

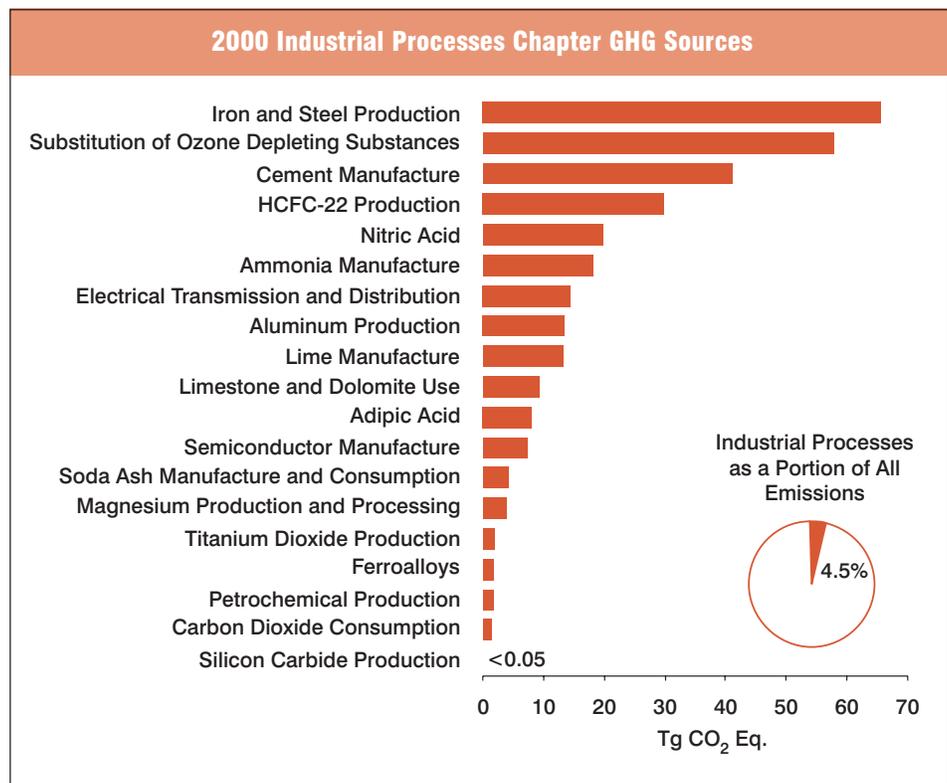
3. Industrial Processes

Greenhouse gas emissions are produced as a by-product of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide (CO₂), methane (CH₄), or nitrous oxide (N₂O). The processes addressed in this chapter include iron and steel production, cement production, ammonia manufacture, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and use, titanium dioxide production, ferroalloy production, CO₂ consumption, aluminum production, petrochemical production, silicon carbide production, nitric acid production, and adipic acid production (see Figure 3-1).

In addition to the three greenhouse gases listed above, there are also industrial sources of several classes of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆). The present contribution of these gases to the radiative forcing

effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, many of them will continue to accumulate in the atmosphere as long as emissions continue. Usage of these gases, especially HFCs, is growing rapidly as they are the primary substitutes for ozone depleting substances (ODS), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to ODS substitutes, HFCs, PFCs, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing. Sulfur hexafluoride is the most potent greenhouse gas the IPCC has evaluated.

Figure 3-1



In 2000, industrial processes generated emissions of 312.8 Tg CO₂ Eq., or 4.5 percent of total U.S. greenhouse gas emissions. Carbon dioxide emissions from all industrial processes were 161.9 Tg CO₂ Eq. (161,940 Gg) in the same year. This amount accounted for only 2.8 percent of national CO₂ emissions. Methane emissions from petrochemical and silicon carbide production resulted in emissions of approximately 1.7 Tg CO₂ Eq. (79 Gg) in 2000, which was less than 1 percent of U.S. CH₄ emissions. Nitrous oxide emissions from adipic acid and nitric acid production were 27.9 Tg CO₂ Eq. (90 Gg) in 2000, or 6.6 percent of total U.S. N₂O emissions. In the same year, combined emissions of HFCs, PFCs and SF₆ totaled 121.3 Tg CO₂ Eq. Overall, emissions from industrial processes increased by 6 percent from 1990 to 2000, which was the result of increases in emissions from several industrial processes—the largest being substitutes for ozone depleting substances—which was offset by decreases in emissions from adipic acid production, aluminum production, and production of HCFC-22.

Greenhouse gases are also emitted from a number of industrial processes not addressed in this chapter. For example, caprolactam—a chemical feedstock for the manufacture of nylon 6,6—and urea production are believed to be industrial sources of N₂O emissions. However, emissions for these and other sources have not been estimated due to a lack of information on the emission processes, manufacturing data, or both. As more information becomes available, emission estimates for these processes will be calculated and included in future greenhouse gas emission inventories, although their contribution is expected to be small.¹

The general method employed to estimate emissions for industrial processes, as recommended by the Intergovernmental Panel on Climate Change (IPCC), involves multiplying production data for each process by an emission factor per unit of production. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically derived emission factors that

are biased and, therefore, may not represent U.S. national averages. Additional sources of uncertainty specific to an individual source category are discussed in each section.

Table 3-1 summarizes emissions for the Industrial Processes chapter in units of teragrams of carbon dioxide equivalents (Tg CO₂ Eq.), while unweighted gas emissions in gigagrams (Gg) are provided in Table 3-2.

Iron and Steel Production

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO₂. Iron is produced by first reducing iron oxide (iron ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron containing about 3 to 5 percent carbon by weight). Metallurgical coke is manufactured in a coke plant using coal as a raw material. Coke oven gas and coal tar are carbon by-products of the coke manufacturing process. The metallurgical coke is a raw material supplied to the blast furnace. Coke oven gas is generally burned as a fuel within the steel mill. Coal tar is used as a raw material in the manufacture of anodes used for primary aluminum production and for other electrolytic processes.

Carbon dioxide is produced as the metallurgical coke used in the blast furnace process is oxidized. Steel (containing less than 2 percent carbon by weight) is produced from pig iron in a variety of specialized steel making furnaces. The majority of CO₂ emissions from the iron and steel process come from the use of coke in the production of pig iron, with smaller amounts evolving from the removal of carbon from pig iron used to produce steel. Some carbon is also stored in the finished iron and steel products.

Emissions of CO₂ from iron and steel production in 2000 were 65.7 Tg CO₂ Eq. (65,709 Gg) (see Table 3-3). Emissions have fluctuated significantly from 1990 to 2000 due to changes in domestic economic conditions and changes in imports and exports. For the past several years, pig iron production has experienced a downward trend, however domestic production recovered somewhat in 2000. Pig iron production in 2000 was 4 percent higher than in 1999, but remains 6 percent below 1995 levels. Asian economic problems and the availability of low-priced imports limit growth in domestic production (USGS 2001).

¹ See Annex V for a discussion of emission sources excluded.

Table 3-1: Emissions from Industrial Processes (Tg CO₂ Eq.)

Gas/Source	1990	1995	1996	1997	1998	1999	2000
CO₂	168.2	164.1	160.4	171.2	164.2	161.4	161.9
Iron and Steel Production	85.4	74.4	68.3	76.1	67.4	64.4	65.7
Cement Manufacture	33.3	36.8	37.1	38.3	39.2	40.0	41.1
Ammonia Manufacture	18.5	18.9	19.5	19.5	20.1	18.9	18.0
Lime Manufacture	11.2	12.8	13.5	13.7	13.9	13.5	13.3
Limestone and Dolomite Use	5.2	7.0	7.4	8.4	8.2	9.1	9.2
Aluminum Production	6.3	5.3	5.6	5.6	5.8	5.9	5.4
Soda Ash Manufacture and Consumption	4.1	4.3	4.2	4.4	4.3	4.2	4.2
Ferroalloy Production	2.0	1.9	2.0	2.0	2.0	2.0	1.7
Titanium Dioxide Production	1.3	1.7	1.7	1.8	1.8	1.9	2.0
Carbon Dioxide Consumption	0.8	1.0	1.1	1.3	1.4	1.6	1.4
CH₄	1.2	1.5	1.6	1.6	1.7	1.7	1.7
Petrochemical Production	1.2	1.5	1.6	1.6	1.6	1.7	1.7
Silicon Carbide Production	+	+	+	+	+	+	+
N₂O	32.7	37.8	38.5	32.7	28.6	27.8	27.9
Nitric Acid Production	17.8	19.9	20.7	21.2	20.9	20.1	19.8
Adipic Acid Production	14.9	17.9	17.8	11.5	7.7	7.7	8.1
HFCs, PFCs, and SF₆	93.6	98.5	111.9	116.9	127.7	120.0	121.3
Substitution of Ozone Depleting Substances	0.9	21.8	30.6	38.0	44.9	51.3	57.8
HCFC-22 Production	35.0	27.0	31.1	30.0	40.2	30.4	29.8
Electrical Transmission and Distribution	31.2	26.5	26.8	24.5	20.1	15.5	14.4
Aluminum Production	18.1	11.8	12.5	11.0	9.0	8.9	7.9
Semiconductor Manufacture	2.9	5.9	5.4	6.5	7.3	7.7	7.4
Magnesium Production and Processing	5.5	5.5	5.5	6.9	6.2	6.1	4.0
Total	295.7	301.9	312.3	322.4	322.1	310.8	312.8

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

Methodology

Since coke is consumed as a reducing agent during the manufacture of pig iron, the corresponding quantity of coal consumed during coking operations was identified. This quantity of coal is considered a non-energy use. Data were also collected on the amount of imported coke consumed in the blast furnace process. These data were converted to their energy equivalents. The carbon content of the combusted coal and imported coke was estimated by multiplying their energy consumption by material specific carbon-content coefficients. The carbon-content coefficients used are presented in Annex A.

