



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.

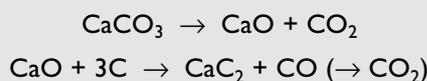
More carbon is actually needed in the process than calculated from a stoichiometric reaction. The suggested emission factors are calculated from coke input in Norwegian plants. The excess carbon is oxidised during the process, little is left as ash (Raanes, 1991).

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:

	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	-
Phtalic 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 Søderberg anode and vertical stud Søderberg anode. Prebaked anodes have been preferred over Søderberg 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.

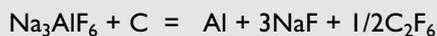
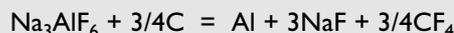
2.13.6 PFCs from Aluminium Production

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:

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

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.