.3 Tier 1b

Tier 1b is an extension of Tier 1a and includes HFCs/PFCs contained in various products which are imported and exported. The following definitions then apply:

Imports = Imported chemical in bulk + quantity of chemical imported in HFC/PFC containing products

Exports = Exported chemical in bulk + quantity of chemical exported in HFC/PFC containing products

Data on production and exports of HFCs/PFCs 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 imports and exports of products and equipment containing HFCs or PFCs. National environmental protection authorities may keep records of HFCs/PFCs destroyed.

To calculate the potential emissions according to Tier 1b, the calculation scheme in Table 2-27 has to be extended to include the import and export of chemicals in products. Table 2-28 demonstrates a possible set-up for calculation of emissions from exports/imports and the results should be added to the emissions calculated using Table 2-27. In Table 2-28, HFC-xxx is used as an example to demonstrate the procedure, which in practice will have to be performed for individual HFCs and PFCs, and with SF₆.



TABLE 2-28
ADDITIONAL CALCULATIONS FOR ESTIMATING
POTENTIAL EMISSIONS ACCORDING TO TIER 1B

Refrigeration

$$G_{\text{HFC-xxx}} = G(\text{Unit } i) \times n(\text{Unit } i) \times F_{\text{HFC-xxx}}(\text{Unit } i) + \dots + G(\text{Unit } m) \times n(\text{Unit } m) \times F_{\text{HFC-xxx}}(\text{Unit } m)$$

where:

- $G_{\text{HFC-xxx}}$ = total import (export) of HFC-xxx in precharged refrigeration units¹⁰
- $G(\text{Unit } i)$ = refrigerant charge in a refrigeration unit of type "i" (i = i → m)
- $n(\text{Unit } i)$ = number of refrigeration units of type "i" imported (exported)
- $F_{\text{HFC-xxx}}$ = fraction of component HFC-xxx¹¹ in the refrigerant (mixture) of a unit of type "i"

Foam products¹²

$$G_{\text{HFC-xxx}} = V(\text{Foam } i) \times J_{\text{HFC-xxx}}(\text{Foam } i) + \dots + V(\text{Foam } m) \times J_{\text{HFC-xxx}}(\text{Foam } m)$$

where:

- $G_{\text{HFC-xxx}}$ = total import (export) of HFC-xxx in foams (flexible and rigid)
- $V(\text{Foam } i)$ = volume of foam of type "i" imported (exported) (i = i → m)
- $J_{\text{HFC-xxx}}$ = remaining amount of blowing agent HFC-xxx per volume unit of foam of type "i"

¹⁰ "Refrigeration units" may be refrigerators, ice machines, AC window units, split-units, chillers etc. Typical charge ranges for various types of equipment are given in Section 2.17.4.2.

¹¹ Many refrigeration units will contain HFC/PFC-mixtures. The fraction of each chemical (HFC-xxx) has to be considered.

¹² Include insulating and non-insulating foams in a variety of products, like refrigerators, insulation panels, pour-in-place sprays, car seats, furniture, bedding, packaging material etc.

Fire extinguishers

$$G_{\text{HFC-xxx}} = G(\text{Unit } i) \times n(\text{Unit } i) \times F_{\text{HFC-xxx}}(\text{Unit } i) + \dots + G(\text{Unit } m) \times n(\text{Unit } m) \times F_{\text{HFC-xxx}}(\text{Unit } m)$$

where:

- $G_{\text{HFC-xxx}}$ = total import (export) of HFC-xxx in precharged fire extinguishers
- $G(\text{Unit } i)$ = charge of fire extinguishing agent in a fire extinguishing unit of type "i" (i = 1 → m)
- $n(\text{Unit } i)$ = number of fire extinguishing units of type "i" imported (exported)
- $F_{\text{HFC-xxx}}$ = fraction of component HFC-xxx¹³ in the fire extinguishing agent of a unit of type "i"

Solvents

$$G_{\text{HFC-xxx}} = G(\text{Solvent } i) \times F_{\text{HFC-xxx}}(\text{Solvent } i) + \dots + G(\text{Solvent } m) \times F_{\text{HFC-xxx}}(\text{Solvent } m)$$

where:

- $G_{\text{HFC-xxx}}$ = total import (export) of HFC-xxx in solvents
- $G(\text{Solvent } i)$ = quantity of solvent of type "i" imported (exported) (i = 1 → m)
- $F_{\text{HFC-xxx}}$ = fraction of component HFC-xxx¹⁴ in solvent of type "i"

Aerosols

$$G_{\text{HFC-xxx}} = G(\text{Can } i) \times n(\text{Can } i) + \dots + G(\text{Can } m) \times n(\text{Can } m)$$

where:

- $G_{\text{HFC-xxx}}$ = total import (export) of HFC-xxx in aerosol cans
- $G(\text{Can } i)$ = charge of HFC-xxx propellant in an aerosol can of type "i" (i = 1 → m)
- $n(\text{Can } i)$ = number of aerosol cans of type "i" imported (exported)

¹³ Most fire extinguishing units will contain HFC/PFC-mixtures. The fraction of each chemical (HFC-xxx) has to be considered.