Emissions from the re-use of scrap steel and imported pig iron in the steel production process were calculated by assuming that all the associated carbon-content of these materials are released on combustion. Steel has an associated carbon-content of approximately 0.4 percent, while pig iron is assumed to contain 4 percent carbon by weight.

Emissions from carbon anodes, used during the production of steel in electric arc furnaces (EAF), were also estimated. Emissions of CO₂ were calculated by multiplying the annual production of steel in electric arc furnaces by an emission factor (4.4 kg CO₂/ton steel_{EAF}). It was assumed that the carbon anodes are composed of 80 percent petroleum coke and 20 percent coal tar pitch (DOE 1997). Since coal tar pitch is a by-product of the coking process and its carbon related emissions are already accounted for during the estimation of emissions from coal combustion, the emission factor was reduced by 20 percent to avoid double counting.

Similarly, an adjustment was made to account for the coal tar pitch component of carbon anodes consumed during the production of aluminum. Again, it was assumed that the carbon anodes have a composition of 80 percent petroleum coke and 20 percent coal tar. These coal tar emissions are accounted for in the aluminum production section of this

Table 3-2: Emissions from Industrial Processes (Gg)

Gas/Source	1990	1995	1996	1997	1998	1999	2000
CO₂	168,165	164,057	160,358	171,156	164,238	161,356	161,940
Iron and Steel Production	85,414	74,357	68,324	76,127	67,429	64,376	65,709
Cement Manufacture	33,278	36,847	37,079	38,323	39,218	39,991	41,067
Ammonia Manufacture	18,510	18,946	19,512	19,477	20,113	18,874	18,017
Lime Manufacture	11,238	12,804	13,495	13,685	13,914	13,466	13,316
Limestone and Dolomite Use	5,181	7,028	7,379	8,401	8,187	9,115	9,196
Aluminum Production	6,315	5,265	5,580	5,621	5,792	5,895	5,410
Soda Ash Manufacture and Consumption	4,142	4,305	4,239	4,355	4,325	4,217	4,181
Ferroalloy Production	1,980	1,866	1,954	2,038	2,027	1,996	1,719
Titanium Dioxide Production	1,308	1,670	1,657	1,836	1,819	1,853	1,963
Carbon Dioxide Consumption	800	968	1,140	1,294	1,413	1,572	1,361
CH₄	57	73	76	78	79	80	79
Petrochemical Production	56	72	75	77	78	79	79
Silicon Carbide Production	1	1	1	1	1	1	1
N₂O	106	122	124	106	92	90	90
Nitric Acid Production	58	64	67	68	67	65	64
Adipic Acid Production	48	58	57	37	25	25	26
HFCs, PFCs, and SF₆	M						
Substitution of Ozone Depleting Substances	M	M	M	M	M	M	M
HCFC-22 Production ^a	3	2	3	3	3	3	3
Electrical Transmission and Distribution ^b	1	1	1	1	1	1	1
Aluminum Production	M	M	M	M	M	M	M
Semiconductor Manufacture	M	M	M	M	M	M	M
Magnesium Production and Processing ^b	+	+	+	+	+	+	+

+ Does not exceed 0.5 Gg
M (Mixture of gases)
^a HFC-23 emitted
^b SF₆ emitted
Note: Totals may not sum due to independent rounding.

chapter. To prevent double counting, 20 percent of the emissions reported in the aluminum section have been subtracted from the estimates for iron and steel production.

Carbon storage was accounted for by assuming that all domestically manufactured steel had a carbon content of 0.4 percent. Furthermore, any pig iron that was not consumed during steel production, but fabricated into finished iron products, was assumed to have a carbon content by weight of 4 percent.

Data Sources

Data relating to the amount of coal consumed at coke plants, for the production of coke for domestic consumption in blast furnaces, as well as, the quantity of coke imported for iron production were taken from Energy Information Administration (EIA), *Quarterly Coal Report* October-December 2000 (EIA 2000); *U.S. Coal Domestic and International Issues* (EIA 2001); *Mineral Yearbook: Iron and Steel* (USGS 2000a, 1999, 1997, 1995a, 1993) and American Iron and Steel Institute (AISI), *Annual Statistical*

Table 3-3: CO₂ Emissions from Iron and Steel Production

Year	Tg CO ₂ Eq.	Gg
1990	85.4	85,414
1995	74.4	74,357
1996	68.3	68,324
1997	76.1	76,127
1998	67.4	67,429
1999	64.4	64,376
2000	65.7	65,709

Report (AISI 2000). Scrap steel and imported pig iron consumption data for 1990 through 2000 were obtained from *Annual Statistical Reports* (AISI 2000, 1995). Crude steel production, as well as pig iron use for purposes other than steel production, was also obtained from *Annual Statistical Reports* (AISI 2001, 1996). Carbon content percentages for pig iron and crude steel and the CO₂ emission factor for carbon anode emissions from steel production were obtained from *IPCC Good Practice Guidance and Uncertainty*

Management (IPCC 2000). Aluminum production data for 1990 through 2000 were obtained from *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995b, 1998, 2000b, 2001). The CO₂ emission factor for carbon anode emissions from aluminum production was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Estimates for the composition of carbon anodes used during steel and aluminum production were obtained from *Energy and Environmental Profile of the U.S. Aluminum Industry* (DOE 1997).

Uncertainty

Estimating CO₂ emissions from coal and coke combustion is based on energy consumption data, average carbon contents, and the fraction of carbon oxidized produce a relatively accurate estimate of CO₂ emissions. However, there are uncertainties associated with each of these factors. For example, carbon oxidation factors may vary depending on inefficiencies in the combustion process, where varying degrees of ash or soot can remain unoxidized.

Simplifying assumptions were made concerning the composition of carbon anodes (80 percent petroleum coke and 20 percent coal tar). For example, within the aluminum industry, the coal tar pitch content of anodes can vary from 15 percent in prebaked anodes to 24 to 28 percent in Soderberg anode pastes (DOE 1997). An average value was assumed and applied to all carbon anodes utilized during aluminum and steel production. The assumption is also made that all coal tar used during anode production originates as a by-product of the domestic coking process. Similarly, it was assumed that all pig iron and crude steel have carbon contents of 4 percent and 0.4 percent, respectively. The carbon content of pig iron can vary between 3 and 5 percent, while crude steel can have a carbon content of up to 2 percent, although it is typically less than 1 percent (IPCC 2000).

There is uncertainty in the most accurate CO₂ emission factor for carbon anode consumption in aluminum production. Emissions vary depending on the specific technology used by each plant (Prebake or Soderberg). The *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) provide CO₂ emission factors for each technology

type. Using information gathered from the Voluntary Aluminum Industrial Partnership (VAIP) program, it was assumed that production was split 80 percent prebake and 20 percent Soderberg for the whole time series. Similarly, the carbon anode emission factor for steel production can vary between 3.7 and 5.5 kg CO₂/ton steel (IPCC 2000). For this analysis, the upper bound value was used.

Cement Manufacture

Cement manufacture is an energy and raw material intensive process resulting in the generation of carbon dioxide (CO₂) from both the energy consumed in making the cement and the chemical process itself.² Cement production has accounted for about 2.4 percent of total global industrial and energy-related CO₂ emissions (IPCC 1996), and the United States is the world's third largest cement producer. Cement is manufactured in almost every U.S. state. Carbon dioxide emitted from the chemical process of cement production represents one of the largest sources of industrial CO₂ emissions in the United States.

