



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

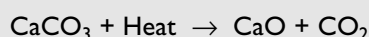
The IPCC Methodology for national GHG inventories requires an intentional double reporting of NMVOCs, methane and carbon monoxide, firstly in their individual inventories, and as CO₂ equivalent in the national CO₂ inventory. Whether an explicit addition to the CO₂ inventory is required depends on how 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.



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

$$=$$

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

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)

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

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

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

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

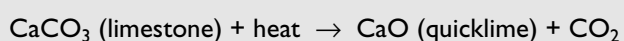
EMEP/CORINAIR has classified cement production as both an industrial combustion and an industrial process (SNAP codes 30311 and 40612, respectively). However, no description of emission factors for the non-combustion emissions are presented. A default methodology is, therefore, presented below.

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.

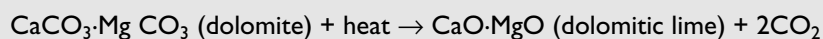
2.4 Lime Production

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 CO₂) 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 ~ 1100° 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 CO₂

The mass of CO₂ 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 CO₂ 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, CO₂ 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.



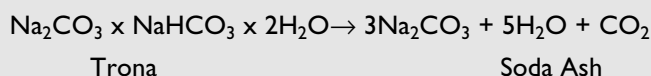
2.6 Soda Ash Production and Use

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.

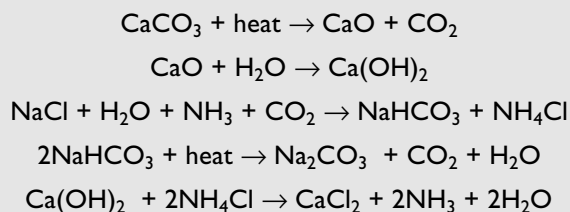
About 25 per cent of the world production is produced from natural sodium carbonate-bearing deposits referred to as natural processes. During the production process, trona (the principal ore from which natural soda ash is made) is calcined in a rotary kiln and chemically transformed into a crude soda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



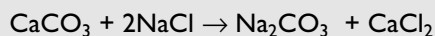
According to this reaction, it takes 10.27 tonnes of trona to produce 1 tonne of carbon dioxide. Hence, for natural soda ash production, emissions of carbon dioxide can be calculated by the following formula:

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

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.

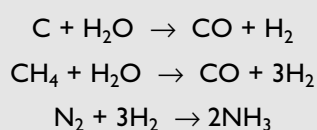
One emission source is the production of concrete pumice stone. As for cement production, SO₂ emissions will originate from the fuel use and sulphur in clay. About 45 per cent of the SO₂ generated in the process will be sequestered in the product. An emission factor of about 0.5kg SO₂/tonne product has 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.

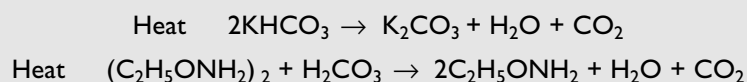
Natural gas is used as the feedstock in most plants, while other fuels (e.g., heavy oils) may be used with the partial oxidation process. In addition, plants may use by-product hydrogen, rather than natural gas, to produce ammonia (thereby eliminating the release of CO₂ from the synthesis process) (CFI,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

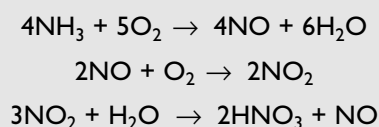
2.9 Nitric acid Production

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.

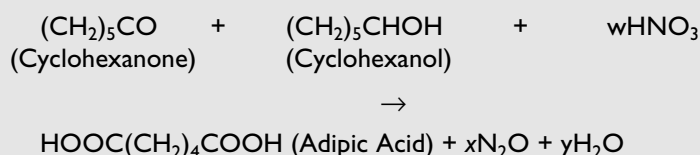


2.10 Adipic Acid Production

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.

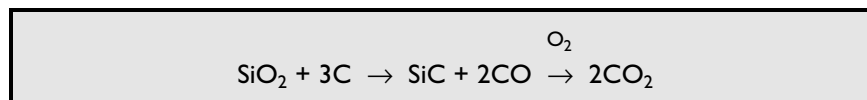
The EMEP/CORINAIR Guidebook indicates that there may be emissions of CO₂, NO and NO₂ in addition to N₂O, but does not propose emission factors at present. Furthermore, European reported emission data indicate that pollutants other than N₂O are not significant (CORINAIR-90). U.S. EPA emission factors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

TABLE 2-8 EMISSION FACTORS FOR ADIPIC ACID PRODUCTION (KG/TONNE PRODUCT)		
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