¹⁴ Solvents will normally not be pure HFCs or PFCs. The fraction of the HFC/PFC in consideration (HFC-xxx) has to be considered.



2.17.4 Tier 2: Advanced Method

2.17.4.1 Overview

The advanced method, Tier 2, contains *actual emission calculations for each individual chemical*, comparable with methods currently applied by AFEAS for CFCs and HCFCs (Gamlen et al., 1986; Fisher and Midgley, 1993; AFEAS, 1995). This is the preferred method if input data are available. Some countries may have the relevant information available already to apply the Tier 2 methodology. However, countries that do not are recommended to establish routines to report HFC/PFC emissions according to Tier 2.

The Tier 2 methodology:

- a) calculates or estimates the consumption of each individual HFC and PFC chemical at a rather detailed level, e.g., refrigerators, other stationary refrigeration/AC equipment, soft foam, hard foam etc., to establish the volume basis for emission calculations.
- b) estimates emissions on the basis of the consumption distribution from (a), and emission characteristics related to various processes and equipment, also taking current service and recovery practices into account.

Table 2-29 gives examples of current HFC/PFC use distribution among various application areas in certain countries. Since HFCs and PFCs have only recently entered the market, the relative size of each area will change over time and will have to be updated. This information may allow countries with similar practices to those in Table 2-29 to make first order estimates for their own HFC/PFC consumption and distribution.

Country	Refrigeration Air Conditioning	Foam Blowing	Solvent	Fire Extinguishing	Aerosol Propellant	Other Applications
Norway	99%	<1%	0%	<1%	0%	0%
Sweden	90%	5%	0%	0%	5%	0%
United Kingdom ^a	76%	12%	0%	7%	5%	0%

^a March Consulting Group (1996), *UK Use and Emissions of Selected Halocarbons*, A Study for the UK Department of Environment.

Any given application area may employ several types of HFC/PFC fluid. Consumption figures should be collected or estimated and the type of HFC/PFC used should be identified.

Nevertheless, real emission data for a given year will never be exactly known, irrespective of the refinement of the estimation methods. 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.

Examples of how the Tier 2 methodology may be applied are given in the remainder of this chapter.

2.17.4.2 Estimation Of Emissions Of HFCs And PFCs From Use In Refrigeration And Air Conditioning Equipment

Overview

HFCs and PFCs are potential replacements to the use of CFCs and HCFCs in refrigeration and air conditioning equipment. A wide array of such equipment is used globally. For the purposes of emission estimation, refrigeration and air-conditioning systems are classified into three categories, according to emission characteristics:

- Household refrigerators and freezers;
- Other stationary refrigeration and air conditioning equipment, including:
 - cold storage warehouses;
 - retail food refrigeration;
 - industrial process refrigeration;
 - commercial and industrial appliances such as refrigerated vending machines, ice machines, dehumidifiers, and water coolers;
 - refrigerated transport including trucks, trains, and ships with refrigerated compartments;
 - commercial and residential air conditioning including chillers, heat pumps, window air conditioners, centralised air conditioners.
- Mobile air conditioners used to cool the passenger compartment of automobiles, trucks, buses, and trains.

HFC-134a is the primary fluorocarbon substitute for CFC-12 in many refrigeration and air-conditioning applications including refrigerators, chillers, and mobile air conditioners.

Other HFCs may also be used in refrigeration applications, particularly as components of blends. These include HFC-23, HFC-32, HFC-125, HFC-143a, and HFC-152a (Du Pont, 1994; Fay, 1995). PFC-218 is used as a component in refrigerant blends from (at least) one manufacturer. PFC-116 may be used in a blend as a substitute for R-503. In addition, a significant portion of the refrigerant market may be taken over by non-halocarbon technologies (McFarland & Kay, 1992).

Calculation methods

Gas emissions from refrigeration and air conditioning systems result from:

- losses during system erection/assembly¹⁵;
- emissions from the stock of existing systems (small leakages, breakdowns, venting at service);
- venting of refrigerant at system disposal.

Methods for estimating average emission rates for the above-mentioned sectors are outlined below.

¹⁵ e.g., losses from using HFC/PFC as tracer gas for checking leak tightness, losses in relation to system development and testing etc.



The quantity of refrigerant emitted during system assembly is related to the amount charged by the following empirical formula:

EQUATION 1

$$E_{\text{assembly}, t} = E_{\text{charged}, t} \cdot (k/100)$$

where:

- $E_{\text{assembly}, t}$ = emissions during system manufacture/assembly in year t
- $E_{\text{charged}, t}$ = the amount of refrigerant charged into new systems in year t
- k = assembly losses in per cent of the amount charged

The amount charged ($E_{\text{charged}, t}$) should include all systems which are charged in the country, including those which are made for export. Systems that are imported precharged should not be considered.

Typical range for the emission factor k is 2-5 per cent (Radian Corp., 1986). For some types of unit production, alternative leak detection methods may be used. Assembly losses may then be less than indicated here, and in some cases may be negligible.