During the cement production process, calcium carbonate (CaCO₃) is heated in a cement kiln at a temperature of about 1,300°C (2,400°F) to form lime (i.e., calcium oxide or CaO) and CO₂. This process is known as calcination or calcining. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO₂ being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make Portland cement. The production of masonry cement from Portland cement requires additional lime and, thus, results in additional CO₂ emissions. However, this additional lime is already accounted for in the Lime Manufacture source category in this chapter; therefore, the additional emissions from making masonry cement from clinker are not counted in this source category's total. They are presented here for informational purposes only.

In 2000, U.S. clinker production—including Puerto Rico—totaled 79,417 thousand metric tons, and U.S. masonry cement production was estimated to be 4,275 thousand metric tons (USGS 2001). The resulting emissions

² The CO₂ emissions related to the consumption of energy for cement manufacture are accounted for under CO₂ from Fossil Fuel Combustion in the Energy chapter.

Table 3-4: CO₂ Emissions from Cement Production*

Year	Tg CO ₂ Eq.	Gg
1990	33.3	33,278
1995	36.8	36,847
1996	37.1	37,079
1997	38.3	38,323
1998	39.2	39,218
1999	40.0	39,991
2000	41.1	41,066

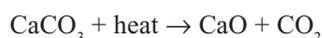
* Totals exclude CO₂ emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

of CO₂ from clinker production were estimated to be 41.1 Tg CO₂ Eq. (41,066 Gg) (see Table 3-4). Emissions from masonry production from clinker raw material were estimated to be 0.1 Tg CO₂ Eq. (96 Gg) in 2000, but again are accounted for under Lime Manufacture.

After falling in 1991 by 2 percent from 1990 levels, cement production emissions have grown every year since. Overall, from 1990 to 2000, emissions increased by 23 percent. In 2000, output by cement plants increased 3 percent over 1999, to 79,417 thousand metric tons. Cement is a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, have had considerable influence on cement production.

Methodology

Carbon dioxide emissions from cement manufacture are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO₂ and lime with the CO₂ released to the atmosphere. The quantity of the CO₂ emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of CaCO₃ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO₂:



Carbon dioxide emissions were estimated by applying an emission factor, in tons of CO₂ released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the

average lime fraction for clinker of 64.6 percent (IPCC 2000) and a constant reflecting the mass of CO₂ released per unit of lime. This calculation yields an emission factor of 0.507 tons of CO₂ per ton of clinker produced, which was determined as follows:

$$\text{EF}_{\text{Clinker}} = 0.646 \text{ CaO} \times \left[\frac{44.01 \text{ g/mole CO}_2}{56.08 \text{ g/mole CaO}} \right] = 0.507 \text{ tons CO}_2/\text{ton clinker}$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO₂ emissions should be estimated as 2 percent of the CO₂ emissions calculated from clinker production. Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2000).

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately 5 percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05 / (1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this percentage (2.86 percent) by the molecular weight ratio of CO₂ to CaO (0.785) to yield 0.0224 metric tons of additional CO₂ emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO₂ emissions from the additional lime added during masonry cement production are accounted for in the section on CO₂ emissions from Lime Manufacture. Thus, these emissions were estimated in this chapter for informational purposes only, and are not included in the cement emission totals.

Data Sources

The activity data for clinker and masonry cement production (see Table 3-5) were obtained from U.S. Geological Survey (USGS 1992, 1995a, 1995b, 1996, 1997, 1998, 1999, 2000, 2001). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

Table 3-5: Cement Production (Gg)

Year	Clinker	Masonry
1990	64,355	3,209
1991	62,918	2,856
1992	63,415	3,093
1993	66,957	2,975
1994	69,786	3,283
1995	71,257	3,603
1996	71,706	3,469
1997	74,112	3,634
1998	75,842	3,989
1999	77,337	4,375
2000	79,417	4,275

Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker, in the amount of lime added to masonry cement, and in the percentage of CKD recycled inside the clinker kiln. The lime content of clinker varies from 64 to 66 percent. CKD loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of CO₂ is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO₂ in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Because the amount of CO₂ reabsorbed is thought to be minimal, it was not estimated.

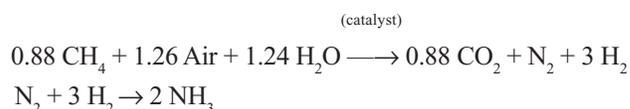
Ammonia Manufacture

Emissions of carbon dioxide (CO₂) occur during the production of synthetic ammonia. In the United States, roughly 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas. The remainder is produced using naphtha (a petroleum fraction) as a feedstock

or through the electrolysis of brine at chlorine plants (EPA 1997). The natural gas-based and naphtha-based processes produce CO₂ and hydrogen (H₂), the latter of which is used in the production of ammonia. The brine electrolysis process does not lead to CO₂ emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts methane to CO₂, carbon monoxide (CO), and H₂ in the presence of a catalyst. Only 30 to 40 percent of the methane feedstock to the primary reformer is converted to CO and CO₂. The secondary reforming step converts the remaining methane feedstock to CO and CO₂. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO₂ in the presence of a catalyst, water, and air in the shift conversion step. Carbon dioxide is removed from the process gas by the shift conversion process, and the hydrogen gas is combined with the nitrogen gas in the process gas during the ammonia synthesis step to produce ammonia. The CO₂ is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO₂ is released.

The conversion process for conventional steam reforming of methane, including primary and secondary reforming and the shift conversion processes, is approximately as follows:



Emissions of CO₂ from ammonia production in 2000 were 18.0 Tg CO₂ Eq. (18,017 Gg). Carbon dioxide emissions from this source are summarized in Table 3-6.

Methodology

Emissions of CO₂ were calculated by multiplying annual estimates of ammonia production by an emission factor (1.2 ton CO₂/ton NH₃). It was assumed that all ammonia was produced using conventional catalytic steam reformation and natural gas feedstock, although small amounts may have been produced using reforming of naphtha feedstock or electrolysis of chlorine brines. The actual amount produced using these alternative methods is not known, but assumed to be small, constituting less than

Table 3-6: CO₂ Emissions from Ammonia Manufacture

Year	Tg CO ₂ Eq.	Gg
1990	18.5	18,510
1995	18.9	18,946
1996	19.5	19,512
1997	19.5	19,477
1998	20.1	20,113
1999	18.9	18,874
2000	18.0	18,017

2 percent of all ammonia production. It was also assumed that 100 percent of the carbon in the natural gas feedstock to the ammonia synthesis process is ultimately converted to CO₂ and emitted to the atmosphere as process exhaust gas.

Data Sources

The emission factor of 1.2 ton CO₂/ton NH₃ was taken from the European Fertilizer Manufacturers Association Best Available Techniques publication, *Production of Ammonia* (EFMA 1995). The EFMA reported an emission factor range of 1.15 to 1.30 ton CO₂/ton NH₃ with 1.2 ton CO₂/ton NH₃ as a typical value. The EFMA reference also indicates that more than 99 percent of the methane feedstock to the catalytic reforming process is ultimately converted to CO₂. Ammonia production data (see Table 3-7) were obtained from the Census Bureau of the U.S. Department of Commerce (Census Bureau 1998, 2000) as reported in *Chemical and Engineering News*, “Facts & Figures for the Chemical Industry.”

Uncertainty

It is uncertain how accurately the emission factor used represents an average across all ammonia plants. The EFMA reported an emission factor range of 1.15 to 1.30 ton CO₂/ton NH₃, with 1.2 ton CO₂/ton NH₃ reported as a typical value. The actual emission factor depends upon the amount

Table 3-7: Ammonia Manufacture

Year	Thousand Metric Tons
1990	15,425
1991	15,576
1992	16,261
1993	15,599
1994	16,211
1995	15,788
1996	16,260
1997	16,231
1998	16,761
1999	15,728
2000	15,014

of air used in the ammonia production process, with 1.15 ton CO₂/ton NH₃ being the approximate stoichiometric minimum that is achievable for the conventional reforming process. By using natural gas consumption data for each ammonia plant, more accurate estimates of CO₂ emissions from ammonia production could be calculated. However, these consumption data are often considered confidential. Also, natural gas is consumed at ammonia plants both as a feedstock to the reforming process and also for generating process heat and steam. Natural gas consumption data, if available, would need to be divided into feedstock use (non-energy) and process heat and steam (fuel) use in order to be used for the Inventory, as CO₂ emissions from fuel use and non-energy use are calculated separately in the Inventory.³

Natural gas feedstock consumption data for the U.S. ammonia industry as a whole is available from the Energy Information Administration (EIA) *Manufacturers Energy Consumption Survey* (MECS) for the years 1985, 1988, 1991, 1994 and 1998 (EIA 1994; EIA 1998). These feedstock consumption data collectively correspond to an effective average emission factor of 1.0 ton CO₂/ton NH₃, which appears to be below the stoichiometric minimum that is achievable for the conventional steam reforming process.

³ It appears, for example, that the IPCC emission factor for ammonia production of 1.5 tonnes CO₂ per tonne ammonia may include both CO₂ emissions from the natural gas feedstock to the process and some CO₂ emissions from the natural gas used to generate process heat and steam for the process. Table 2-5, Ammonia Production Emission Factors, in Volume 3 of the Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories Reference Manual (IPCC, 1997) includes two emission factors, one reported for Norway and one reported for Canada. The footnotes to the table indicate that the factor for Norway does not include natural gas used as fuel but that it is unclear whether the factor for Canada includes natural gas used as fuel. However, the factors for Norway and Canada are nearly identical (1.5 and 1.6 tonnes CO₂ per tonne ammonia, respectively) and it is likely that if one value includes fuel use the other value also does. Further, for the conventional steam reforming process the EFMA reports an emission factor range for feedstock CO₂ of 1.15 to 1.30 tonnes per tonne (with a typical value of 1.2 tonne per tonne) and a emission factor for fuel CO₂ of 0.5 tonnes per tonne. This corresponds to a total CO₂ emission factor for the ammonia production process, including both feedstock CO₂ and process heat CO₂, of 1.7 tonne per tonne, which is closer to the emission factors reported in the IPCC 1996 Reference Guidelines than to the feedstock-only CO₂ emission factor of 1.2 tonne CO₂ per tonne ammonia reported by the EFMA.

The EIA data for natural gas consumption for the years 1994 and 1998 correspond more closely to the CO₂ emissions calculated using the EFMA emission factor than do data for previous years. The 1994 and 1998 data alone yield an effective emission factor of 1.1 ton CO₂/ton NH₃, corresponding to CO₂ emissions estimates that are approximately 1.5 Tg CO₂ Eq. below the estimates calculated using the EFMA emission factor of 1.2 ton CO₂/ton NH₃. Natural gas feedstock consumption data are not available from EIA for other years, and data for 1991 and previous years may underestimate feedstock natural gas consumption, and therefore the emission factor was used to estimate CO₂ emissions from ammonia production, rather than EIA data.

All ammonia production in this analysis was assumed to be from the same process; conventional catalytic reforming of natural gas feedstock. However, actual emissions could differ because processes other than catalytic steam reformation and feedstocks other than natural gas may have been used for ammonia production.

Lime Manufacture

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) at coal-fired electric power plants, construction, pulp and paper manufacturing, and water purification. Lime has historically ranked fifth in total production of all chemicals in the United States. For U.S. operations, the term “lime” actually refers to a variety of chemical compounds. These include calcium oxide (CaO), or high-calcium quicklime; calcium hydroxide (Ca(OH)₂), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([Ca(OH)₂•MgO] or [Ca(OH)₂•Mg(OH)₂]).

Lime production involves three main processes: stone preparation, calcination, and hydration. Carbon dioxide is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO₃)—is roasted at high temperatures in a kiln to produce CaO and CO₂. The CO₂ is driven off as a gas and is normally emitted to the atmosphere. Some of the CO₂ generated during the production process, however, is recovered at some facilities for use in sugar

refining and precipitated calcium carbonate (PCC)⁴ production. It is also important to note that, for certain applications, lime reabsorbs CO₂ during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 19,541 thousand metric tons in 2000 (USGS 2001). This resulted in an estimated CO₂ emissions of 13.3 Tg CO₂ Eq. (13,316 Gg) (see Table 3-8 and Table 3-9).

Table 3-8: CO₂ Emissions from Lime Manufacture

Year	Tg CO ₂ Eq.
1990	11.2
1995	12.8
1996	13.5
1997	13.7
1998	13.9
1999	13.5
2000	13.3

Table 3-9: CO₂ Emissions from Lime Manufacture (Gg)

Year	Potential	Recovered*	Emissions
1990	11,730	(493)	11,238
1995	13,701	(896)	12,804
1996	14,347	(852)	13,495
1997	14,649	(964)	13,685
1998	14,975	(1,061)	13,914
1999	14,655	(1,188)	13,466
2000	14,549	(1,233)	13,316

* For sugar refining and precipitated calcium carbonate production
 Note: Totals may not sum due to independent rounding.

At the turn of the 20th Century, over 80 percent of lime consumed in the United States went for construction uses. The contemporary quicklime market is distributed across its four end-use categories as follows: metallurgical uses, 38 percent; environmental uses, 26 percent; chemical and industrial uses, 24 percent; and construction uses, 11 percent. Construction end-uses are still important to the hydrated lime market, accounting for 52 percent of consumption. However, hydrated lime constitutes only 8 percent of the total lime market (USGS 2001).

⁴ Precipitated calcium carbonate is a specialty filler used in premium-quality coated and uncoated papers.

Lime production in 2000 declined less than 1 percent from 1999, the second consecutive drop in annual production. Overall, from 1990 to 2000, lime production increased by 23 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization (FGD) technologies. In 1993, the U.S. Environmental Protection Agency (EPA) completed regulations under the Clean Air Act capping sulfur dioxide (SO₂) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the FGD end-use to expand from 10 percent of total lime consumption in 1990 to 16 percent in 2000 (USGS 1992, 2001).

Methodology

During the calcination stage of lime manufacture, CO₂ is driven off as a gas and normally exits the system with the stack gas. To calculate emissions, the amounts of high-calcium and dolomitic lime produced were multiplied by their respective emission factors. The emission factor is the product of a constant reflecting the mass of CO₂ released per unit of lime and the average calcium plus magnesium oxide (CaO + MgO) content for lime (95 percent for both types of lime). The emission factors were calculated as follows:

For high-calcium lime:

$$(44.01 \text{ g CO}_2/\text{mole}) \div [(56.08 \text{ g CaO}/\text{mole}) \div (0.95 \text{ g CaO}/\text{lime})] = 0.75 \text{ g CO}_2/\text{g lime}$$

For dolomitic lime:

$$(88.02 \text{ g CO}_2/\text{mole}) \div [(97.01 \text{ g CaO}\cdot\text{MgO}/\text{mole}) \div (0.95 \text{ g CaO}\cdot\text{MgO}/\text{g lime})] = 0.86 \text{ g CO}_2/\text{g lime}$$

Production is adjusted to remove the mass of chemically combined water found in hydrated lime (see Table 3-11), using the midpoint of default ranges provided by the *IPCC Good Practice Guidance* (IPCC 2000). These factors set the chemically combined water content to 27 percent for high-calcium hydrated lime, and 24 percent for dolomitic hydrated lime.

Lime production in the United States was 19,541 thousand metric tons in 2000 (USGS 2001), resulting in potential CO₂ emissions of 14,549 Gg. Some of the CO₂ generated during the production process, however, was recovered for use in sugar refining and precipitated calcium carbonate (PCC) production. Combined lime manufacture by these producers was 2,067

thousand metric tons in 2000, generating 1.5 Tg of CO₂. It was assumed that approximately 80 percent of the CO₂ involved in sugar refining and PCC was recovered.

Data Sources

The activity data for lime manufacture and lime consumption by sugar refining and precipitated calcium carbonate (PCC) for 1990 through 2000 (see Table 3-10) were obtained from USGS (1992, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001). The CaO and CaO•MgO contents of lime were obtained from the *IPCC Good Practice Guidance* (IPCC 2000). Since data for the individual lime types was not provided prior to 1997, total lime production for 1990 through 1996 was allocated according to the 1997 distribution. For lime consumption, it was assumed that 100 percent was high-calcium based on communication with the National Lime Association (Males 2001).

Table 3-10: Lime Production and Lime Use for Sugar Refining and PCC (Thousand Metric Tons)

Year	High-Calcium Production ^a	Dolomite Production ^{a,b}	Use
1990	12,947	2,895	826
1991	12,840	2,838	964
1992	13,307	2,925	1,023
1993	13,741	3,024	1,279
1994	14,274	3,116	1,374
1995	15,193	3,305	1,503
1996	15,856	3,434	1,429
1997	16,120	3,552	1,616
1998	16,750	3,423	1,779
1999	16,110	3,598	1,992
2000	16,350	3,191	2,067

^a Includes hydrated limes.
^b Includes dead-burned dolomite.

Table 3-11: Hydrated Lime Production (Thousand Metric Tons)

Year	High-Calcium Hydrate	Dolomitic Hydrate
1990	1,781	319
1991	1,841	329
1992	1,892	348
1993	1,908	342
1994	1,942	348
1995	2,027	363
1996	1,858	332
1997	1,820	352
1998	1,950	383
1999	2,010	298
2000	1,550	421

Uncertainty

Uncertainties in the emission estimate can be attributed to slight differences in the chemical composition of these products. Although the methodology accounts for various formulations of lime, it does not account for the trace impurities found in lime, such as iron oxide, alumina, and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO₂ emitted during lime manufacture will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction applications. In many processes, CO₂ reacts with the lime to create calcium carbonate (e.g., water softening). Carbon dioxide reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate (PCC) reacts with CO₂; whereas most of the lime used in steelmaking reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO₂ that is reabsorbed.⁵ As more information becomes available, this emission estimate will be adjusted accordingly.