Annual leakage from the stock, including venting during service, is commonly expressed in per cent of total amount of "banked" refrigerant in the existing stock of systems. Emission rates related to current system design and service practices are available from half a century of CFC and HCFC refrigeration. The following calculation formula applies:

EQUATION 2

$$E_{\text{operation}, t} = E_{\text{stock}, t} \cdot (x/100)$$

where:

- $E_{\text{operation}, t}$ = amount of HFC/PFC emitted during system operation in year t
- $E_{\text{stock}, t}$ = amount of HFC/PFC stocked in existing systems in year t
- x = annual leakage rate in per cent of total HFC/PFC charge in the stock, per cent.

In calculating the refrigerant "bank" ($E_{\text{stock}, t}$) all systems in operation in the country (home-made and imported) have to be considered.

Examples of typical leakage rates (x) for various types of equipment describing the respective refrigeration sectors are given later in this section.

The amount of refrigerant released from scrapped systems depends on the amount of refrigerant left at the time of disposal, and the portion recovered. Normally, less refrigerant is left than was originally charged. From a technical point of view, the major part of the remaining fluid can be recovered.

To estimate emissions at system disposal, the following calculation formula is applicable:

EQUATION 3

$$E_{\text{disposal, } t} = E_{\text{charge (} t - n)} \cdot (y/100) \cdot (100 - z)/100$$

or

$$E_{\text{disposal, } t} = E_{\text{charge (} t - n)} \cdot Q$$

where:

$E_{\text{disposal, } t}$	=	amount of HFC/PFC emitted at system disposal in year t
$E_{\text{charge (} t - n)}$	=	amount of HFC/PFC initially charged into new systems installed in year (t-n)
n	=	average equipment lifetime, years
y	=	amount of HFC/PFC in systems at time of disposal in per cent of initial charge, per cent
z	=	amount of HFC/PFC recovered in per cent of actual charge ("recovery efficiency"), per cent
Q	=	amount of HFC/PFC emitted at system disposal in per cent of the quantity of chemical originally charged into the system, per cent $Q = y(100 - z)/100$

In estimating the amount of refrigerant initially charged into the systems ($E_{\text{charged, (} t - n)}$), both systems charged in the country (for home market) and systems imported precharged should be taken into account. First charge of systems made for export should not be considered.

Values applicable to n, y and z are discussed later in this section when dealing with the respective sectors.

Total emissions in year t will then be found as the sum of emissions at assembly, during operational life and at disposal:

EQUATION 4

$$E_{\text{total, } t} = E_{\text{assembly, } t} + E_{\text{operation, } t} + E_{\text{disposal, } t}$$

Estimating input data for actual emission calculations

To provide a good basis for emission calculations according to Tier 2, it appears that much detailed information (Equations 1-3) about HFC/PFC use is required. The most important information is reliable estimates for the overall consumption and consumption distribution.

In principle, there are two different approaches to determine consumption figures. One is to estimate the amounts and types of each chemical from the number of refrigerating and air conditioning systems in question ("bottom-up approach").

Alternatively, one may start with more general registrations or estimates of HFC/PFC use for refrigeration purposes, and distribute these figures among the various sectors according to the relative magnitude of each sector ("top-down approach"). A reasonably good distribution key has to be developed also with respect to the individual types of



HFCs/PFCs. Refrigeration and air conditioning organisations in the country may possess useful data with respect to the information required.

A bottom-up approach may work well when estimating emissions from refrigerating units of similar type and design, the number of which may be large but known (such as refrigerators, AC units, mobile air conditioners etc.).

The top-down approach is more general, and probably more practical for systems which are erected and charged at site, and for production of systems with large variations in purpose, design and charge. This approach is less likely to under-estimate emissions, since it is based on total HFC/PFC consumption figures.

It may be practicable to apply elements from both approaches. However, one has to be cautious about double counting.

Examples demonstrating the top-down approach are provided in Table 2-30, which shows distribution of individual HFCs/PFCs within the same sectors.

		HFC-23	HFC-32	HFC-125	HFC-134A	HFC-143A	HFC-152A	PFC-218
Household refrigeration	Norway	0	0	0	100%	0	0	0
	Sweden	0	0	0	100%	0	0	0
Other stationary equipment	Norway	<1%	<1%	19%	71%	7%	2%	<1%
	Sweden	<1%	<1%	<5%	95%	<5%	<1%	<1%
Mobile air conditioning	Norway	0	0	0	100%	0	0	0
	Sweden	0	0	0	100%	0	0	0

Estimated amounts of the various "base chemicals" going into each specified sector may follow from total quantities HFCs/PFCs consumed and the distribution keys laid down in Table 2-29. Since HFCs and PFCs have only recently entered the market, consumption figures for the various chemicals relative to each other may change somewhat over time.

These figures may be useful for countries with similar practices as those shown in the table, to make first estimates for their own HFC/PFC consumption distribution in refrigeration.

Estimating emissions from household refrigeration

Information for household refrigerators and freezers is very reliable, and emission rates in the form of leakages and service losses are very low. Average lifetime is expected to be 15 years (n in Equation 3 is equal to 15). Even though a refrigerator is sensitive with respect to low charge, it is estimated that only 1 per cent of the units in operation fail each year due to loss of charge (U.S. EPA, 1992a), resulting in an average refrigerant loss per year of 1 per cent of the total quantity banked in the stock.

A certain, but small amount of the charge of those refrigerators reaching the average lifetime will have escaped during operation. The remaining charge is emitted upon disposal of the refrigerator (Kroeze 1995; U.S. EPA 1992a). This was common practice until recently. Over the past 2-4 years, recovery and recycling practices have been

established in many countries to minimise CFC emission. Similar practices may be applied to reduce HFC/PFC emission as well.

In the industrialised world, the overwhelming majority of household refrigerators are not serviced during their lifetime (U.S. EPA, 1992a). However, recharging is very common in many developing countries, and 2 to 3 charges during the lifetime of a fridge may be typical. From this it may be deduced that the average failure rate is higher in these countries, and the physical lifetime of a refrigerator may be longer.

Emission of HFCs/PFCs during assembly, operation and disposal of household refrigerators and freezers in the year t are to be calculated according to Equations 1-4. Emission factors related to system assembly, operation and disposal (k , x and Q respectively) should be chosen according to each country's experience.

Example of common range of variation for k in the past is given under Calculation Methods earlier in this section. It is believed that k for household refrigerators and freezers belongs to the lower part of the range (2 per cent). In those cases where trace gases other than the refrigerant itself are used for leak detection, e.g., helium, k becomes practically zero.

American experience with respect to annual leakage rate, as referenced above, indicates that a typical value for x in developed countries may be 1 per cent.

The remaining charge after 15 years (y in Equation 2) is not well known, but is believed to be in the order of 90 per cent. If recovery and recycling are not practised (z in Equation 3 is equal to zero), Q becomes equal to 90 per cent. However, if one allowed for the recovery and recycling which is possible now, Q could decrease to 40 per cent. The practical recovery rate (z) for refrigerant in refrigerators is just below 50 per cent (McCulloch, 1994). Kroeze indicates a range of recovery of 30-60 per cent (Kroeze, 1995), which is consistent with the figure given by McCulloch (1994).

Reasonable estimates for the number of refrigerators and freezers manufactured in a country are generally available, as well as the number of imported and exported units and the total stock. The amount of refrigerant banked in the stock can be calculated by multiplying the number of units with average charge sizes. American refrigerators have an average charge of 170 grams, while the corresponding figures for Europe and Japan are 140 grams and 137 grams respectively (Fischer et al., 1991; Fujimoto, 1991).

Refrigerators made in developing countries may have different (probably larger) average charges than those values indicated above.

Emissions from Other Stationary Refrigeration and Air Conditioning Equipment

Other stationary refrigeration and air conditioning equipment is not usually hermetically sealed and therefore has higher leak rates and requires servicing on a regular basis to replace refrigerant leaked over time. In addition, these units typically have much larger charge sizes than household refrigeration equipment.

Emissions of HFCs/PFCs during assembly, operation and disposal of other stationary refrigeration and air conditioning equipment in the year t are to be calculated according to Equations 1 to 4. Emission factors related to system assembly, operation and disposal (k , x and Q respectively) should be chosen according to each country's experience. Average system lifetime is expected to be 15 years (n in Equation 3 is equal to 15).

An example of a common range of historical variation for k is given under Calculation Methods earlier in this section. It is believed that k for factory built systems (unit



systems) belongs to the lower part of the range (2-3 per cent), while k for systems erected and charged at site are higher (4-5 per cent).

Various references (Enquete Commission, 1994; U.S. EPA, 1993; McCulloch, 1994) seem to agree that leakage emissions from other stationary equipment are approximately 17 per cent on average ($x = 17\%$).

Since all systems leak, the average charge at the point of disposal will be less than the amount initially charged into the systems (and after topping up at service). However, exact figures are not known. If country specific data are not available, 90 per cent of that initially charged may be assumed for calculation purposes (y in Equation 2 represents 90 per cent). The charge remaining in the equipment upon retirement is normally vented (z in Equation 3 is equal to zero), which means that Q equals 90 per cent.

Emissions at assembly, during operation, and at disposal may be reduced through the implementation of future actions designed to reduce leakage and disposal emissions. Specifically, leakage rates in other stationary refrigeration and air conditioning equipment can be reduced through the use of improved valves and fittings that minimise such emissions, and emissions that occur upon service and disposal of equipment can be reduced through the use of recovery or recycling technologies.

Assuming the implementation of these technologies, leakage emissions can be reduced to as low as 3 per cent ($x = 3\%$) per year and emissions upon retirement of equipment can be reduced by as much as 80 per cent ($z = 80\%$, $Q = 18\%$).

Refrigerant charge may vary over a wide range, dependent upon system size and design. The following range may indicate orders of magnitude (U.S. EPA, 1993):

- Residential air conditioning: 2 to 3 kg
- Transport Refrigeration: 8 kg
- Retail Food Refrigeration: 10 to 230 kg
 - Chillers: 75 to 900 kg
 - Industrial Process Refrigeration: 340 to 9100 kg
 - Commercial and industrial appliances: 0.10 to 0.50 kg

To apply the bottom-up approach, reliable average values for system charge sizes valid for each country will be required to develop useful estimates.