In some cases, lime is generated from calcium carbonate by-products at paper mills and water treatment plants.⁶ The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the paper industry, mills that employ the sulfate process (i.e., Kraft) consume lime in order to causticize a waste sodium carbonate solution (i.e., black liquor). Most sulfate mills recover the waste calcium carbonate after the causticizing operation and calcine it back into lime—thereby generating CO₂—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO₂ emitted

during this process is biogenic in origin, and therefore would not be included in Inventory totals.

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

Limestone and Dolomite Use

Limestone (CaCO₃) and dolomite (CaCO₃MgCO₃)⁷ are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every State in the United States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process to generate CO₂ as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization (FGD) systems for utility and industrial plants, as a raw material in glass manufacturing, or in magnesium production.

In 2000, approximately 16,314 thousand metric tons of limestone and 4,019 thousand metric tons of dolomite were used for these applications. Overall, both limestone and dolomite usage resulted in aggregate CO₂ emissions of 9.2 Tg CO₂ Eq. (9,196 Gg) (see Table 3-12 and Table 3-13).

Emissions in 2000 increased 1 percent from the previous year and 77 percent since 1990. In the future, increases in demand for crushed stone are anticipated. Demand for crushed stone from the transportation sector continues to drive growth in limestone and dolomite use. The Transportation Equity Act

⁵ Representatives of the National Lime Association estimate that CO₂ reabsorption that occurs from the use of lime may offset as much as a third of the CO₂ emissions from calcination.

⁶ Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO₂. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime) [CaC₂ + 2H₂O → C₂H₂ + Ca(OH)₂], not calcium carbonate [CaCO₃]. Thus, the calcium hydroxide is heated in the kiln to simply expel the water [Ca(OH)₂ + heat → CaO + H₂O] and no CO₂ is released to the atmosphere.

⁷ Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

Table 3-12: CO₂ Emissions from Limestone & Dolomite Use (Tg CO₂ Eq.)

Activity	1990	1995	1996	1997	1998	1999	2000
Flux Stone	3.0	3.9	4.2	5.0	5.1	6.1	6.1
Glass Making	0.2	0.5	0.4	0.4	0.2	0.2	0.2
FGD	1.9	2.6	2.7	2.9	2.8	2.8	2.8
Magnesium Production	0.1	+	0.1	0.1	0.1	0.1	0.1
Total	5.2	7.0	7.4	8.4	8.2	9.1	9.2

Note: Totals may not sum due to independent rounding.

Table 3-13: CO₂ Emissions from Limestone & Dolomite Use (Gg)

Activity	1990	1995	1996	1997	1998	1999	2000
Flux Stone	3,005	3,903	4,249	5,042	5,142	6,065	6,144
Limestone	2,554	2,523	3,330	3,970	4,298	4,273	4,329
Dolomite	452	1,380	919	1,072	844	1,792	1,816
Glass Making	189	526	362	383	191	194	197
Limestone	189	421	251	266	65	67	67
Dolomite	NA	105	110	117	125	128	129
FGD	1,922	2,558	2,695	2,902	2,781	2,781	2,781
Magnesium Production	64	41	73	73	73	73	73
Total	5,182	7,028	7,379	8,401	8,187	9,115	9,196

NA (Not Available)
Note: Totals may not sum due to independent rounding.

for the 21st Century, which commits over \$200 billion dollars to highway work through 2003, is expected to maintain the upward trend in consumption.

Methodology

Carbon dioxide emissions were calculated by multiplying the amount of limestone consumed by an average carbon content for limestone, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). Assuming that all of the carbon was oxidized and released to the atmosphere, the appropriate emission factor was multiplied by the annual level of consumption for flux stone, glass manufacturing, and FGD systems to determine emissions.

Carbon dioxide emitted during the thermic reduction of dolomite (CaMg (CO₃)₂) to magnesium metal vapor were estimated based on magnesium production capacity and the magnesium to carbon molar ratio. Operation at maximum operational capacity is assumed, this overestimation accounts for less than ideal (chemically) production. Stoichiometrically, two carbon molecules are emitted per magnesium molecule. One plant in the United States produces magnesium metal from

the dolomitic process, the other production method used in the United States produces magnesium from magnesium chloride (electrolytic reduction). Capacity fluctuations are due to variable furnace availability.

Data Sources

Consumption data for 1990 through 2000 of limestone and dolomite used as flux stone and in glass manufacturing (see Table 3-14) and production capacity of dolomitic magnesium metal (see Table 3-15) were obtained from the USGS (1993, 1995a, 1995b, 1996, 1997, 1998, 1999, 2000, 2001). Consumption data for limestone used in FGD were taken from unpublished survey data in the Energy Information Administration's Form EIA-767, "Steam Electric Plant Operation and Design Report," (EIA 1997, 1998, 1999). For 1990 and 1994, the USGS did not provide a breakdown of limestone and dolomite production by end-use and for 2000 the end-use breakdowns had not yet been finalized at the time of publication. Consumption figures for these years were estimated by assuming that limestone and dolomite accounted for the same percentage of total crushed stone consumption for a given year as the average

Table 3-14: Limestone and Dolomite Consumption (Thousand Metric Tons)

Activity	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
Flux Stone	6,737	6,052	5,185	4,263	5,487	8,586	9,468	11,239	11,512	13,415	13,590
Limestone	5,804	5,213	4,447	3,631	3,149	5,734	7,569	9,024	9,769	9,712	9,838
Dolomite	933	838	738	632	2,339	2,852	1,899	2,215	1,743	3,703	3,751
Glass Making	430	386	495	622	949	1,174	799	847	407	415	421
Limestone	430	386	495	622	949	958	571	605	148	151	153
Dolomite	NA	NA	NA	NA	NA	216	228	242	259	264	267
FGD	4,369	4,606	4,479	4,274	5,080	5,815	6,125	6,595	6,322	6,322	6,322

NA (Not Available)

Table 3-15: Dolomitic Magnesium Metal Production Capacity (Metric Tons)

Year	Production Capacity
1990	35,000
1991	35,000
1992	14,909
1993	12,964
1994	21,111
1995	22,222
1996	40,000
1997	40,000
1998	40,000
1999	40,000
2000	40,000
2001	29,167

of the percentages for the years before and after.⁸ Furthermore, following 1996, limestone used in glass manufacture has only been reported for 1998. For 1996 and 1997, limestone used in glass manufacture was estimated based on the percent of total crushed stone for 1995 and 1998. For 1999 and 2000, limestone used in glass manufacture was estimated based on the percent of total crushed stone for 1998.

It should be noted that there is a large quantity of crushed stone reported to the USGS under the category “unspecified uses.” A portion of this consumption is believed to be limestone or dolomite used as flux stone and for glass manufacture. The quantity listed for “unspecified uses” was, therefore, allocated to each reported end-use according to each end-uses fraction of total consumption in that year.⁹

⁸ Exception: 1990 and 2000 consumption were estimated using the percentages for only 1991 and 1999, respectively.

⁹ This approach was recommended by USGS.

Uncertainty

Uncertainties in this estimate are due in part, to variations in the chemical composition of limestone. In addition to calcite, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured.

Uncertainties also exist in the activity data. Much of the limestone consumed in the United States is reported as “other unspecified uses;” therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Also, some of the limestone reported as “limestone” is believed to actually be dolomite, which has a higher carbon content than limestone. Lastly, the uncertainty of the estimates for limestone used in glass making are especially high. Large fluctuations in reported consumption exist, reflecting year-to-year changes in the number of survey respondees. The uncertainty resulting from a shifting survey population is exacerbated by the gaps in the time series of reports. However, since glass making accounts for no more than 10 percent of limestone consumption, its contribution to the overall emissions estimate is low.

Soda Ash Manufacture and Consumption

Soda ash (sodium carbonate, Na_2CO_3) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is the largest soda ash-producing country in the world. Trona is the principal ore from which natural soda ash is made.

Only two States produce natural soda ash: Wyoming and California. Of these two States, only Wyoming has net emissions of CO_2 . This difference is a result of the production processes employed in each State.¹⁰ During the production process used in Wyoming, natural sources of sodium carbonate are heated and transformed into a crude soda ash that requires further refining. Carbon dioxide (CO_2) is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO_2 may also be released when soda ash is consumed.