Emissions from Mobile Air Conditioning (MAC)

Car air conditioners are relatively leaky systems that require frequent servicing. Estimates for current applications are that approximately one-third of the charge is leaked each year (McCulloch, 1994), and that the remaining charge in equipment is emitted upon its retirement. Car air conditioners have typical lifetimes of 11 years (small cars) to 15 years (trucks) (UNEP, 1989). On average, a lifetime of 12 years may be assumed (n in Equation 3 is equal to 12).

Emission of HFCs/PFCs during assembly, operation and disposal of mobile air conditioners in the year t are to be calculated according to Equations 1-4. Emission factors related to system assembly, operation and disposal (k , x and Q respectively) should be chosen according to each country's experience.

New HFC systems may have less leakage, e.g., 10-20 per cent ($x = 10\text{-}20\%$) (Arai, personal communication, 1996).

Example of common range of variation for k in the past is given under Calculation Methods earlier in this section. It is believed that k for MACs belongs to the upper part of the range (4-5 per cent).

With respect to x , a typical value according to past CFC/HCFC experience, as referenced above, is, about one third ($x = 30\%$).

Since MACs are generally more leaky than stationary systems, average charge at the point of disposal will most probably be less than typical values for stationary systems. However, exact figures are not known. If country specific data are not available, 75 per cent of that initially charged may be assumed for calculation purposes (y in Equation 2 is equal to 75 per cent). In most cases, the refrigerant is vented at disposal (z in Equation 3 is zero), which means that Q equals 75 per cent.

With improved system components, such as improved seals, fittings, and hosing, and the use of recycling at service, emissions from MACs during normal use (x) should eventually be reduced to 10 per cent of the charge per year

In addition, recycling at disposal provides the opportunity to reduce emissions upon retirement by more than 80 per cent. If recycling is fully utilised, emission at disposal may decrease to 15 per cent of the amount originally charged ($Q = 15\%$).

According to UNEP Technical Options Report (UNEP, 1989), typical refrigerant charges in mobile air conditioners are 1.2 kg/unit for cars and 1.5 kg/unit for trucks. MACs in newer cars may have a lower charge, e.g., 800 g which is typical for Japanese passenger cars (Nagayama, 1996).

2.17.4.3 Estimation of Emissions of HFCs and PFCs from Foam Blowing

HFCs are potential replacements for CFCs and HCFCs in the manufacture of insulating, cushioning, and packaging foams. The specific compounds that may be used include HFC-125, HFC-134a, HFC-143a, and HFC-152a (Kroeze, 1995; U.S. EPA, 1992b).

HFCs and PFCs may potentially be used as alternative blowing agents in the manufacture of open cell foam products such as cushioning and packaging foams. For open cell foams, HFC and PFC emissions occur at the time of manufacture and are equal to 100 per cent of the total quantity of chemical used as the blowing agent (U.S. EPA, 1992a; Fisher and Midgley, 1993). As a result total HFC or PFC emissions in year t for open cell foam can be calculated as follows:

Emissions of HFCs or PFCs in year t
=
100% of the quantity of HFCs or PFCs sold for blowing open cell foam in year t

The total quantity of HFCs or PFCs used in blowing open cell foam can be calculated as the quantity (in kg or tonnes) of foam manufactured in a given year times the quantity of HCF or PFC used per kilogram or tonne of open cell foam produced.

Kroeze (1995) estimates that approximately 55 per cent of the HFC or PFC used as blowing agent in the manufacture of open cell foams could potentially be recycled. If such recycling occurs, total emissions from open cell foam manufacture would still be 100 per cent of the chemical *sold* for foam blowing purposes but this would be less because the



amount in use would be reduced by a quantity equal to that recycled. Provided that 55 per cent of the blowing agent is recycled, the gas used for the blowing process will be a mixture of 45 per cent virgin chemical and 55 per cent recycled chemical.

For insulating (closed cell) foams, only about 10 per cent of the blowing agent is released during the blowing of the foam, while the remaining chemical is contained in the insulation. This quantity remaining in the foam is slowly released over the 20 to 25 year lifetime of the foam (Gamlen et al., 1986). HFC or PFC emissions from insulating foam in year t are therefore calculated as follows:

Emissions of HFCs or PFCs in year t
=
10 per cent of the total quantity of HFC or PFC used in manufacturing new insulating foam in year t
+
4.5 per cent of the quantity of original HFC or PFC charge blown into the insulated foam manufactured between year t and year $t-20$

The total quantity of HFCs or PFCs used in blowing insulating foam can be calculated as the quantity (in kg or tonnes) of new foam manufactured in a given year times the quantity of HFC or PFC used per kilogram or tonne of new insulating foam produced and with 10 per cent production lost added. Typically, the blowing agent accounts for 6-15 per cent of the total foam weight (Fischer et al., 1991).

The total quantity of HFC or PFC contained in the existing stock of insulating foam can be calculated as the product of the total quantity of insulating foam in use in year t and the average charge of chemical contained in each tonne of such installed insulating foam.

Finally, Kroeze (1995) estimates that approximately half of the quantity of chemical emitted during the blowing of insulating foam could be reduced through recycling and/or leakage control and that approximately 80 per cent of the HFCs or PFCs contained in insulating foam at retirement could be recycled or destroyed (approximately 30 to 40 per cent of the charge remains in the foam upon retirement). If such potential future actions are implemented, then emissions in year t from insulating foam can be calculated as follows:

Emissions of HFCs or PFCs in year t
=
5% of the total quantity of HFC or PFC sold for use in manufacturing new insulating foam in year t
+
3.6% of the total HFC or PFC contained in the existing stock of insulating foam in year t .

The production losses of 5 per cent represents net losses, that is the amount of blowing agent escaped from the process minus the amount of blowing agent recovered.

2.17.4.4 Estimation of Emissions of HFCs, PFCs, and SF₆ from Fire Extinguishing

HFCs and PFCs are potential replacements for Halon 1211 in portable fire extinguishers and Halon 1301 in total flooding fixed fire extinguishing systems. Potential substitutes include HFC-23, HFC-125, HFC-227ea, PFC-410, and PFC-614 (U.S. EPA, 1992b; Kroeze, 1995).

McCulloch (1992) estimates that total halon emissions can be estimated as 60 per cent of total halon 1211 contained in new portable halon fire extinguishers installed each year, and as 35 per cent of total Halon 1301 contained in new total flooding equipment installed each year. The remaining amounts of chemical, 40 per cent for portable fire extinguishers and 65 per cent for total flooding equipment respectively, add to the bank of fire extinguishing chemicals.

Replacement HFCs and PFCs for fire extinguishing equipment are likely to be emitted at lower rates than the halons they replace, due to improved testing and practising procedures. Until these new procedures are adopted, however, emission rates for replacement chemicals may be similar to those for existing systems.

The method used to estimate emissions here is appropriate for the mature market for fire extinguishing agents. Transition to HFCs and PFCs in this market would result in a relatively rapid increase in the banks of these materials held in equipment while the bank of halons would decline. Unless there is a requirement to replace the halons bank, the equations developed for halon emissions should be appropriate for HFCs and PFCs in this application and so the estimate for HFC or PFC emissions from portable equipment in year t would be:

$$\begin{array}{c} \text{Emissions of HFCs or PFCs in year } t \\ = \\ \text{60 per cent of the total quantity of HFC or PFC used in new portable} \\ \text{halocarbon fire extinguishing equipment installed in year } t \end{array}$$

Similarly, emissions estimates in year t for total flooding equipment can be calculated as:

$$\begin{array}{c} \text{Emissions of HFCs or PFCs in year } t \\ = \\ \text{35 per cent of the total quantity of HFC or PFC used new fixed halocarbon} \\ \text{fire extinguishing equipment installed in year } t \end{array}$$

Finally, McCulloch estimates that HFC and PFC emissions from the fire extinguishing equipment sector could eventually be reduced to 30 per cent of total sales for portable systems and 15 per cent of sales for fixed systems based on improved housekeeping, servicing, and bank management practices.



Emission of sulphur hexafluoride from fire extinguishing equipment

Some of the new substitutes for halon in fire extinguishing equipment contain sulphur hexafluoride, SF₆, probably in blends with HFC. If the products contain SF₆, it is emitted to the atmosphere in the same manner as HFC or PFC. The equations for the estimation of HFC and PFC emissions from fire extinguishing equipment are therefore also valid for SF₆, since they have to be adjusted for the proportion of the SF₆ in the original blend. Emissions of SF₆ are to be calculated according to the proportion of this chemical in the blend.

2.17.4.5 Estimation of Emissions of HFCs and PFCs from Aerosol Products

HFCs may be used as replacements for CFCs and HCFCs in aerosol propellants in industrial and technical applications, and household, medical and personal care products. The HFCs that may be used include HFC-125, HFC-134a, 152a, and HFC-227ea (Kroeze, 1995; U.S. EPA, 1992b).

Gases from aerosols are usually released shortly after production, on average six months after sale in the United States and Europe. During use of aerosols, 100 per cent of the chemical is emitted (Gamlen et al., 1986; U.S. EPA, 1992a). For this methodology, aerosol emissions are estimated to be one half of the current year sales of the aerosol plus one half of the previous year sales (Gamlen et al., 1986). In other words, aerosol emissions in year t can be calculated as follows:

Emissions of HFCs in year t
=
50% of the quantity of HFCs contained in aerosols sold in year t
+
50% of the quantity of HFC contained in aerosols sold in year t-1

This calculation accounts for the six month lag from purchase to use. Total aerosol use each year can be calculated as the number of aerosol cans sold in a given year times the charge of HFC or PFC in each can. Finally, Kroeze (1995) points out that technologies do not exist to reduce emissions from aerosol cans.

2.17.4.6 Estimation of Emissions of HFCs and PFCs from Solvents

HFCs and PFCs may be used as replacements for CFC-113 in metal cleaning, electronics, and precision cleaning applications and as replacements for aerosol cleaning. The compounds that may be used include HFC-43-10, PFC-614, PFC-512, PFC-612, PFC-716, and PFC-819 (Kroeze, 1995; U.S. EPA, 1992b).