In 2000, CO_2 emissions from the manufacture of soda ash from trona were approximately 1.5 Tg CO_2 Eq. (1,529 Gg). Soda ash consumption in the United States also generated 2.7 Tg CO_2 Eq. (2,652 Gg) in 2000. Total emissions from this source in 2000 were then 4.2 Tg CO_2 Eq. (4,181 Gg) (see Table 3-16 and Table 3-17). Emissions have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 2000 decreased by 1 percent from the previous year, and have increased 1 percent since 1990.

The United States has the world's largest deposits of trona and represents about one-third of total world soda ash output. The distribution of soda ash by end-use in 2000 was glass making, 50 percent; chemical production, 27 percent; soap and detergent manufacturing, 11 percent;

¹⁰ In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO_2 in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO_2 is generated as a by-product, the CO_2 is recovered and recycled for use in the carbonation stage and is not emitted.

Table 3-16: CO_2 Emissions from Soda Ash Manufacture and Consumption

Year	Tg CO_2 Eq.
1990	4.1
1995	4.3
1996	4.2
1997	4.4
1998	4.3
1999	4.2
2000	4.2

Table 3-17: CO_2 Emissions from Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture	Consumption	Total
1990	1,432	2,710	4,142
1995	1,607	2,698	4,305
1996	1,588	2,652	4,239
1997	1,666	2,689	4,355
1998	1,607	2,718	4,325
1999	1,549	2,668	4,217
2000	1,529	2,652	4,181

Note: Totals may not sum due to independent rounding.

distributors, 6 percent; flue gas desulfurization, and pulp and paper production, 2 percent each; and water treatment and miscellaneous, 1 percent each (USGS 2001).

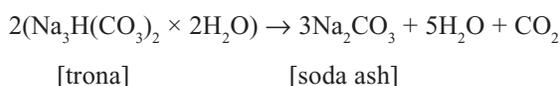
Soda ash production and consumption decreased by 1 percent from 1999 values. Exports were a driving force behind U.S. soda ash production and the Asian economic crisis beginning in late 1997 has been cited as a major cause for the drop in world soda ash demand. However, growing demand in Asia and South America is expected to lead to moderate growth (between 0.5 and 1 percent) in U.S. soda ash production.

Construction is currently underway on a major soda ash plant that will use a new feedstock—nahcolite, a natural sodium bicarbonate found in deposits in Colorado's Piceance Creek Basin. The new facility will have an annual capacity of 900,000 tons of soda ash and is slated to open in January 2001 (USGS 2000). Part of this production

process involves the stripping of CO₂. At this point, however, it is unknown whether any CO₂ will be released to the atmosphere or captured and used for conversion back to sodium bicarbonate.

Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. Carbon dioxide and water are generated as by-products of the calcination process. Carbon dioxide emissions from the calcination of trona can be estimated based on the following chemical reaction:



Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO₂. Thus, the 15.7 million metric tons of trona mined in 2000 for soda ash production (USGS 2001) resulted in CO₂ emissions of approximately 1.5 Tg CO₂ Eq. (1,529 Gg).

Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO₂ is usually emitted. In these applications, it is assumed that one mole of carbon is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of carbon (or 0.415 metric tons of CO₂) are released for every metric ton of soda ash consumed.

Data Sources

The activity data for trona production and soda ash consumption (see Table 3-18) were taken from USGS (1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001). Soda ash manufacture and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry. All six of the soda ash manufacturing operations in the United States completed surveys to provide data to the USGS.

Uncertainty

Emissions from soda ash manufacture are considered to be relatively certain. Both the emissions factor and activity data are reliable. However, emissions from soda ash

Table 3-18: Soda Ash Manufacture and Consumption (Thousand Metric Tons)

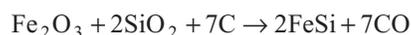
Year	Manufacture*	Consumption
1990	14,734	6,527
1991	14,674	6,278
1992	14,900	6,360
1993	14,500	6,350
1994	14,600	6,240
1995	16,500	6,510
1996	16,300	6,470
1997	17,100	6,670
1998	16,500	6,550
1999	15,900	6,430
2000	15,700	6,390

* Soda ash manufactured from trona ore only.

consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited. Therefore, uncertainty exists as to the accuracy of the emission factors.

Ferroalloy Production

Carbon dioxide is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements often including silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (25 to 55 percent and 56 to 95 percent silicon), silicon metal (about 98 percent silicon), and miscellaneous alloys (36 to 65 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials. As a result, government information disclosure rules prevent the publication of production data for them. Similar to emissions from the production of iron and steel, CO₂ is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced. The CO is eventually oxidized, becoming CO₂. A representative reaction equation for the production of 50 percent ferrosilicon is given below:



Emissions of CO₂ from ferroalloy production in 2000 were 1.7 Tg CO₂ Eq. (1,719 Gg) (see Table 3-19).

Table 3-19: CO₂ Emissions from Ferroalloy Production

Year	Tg CO ₂ Eq.	Gg
1990	2.0	1,980
1995	1.9	1,866
1996	2.0	1,954
1997	2.0	2,038
1998	2.0	2,027
1999	2.0	1,996
2000	1.7	1,719

Methodology

Emissions of CO₂ from ferroalloy production were calculated by multiplying annual ferroalloy production by material-specific emission factors. Emission factors taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) were applied to ferroalloy production. For ferrosilicon alloys containing 25 to 55 percent silicon and miscellaneous alloys (including primarily magnesium-ferrosilicon, but also including other silicon alloys) containing 32 to 65 percent silicon, an emission factor for ferrosilicon 50 percent (2.35 tons CO₂/ton of alloy produced) was applied. Additionally, for ferrosilicon alloys containing 56 to 95 percent silicon, an emission factor for ferrosilicon 75 percent (3.9 tons CO₂ per ton alloy produced) was applied. The emission factor for silicon metal was assumed to be 4.3 tons CO₂/ton metal produced. It was assumed that 100 percent of the ferroalloy production was produced using petroleum coke using an electric arc furnace process (IPCC/UNEP/OECD/IEA 1997) although some ferroalloys may have been produced with coking coal, wood, other biomass, or graphite carbon inputs. The amount of petroleum coke consumed in ferroalloy production was calculated assuming that the petroleum coke used is 90 percent carbon and 10 percent inert material.

Data Sources

Emission factors for ferroalloy production were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Ferroalloy production data for 1990 through 1999 (see Table 3-20) were obtained from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Silicon Annual Report* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000).

Data for 2000 were obtained from USGS (2001) *Mineral Industry Surveys – Silicon in December 2000*. Until 1999, the USGS reported production of ferrosilicon 25 to 55 percent separately from production of miscellaneous alloys containing 32 to 65 percent silicon; beginning in 1999, the USGS reported these as a single category (see Table 3-20). The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

Uncertainty

Although some ferroalloys may be produced using wood or other biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood or other biomass would not be counted under this source because wood-based carbon is of biogenic origin.¹¹ Emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, but may generate differing amounts of CO₂ per unit of ferroalloy produced compared to the use of petroleum coke. The most accurate method for these estimates would be basing calculations on the amount of reducing agent used in the process, rather than the amount of ferroalloys produced. These data were not available, however.

Also, annual ferroalloy production is now reported by the USGS in three broad categories: ferroalloys containing 25 to 55 percent silicon (including miscellaneous alloys), ferroalloys containing 56 to 95 percent silicon, and silicon metal. It was assumed that the IPCC emission factors apply to all of the ferroalloy production processes, including miscellaneous alloys. Finally, production data for silvery pig iron (alloys containing less than 25 percent silicon) are not reported by the USGS to avoid disclosing company proprietary data. Emissions from this production category, therefore, were not estimated.

Titanium Dioxide Production

Titanium dioxide (TiO₂) is a metal oxide manufactured from titanium ore, and is principally used as a pigment. Titanium dioxide is a principal ingredient in white paint, and TiO₂ is also used as a pigment in the manufacture of white paper, foods, and other products. There are two processes for making TiO₂, the chloride process and the

¹¹ Emissions and sinks of biogenic carbon are accounted for in the Land-Use Change and Forestry chapter.

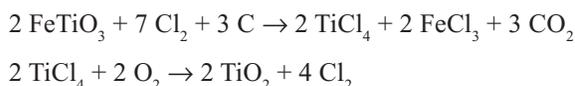
Table 3-20: Production of Ferroalloys (Metric Tons)

Year	Ferrosilicon 25%-55%	Ferrosilicon 56%-95%	Silicon Metal	Misc. Alloys (32-65%)
1990	321,385	109,566	145,744	72,444
1995	181,000	128,000	163,000	99,500
1996	182,000	132,000	175,000	110,000
1997	175,000	147,000	187,000	106,000
1998	162,000	147,000	195,000	99,800
1999	252,000	145,000	195,000	NA
2000	229,000	100,000	184,000	NA

NA (Not Available)

sulfate process. Carbon dioxide is emitted from the chloride process, which uses petroleum coke and chlorine as raw materials and emits process-related CO₂. The sulfate process does not use petroleum coke or other forms of carbon as a raw material and does not emit CO₂. In 2000, approximately 93 percent of the titanium dioxide production capacity was chloride process and the remainder was sulfate process.