Chemicals used as cleaning agents are emitted during, or shortly after, use and are typically 100 per cent of total use (Fisher and Midgley, 1993; U.S. EPA, 1992a). This methodology assumes that solvents, on average, are used six months after they are sold. Total HFC or PFC emissions in year t can therefore be calculated as follows:

$$\begin{aligned} & \text{Emissions of HFCs or PFCs in year } t \\ & = \\ & \text{50\% of the quantity of HFCs or PFC} \\ & \text{sold for use in solvent applications in year } t \\ & + \\ & \text{50\% of the quantity of HFCs sold for use in solvent applications in year } t-1 \end{aligned}$$

It has been estimated that solvent emissions can be reduced by up to 80 per cent through the use of improved housekeeping and recycling practices.

2.17.4.7 Estimation of Emissions of HFCs and PFCs from Other Applications

Other Applications

Other applications in which HFCs and PFCs may replace CFCs and HCFCs include sterilisation equipment, tobacco expansion applications, and use as solvents in the manufacture of adhesives, coatings, and inks. The specific compounds include HFC-125, HFC-134a, and HFC-227ea (Kroeze, 1995; U.S. EPA, 1992b).

For other applications, it is assumed that all HFCs and PFC are released within 6 months after production. Emissions in the year t can be calculated as follows:

$$\begin{aligned} & \text{Emissions of HFCs or PFCs in year } t \\ & = \\ & \text{50\% of the quantity of HFCs/PFCs sold for other applications in year } t \\ & + \\ & \text{50\% of the quantity of HFCs/PFCs sold in year } t-1 \end{aligned}$$

2.17.4.8 Sulphur Hexafluoride (SF₆) Emissions

Primary uses of SF₆

Primary uses of SF₆ include the following:

Gas-Insulated Switchgear and Circuit Breakers

SF₆ is used as an insulation medium in high tension electrical equipment including gas insulated switchgear (GIS) and circuit breakers.

Fire suppression and explosion protection

Some of the new gases placed on the market as substitutes for halons in fire extinguishing equipment, may contain up to 20 per cent sulphur hexafluoride, SF₆. These applications are described in Section 2.17.4.4.

Globally, it is estimated that about 80 per cent of SF₆ is used in gas-insulated switchgear and circuit breakers, 5 to 10 per cent in the magnesium and aluminium industries, and 5 to 10 per cent in a number of smaller applications (Ko et al., 1993).



Other applications

SF₆ is used in a variety of additional applications including as an insulating medium in sound proof windows, in leak detectors, gas-air tracers, and various electronic applications. The use of SF₆ in production of aluminium and magnesium is covered under Section 2.13.8.

Recommended methodology for estimating SF₆ emissions

Total emissions of SF₆ used in GIS application and circuit breakers can be assumed to be approximately 1 per cent of the total quantity of SF₆ contained in such equipment each year (NILU, 1993). In addition, if it is assumed that GIS equipment has a lifetime of 30 years, then approximately 70 per cent of the SF₆ will remain in the equipment upon retirement and will then be released upon disposal of the equipment (NILU, 1993). Total emissions from GIS applications can therefore be estimated as:

Emissions of SF ₆ in year t
=
1% of the total charge of SF ₆ contained in the existing stock of equipment in year t
+
70% of the quantity of equipment manufactured in year t-30.

The total charge of SF₆ contained in equipment can be estimated as the product of the total quantity of equipment in operation and the typical charge size of equipment. Charge sizes for GIS equipment rated to 50 kV or more can range from hundreds to thousands of kilos per installation, and for low-voltage switches contain 1-2 kg per installation (Kroeze, 1995).

If data on the total stock of GIS are unavailable, then it should be assumed that emissions equal consumption.

2.18 References

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CHAPTER 3
SOLVENT AND OTHER
PRODUCT USE



3 SOLVENT AND OTHER PRODUCT USE

3.1 Overview

Solvents and related compounds are important for greenhouse gas (GHG) and other emission inventories because they are a significant source of emissions of non-methane volatile organic compounds (NMVOCs). No other GHGs are emitted in significant amounts from the use of solvents and related compounds, which include chemical cleaning substances used in dry cleaning, printing, metal degreasing, and a variety of industrial applications as well as household use. Also included in this category are paints, lacquers, thinners and related materials used in coatings in a variety of industrial, commercial and household applications. Table 3-1 lists some of the potentially important subcategories included under this source category.

This category also includes evaporative emissions of greenhouse gases arising from other types of product use. This included, for example, N₂O emissions from medical use. Emissions arising from the use of hydrofluorocarbons (HFCs) in applications like refrigeration, air conditioning, fire extinguishers, solvents foam-blowing, cooling and aerosols should be reported in Industrial Processes under category 2F.

All of the substances included here contain significant amounts of NMVOC. Emissions are produced through evaporation of the volatile chemicals when these products are exposed to air. Non-methane volatile organic compounds (NMVOCs) are often emitted in significant quantities from evaporation during the variety of dispersed activities discussed above. These emissions are sometimes referred to as "area" sources because they occur in large numbers of small dispersed applications, rather than from large centralised industrial processes (or "point" sources).

Solvent and other product use is treated as a separate category in detailed inventory procedures (e.g., CORINAIR) because the nature of this area source requires a somewhat different approach to emissions estimation than that used for calculating other emissions categories. The IPCC *Guidelines* treats the category separately for this reason.

3.2 NMVOC Emissions from Solvent and Other Product Use

NMVOC emissions estimates are characterised by high uncertainty. This is especially true for the solvent use source category on a global scale. The contribution of this source category is believed to be quite significant. A preliminary analysis estimated total global NMVOC release from solvent use to be about 11 per cent of total NMVOC emissions (Watson, et al., 1991).

Based on national GHG emissions inventories, NMVOC emissions from these sources can represent a much larger share of the total NMVOC emissions for some countries. NMVOC from solvent use represents 31 per cent of the total NMVOC emissions for both Italy and Denmark. (ENEA, 1991, Fenger et al., 1990) The Netherlands estimates solvent use to account for 25 per cent, and both Finland and the United States estimate emissions to be 24 per cent of their total NMVOC emissions (van den Born et al., 1991, Boström et al., 1992, US EPA, 1991). By contrast, emissions from solvent use in Nigeria were only 3 per cent of the total NMVOC (Obioh et al., 1992).

3.2.1 Estimating Emissions

The wide variations in national emissions from solvent and other product use highlight the differences in their use between countries and some of the difficulties associated with accurately estimating emissions from these sources.

There are two basic approaches to estimation of emissions from Solvent and Other Product Use, which depend on the availability of data on the activities producing emissions and the emission factors.

- 1 Production-based** - In some cases, solvent or coating use is associated with centralised industrial production activities, such as automobile and ship production, textile manufacture, paper coating, chemical products manufacture, etc. In these cases it is generally possible to develop NMVOC emission factors based on unit of product output. These are based on the amount of paint, solvents, or other chemically volatile products consumed per unit of production of the final products. Once reasonable factors are developed it is straightforward to estimate annual emissions based on production data which are generally available on an annual basis for most countries. Industrial production data is also compiled and published by international organisations (e.g., United Nations, 1992) and these data can be used to supplement locally available data.
- 2 Consumption-based** - In many applications of paints, solvents and similar products, the end uses are too small-scale, diverse, and dispersed to be tracked directly. Therefore emissions estimates are generally based on total consumption (i.e., sales) of the solvents, paints, etc. used in these applications. The assumption is that once these products are sold to end users, they are applied and emissions produced relatively rapidly. For most surface coating and general solvent use, this approach is used. Emission factors are developed based on the likely ultimate release of NMVOC to the atmosphere per unit of product consumed. These emission factors can then be applied to sales data for the specific solvent or paint products.

The IPCC/OECD joint programme has not produced any original work on estimation of NMVOCs from the use of these products. This is for two reasons. First, NMVOC is a greenhouse gas (actually a class of gases) covered under the programme, but it has been



assigned a lower priority for national experts just initiating greenhouse gas inventory work. Most methods development work within the IPCC/OECD programme has focused on providing methods and default information for the first priority gases - CO₂, CH₄, and N₂O, which are direct greenhouse gases. Second, NMVOCs are among the gases already under heavy scrutiny in national and international inventory programmes because of their role as local and regional air pollutants. Hence there is a large and growing body of literature containing guidance on estimation procedures and emission factors for NMVOCs from a number of source categories, including from solvents and other products.

National experts who are already familiar with these procedures and have emissions data available or under development, should report these data to the IPCC/OECD programme, as discussed in *Volume 1: Reporting Instructions*.

Other experts needing information should consult the existing major references such as:

- Default Emission Factor Handbook (EEATF, 1992);
- US EPA's Compilation of Air Pollutant Emissions Factors (AP-42) (US EPA, 1985) and Supplement F (AP-42) (US EPA, 1993);
- Criteria Pollutant Emission Factors for the 1985 NAPAP Emissions Inventory (Stockton and Stelling, 1987).
- Proceedings of the TNO/EURASAP Workshop (TNO Inst. of Environmental Sciences, 1993).
- EMER/CORINAIR (1996) Joint Emission Inventory Guidebook (1st edition).

3.2.2 Uncertainties

Because NMVOC emission controls vary widely throughout the world, it is important for national experts to account for the level of emission control application in their country. Also, there may be significant differences among countries regarding the processes and equipment used. These differences can affect the level of NMVOC emissions. Finally, because estimates based on consumption data provide only an approximation of the activities associated with the manufacture of all products within a particular subcategory, there is a degree of uncertainty in the estimates (Watson, et al., 1991).

Surface coating (e.g., painting) operations	Applications of paints, lacquer, enamel and primer to cans, wood products, metal parts, buildings, etc. Use of thinning solvents.
Paper coating operations	Coating operations, mixing and use of thinning solvents.
Printing and Publishing	Press operations, lithography, use of thinning solvents.
General Solvent Use	Vapour degreasing, dry cleaning, textile manufacture, household solvent use.
Production of Automobiles and Trucks	Surface coating, cleaning/degreasing operations.
Ship building	Surface coating, cleaning/degreasing operations.
Chemical Products Manufacture and Processing	Solvents are used in a variety of applications in the manufacturing of chemicals and chemical products.

3.3 References

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