The chloride process is based on the following chemical reactions:



The carbon in the first chemical reaction is provided by petroleum coke, which is oxidized in the presence of the chlorine and FeTiO₃ (the Ti-containing ore) to form CO₂. More than 90 percent of U.S. TiO₂ was produced through chloride process, and a special grade of petroleum coke is manufactured specifically for this purpose. Emissions of CO₂ from titanium dioxide production have grown from 1.3 Tg CO₂ Eq. (1,308 Gg) in 1990 to 2.0 Tg CO₂ Eq. (1,963 Gg) in 2000, due to growth in titanium dioxide production (see Table 3-21).

Table 3-21: CO₂ Emissions from Titanium Dioxide

Year	Tg CO ₂ Eq.	Gg
1990	1.3	1,308
1995	1.7	1,670
1996	1.7	1,657
1997	1.8	1,836
1998	1.8	1,819
1999	1.9	1,853
2000	2.0	1,963

Methodology

Emissions of CO₂ from titanium dioxide production were calculated by multiplying annual titanium dioxide production by chlorine process-specific emission factors.

Data were obtained for the total amount of titanium dioxide produced each year, and it was assumed that 93 percent of the total production in 2000 was produced using the chloride process. An emission factor of 0.4 metric tons C/metric ton TiO₂ was applied to the estimated chloride process production. It was assumed that all titanium dioxide produced using the chloride process was produced using petroleum coke, although some titanium dioxide may have been produced with graphite or other carbon inputs. The amount of petroleum coke consumed annually in titanium dioxide production was calculated based on the assumption that petroleum coke used in the process is 90 percent carbon and 10 percent inert materials.

Data Sources

The emission factor for the titanium dioxide chloride process was taken from the report *Everything You've Always Wanted to Know about Petroleum Coke* (Onder and Bagdoyan 1993). Titanium dioxide production data for 1990 through 1999 (see Table 3-22) were obtained from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Titanium Annual Report* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000). Data for 2000 were obtained from USGS (2001) *Mineral Industry Surveys – Titanium in December 2000*. Data for the percentage of the total titanium dioxide production capacity that is chloride process for 1994 through 1999 were also taken from the USGS *Minerals Yearbook*. Percentage chloride process data were not available for 1990 through 1993, and data from the 1994

Table 3-22: Titanium Dioxide Production

Year	Metric Tons
1990	979,000
1991	992,000
1992	1,140,000
1993	1,160,000
1994	1,250,000
1995	1,250,000
1996	1,230,000
1997	1,340,000
1998	1,330,000
1999	1,350,000
2000	1,440,000

USGS *Minerals Yearbook* were used for these years. The chloride process percentage for 2000 was estimated from data published in the *Chemical Market Report* (2000). The composition data for petroleum coke were obtained from Onder and Bagdoyan (1993).

Uncertainty

Although some titanium dioxide may be produced using graphite or other carbon inputs, information and data regarding these practices were not available. Titanium dioxide produced using graphite inputs may generate differing amounts of CO₂ per unit of titanium dioxide produced compared to the use of petroleum coke. The most accurate method for these estimates would be basing calculations on the amount of reducing agent used in the process, rather than the amount of titanium dioxide produced. These data were not available, however.

Also, annual titanium production is not reported by USGS by the type of production process used (chloride or sulfate). Only the percentage of total production capacity is reported. It was assumed that titanium dioxide was produced using the chloride process and the sulfate process in the same ratio as the ratio of the total U.S. production capacity for each process. This assumes that the chloride process plants and sulfate process plants operate at the same level of utilization. Finally, the emission factor was applied uniformly to all chloride process production, and no data were available to account for differences in production

efficiency among chloride process plants. In calculating the amount of petroleum coke consumed in chloride process titanium dioxide production, literature data were used for petroleum coke composition. Certain grades of petroleum coke are manufactured specifically for use in the titanium dioxide chloride process, however this composition information was not available.

Carbon Dioxide Consumption

Carbon dioxide (CO₂) is used for a variety of applications, including food processing, chemical production, carbonated beverages, and enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the ground to increase reservoir pressure, and is therefore considered sequestered.¹² For the most part, however, CO₂ used in non-EOR applications will eventually be released to the atmosphere.

Carbon dioxide is produced from a small number of natural wells, as a by-product from the production of chemicals (e.g., ammonia), or separated from crude oil and natural gas. Depending on the raw materials that are used, the by-product CO₂ generated during these production processes may already be accounted for in the CO₂ emission estimates from fossil fuel consumption (either during combustion or from non-fuel uses). For example, ammonia is primarily manufactured using natural gas as a feedstock. Carbon dioxide emissions from this process are accounted for in the Energy chapter under Fossil Fuel Combustion and, therefore, are not included here.

In 2000, CO₂ emissions from this source not accounted for elsewhere were 1.4 Tg CO₂ Eq. (1,361 Gg) (see Table 3-23). This amount represents a decrease of 13 percent from the previous year and is 70 percent higher than emissions in 1990.

Methodology

Carbon dioxide emission estimates were based on CO₂ consumption with the assumption that the end-use applications, except enhanced oil recovery, eventually release 100 percent of the CO₂ into the

¹² It is unclear to what extent the CO₂ used for EOR will be re-released. For example, the CO₂ used for EOR may show up at the wellhead after a few years of injection (Hangebrauk et al. 1992). This CO₂, however, is typically recovered and re-injected into the well. More research is required to determine the amount of CO₂ that in fact escapes from EOR operations. For the purposes of this analysis, it is assumed that all of the CO₂ remains sequestered.

Table 3-23: CO₂ Emissions from Carbon Dioxide Consumption

Year	Tg CO ₂ Eq.	Gg
1990	0.8	800
1995	1.0	968
1996	1.1	1,140
1997	1.3	1,294
1998	1.4	1,413
1999	1.6	1,572
2000	1.4	1,361

atmosphere. Carbon dioxide consumption for uses other than enhanced oil recovery was about 6,807 thousand metric tons in 2000. The Freedonia Group estimates that, in the United States, there is an 80 percent to 20 percent split between CO₂ produced as a by-product and CO₂ produced from natural wells. Thus, emissions are equal to 20 percent of CO₂ consumption. The remaining 80 percent was assumed to already be accounted for in the CO₂ emission estimates from other categories (the most important being Fossil Fuel Combustion).

Data Sources

Carbon dioxide consumption data (see Table 3-24) were obtained from *Industrial Gases to 2004*, published by the Freedonia Group Inc. (1994, 1996, 1999a, 1999b, 2000). The 2000 report contains actual data for 1999 only. Data for 1996 were obtained by personal communication with Paul Ita of the Freedonia Group Inc. (Ita 1997). Data for 1997 and 2000 production were calculated from annualized growth rates for 1994 through 1996 and 1997 through 1999 respectively. The 1997 and 2000 values for enhanced oil recovery were set equal

Table 3-24: Carbon Dioxide Consumption

Year	Thousand Metric Tons
1990	4,000
1991	4,200
1992	4,410
1993	4,559
1994	4,488
1995	4,842
1996	5,702
1997	6,468
1998	7,067
1999	6,512
2000	6,807

to the 1998 and 1999 values, respectively. The percent of carbon dioxide produced from natural wells was obtained from Freedonia Group Inc. (1991).

Uncertainty

Uncertainty exists in the assumed allocation of carbon dioxide produced from fossil fuel by-products (80 percent) and carbon dioxide produced from wells (20 percent). In addition, it is possible that CO₂ recovery exists in particular end-use sectors. Contact with several organizations did not provide any information regarding recovery. More research is required to determine the quantity, if any, that may be recovered.

Petrochemical Production

Small amounts of methane (CH₄) are released during the production of some petrochemicals. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. Emissions are presented here from the production of five chemicals: carbon black, ethylene, ethylene dichloride, styrene, and methanol.

Carbon black is an intensely black powder made by the incomplete combustion of an aromatic petroleum feedstock. Most carbon black produced in the United States is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes of the plastics industry including polymers such as high, low, and linear low density polyethylene (HDPE, LDPE, LLDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Styrene is a common precursor for many plastics, rubber, and resins. It can be found in many construction products, such as foam insulation, vinyl flooring, and epoxy adhesives. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers. The United States produces close to one quarter of the world's supply of methanol.

Aggregate emissions of CH₄ from petrochemical production in 2000 were 1.7 Tg CO₂ Eq. (79 Gg) (see Table 3-25).

Table 3-25: CH₄ Emissions from Petrochemical Production

Year	Tg CO ₂ Eq.	Gg
1990	1.2	56
1995	1.5	72
1996	1.6	75
1997	1.6	77
1998	1.6	78
1999	1.7	79
2000	1.7	79

Methodology

Emissions of CH₄ were calculated by multiplying annual estimates of chemical production by an emission factor. The following factors were used: 11 kg CH₄/metric ton carbon black, 1 kg CH₄/metric ton ethylene, 0.4 kg CH₄/metric ton ethylene dichloride,¹³ 4 kg CH₄/metric ton styrene, and 2 kg CH₄/metric ton methanol. These emission factors were based upon measured material balances. Although the production of other chemicals may also result in methane emissions, there were not sufficient data to estimate their emissions.

Data Sources

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data for 1990 through 1998 (see Table 3-26) were obtained from the Chemical Manufacturer's Association *Statistical Handbook* (CMA 1999). Production for 1999 and 2000 was projected by the American Chemistry Council (2001).

Table 3-26: Production of Selected Petrochemicals (Thousand Metric Tons)

Chemical	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
Carbon Black	1,306	1,225	1,365	1,452	1,492	1,524	1,560	1,588	1,610	1,642	1,674
Ethylene	16,542	18,124	18,563	18,709	20,201	21,199	22,197	23,088	23,474	25,119	24,971
Ethylene Dichloride	6,282	6,221	6,872	8,141	8,482	7,829	9,303	10,324	11,080	10,309	9,866
Styrene	3,637	3,681	4,082	4,565	5,112	5,167	5,387	5,171	5,183	5,410	5,421
Methanol	3,785	3,948	3,666	4,782	4,904	4,991	5,280	5,743	5,861	5,303	5,221

¹³ The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be dichloroethylene (C₂H₂Cl₂) instead of ethylene dichloride (C₂H₄Cl₂).

Uncertainty

The emission factors used here were based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emissions estimates, however, such data were not available. There may also be other significant sources of methane arising from petrochemical production activities that have not been included in these estimates.

Silicon Carbide Production

Methane is emitted from the production of silicon carbide, a material used as an industrial abrasive. To make silicon carbide (SiC), quartz (SiO₂) is reacted with carbon in the form of petroleum coke. Methane is produced during this reaction from volatile compounds in the petroleum coke. Although CO₂ is also emitted from this production process, the requisite data were unavailable for these calculations. Regardless, they are already accounted for under CO₂ from Fossil Fuel Combustion in the Energy chapter. Emissions of CH₄ from silicon carbide production in 2000 (see Table 3-27) were 1 Gg CH₄ (0.01 Tg CO₂ Eq.).

Table 3-27: CH₄ Emissions from Silicon Carbide Production

Year	Tg CO ₂ Eq.	Gg
1990	+	1
1995	+	1
1996	+	1
1997	+	1
1998	+	1
1999	+	1
2000	+	1

+ Does not exceed 0.05 Tg CO₂ Eq.

Methodology

Emissions of CH₄ were calculated by multiplying annual silicon carbide production by an emission factor (11.6 kg CH₄/metric ton silicon carbide). This emission factor was derived empirically from measurements taken at Norwegian silicon carbide plants (IPCC/UNEP/OECD/IEA 1997).

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 2000 (see Table 3-28) were obtained from the *Minerals Yearbook: Volume I-Metals and Minerals, Manufactured Abrasives* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001).

Table 3-28: Production of Silicon Carbide

Year	Metric Tons
1990	105,000
1991	78,900
1992	84,300
1993	74,900
1994	84,700
1995	75,400
1996	73,600
1997	68,200
1998	69,800
1999	65,000
2000	45,000

Uncertainty

The emission factor used here was based on one study of Norwegian plants. The applicability of this factor to average U.S. practices at silicon carbide plants is uncertain. A better alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. These data were not available, however.

Adipic Acid Production

Adipic acid production has been identified as an anthropogenic source of nitrous oxide (N₂O) emissions. Worldwide, there are few adipic acid plants. The United States is the major producer with three companies in four locations accounting for approximately forty percent of world production. Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. Approximately 80 percent of all adipic acid produced in the United States is used in the production of nylon 6,6. Food grade adipic acid is also used to provide some foods with a “tangy” flavor.

Adipic acid is produced through a two-stage process during which N₂O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone/cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. Nitrous oxide is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream. Process emissions from the production of adipic acid will vary with the types of technologies and level of emissions controls employed by a facility. In 1990, two of the three major adipic acid producing plants had N₂O abatement technologies in place and as of 1998, the three major adipic acid production facilities had control systems in place.¹⁴ Only one small plant, representing approximately two percent of production, does not control for N₂O.

Nitrous oxide emissions from this source were estimated to be 8.11 Tg CO₂ Eq. (26.2 Gg) in 2000 (see Table 3-29).

¹⁴ During 1997, the N₂O emission controls installed by the third plant operated for approximately a quarter of the year.

Table 3-29: N₂O Emissions from Adipic Acid Production

Year	Tg CO ₂ Eq.	Gg
1990	14.9	48
1995	17.9	58
1996	17.8	57
1997	11.5	37
1998	7.7	25
1999	7.7	25
2000	8.1	26

National adipic acid production has increased about 50 percent over the period of 1990 through 2000, to approximately 1.1 million metric tons. This increase was primarily due to a 120,000 metric ton expansion in production capacity and rising demand for engineering plastics. At the same time, emissions have been significantly reduced due to the widespread installation of pollution control measures.

Methodology

For two plants, emission estimates were based on information obtained directly from the plant engineer. For the other two plants, N₂O emissions were calculated by multiplying adipic acid production by the ratio of N₂O emitted per unit of adipic acid produced and adjusting for the actual percentage of N₂O released as a result of plant-specific emission controls. Because emissions of N₂O in the United States are not regulated, emissions have not been well characterized. However, on the basis of experiments (Thiemens and Trogler 1991), the overall reaction stoichiometry for N₂O production in the preparation of adipic acid was estimated at approximately 0.3 kg of N₂O per kilogram of product. Emissions are estimated using the following equation:

$$\text{N}_2\text{O emissions} = [\text{production of adipic acid}] \times [0.3 \text{ kg N}_2\text{O} / \text{kg adipic acid}] \times [1 - (\text{N}_2\text{O destruction factor} \times \text{abatement system utility factor})]$$

The “N₂O destruction factor” represents the amount of N₂O expressed as a percentage of N₂O emissions that are destroyed by the currently installed abatement technology. The “abatement system utility factor” represents the percent

Table 3-30: Adipic Acid Production

Year	Thousand Metric Tons
1990	735
1991	771
1992	708
1993	765
1994	815
1995	816
1996	835
1997	860
1998	866
1999	1,100
2000	1,128

of time that the abatement equipment operates. Overall, in the United States, two of the plants employ catalytic destruction, one plant employs thermal destruction, and the smallest plant uses no N₂O abatement equipment. The N₂O abatement system destruction factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer et al. 1999, Reimer 1999).

Data Sources

National adipic acid production data for 1990 through 1995 (see Table 3-30) were obtained from *Chemical and Engineering News*, “Facts and Figures” and “Production of Top 50 Chemicals” (C&EN 1992, 1993, 1994, 1995, 1996). For 1996 and 1997 data were projected from the 1995 manufactured total based upon suggestions from industry contacts. For 1998, production data were obtained from *Chemical Week*, Product focus: adipic acid/adiponitrile (CW 1999). Production data for 1999 are based on an estimate provided by the adipic acid industry (Reimer 2000). The production data for the smallest plant in 2000 was obtained from *Chemical Week* (Westervelt 2000). The emission factor was taken from Thiemens and Trogler (1991). Adipic acid plant capacities for 1998, 1999, and 2000 were updated using *Chemical Week*, Product focus: adipic acid/adiponitrile (CW 1999, 2001). Plant capacities for previous years were obtained from *Chemical Market Reporter* (1998). The national production and plant capacities were utilized for two of the four plants. Information for the other two plants was taken directly from the plant engineer (Childs 2000).

Uncertainty

Because N₂O emissions are controlled in some adipic acid production facilities, the amount of N₂O that is actually released will depend on the level of controls in place at a specific production plant. Thus, in order to calculate emissions, it is necessary to have production data on a plant-specific basis. In most cases, however, these data are confidential. As a result, plant-specific production figures were estimated by allocating total adipic acid production using existing plant capacities. This creates a degree of uncertainty in the adipic acid production data used to derive the emission estimates as it is necessary to assume that all plants operate at equivalent utilization levels. For two of the plants, estimates were calculated based on information obtained directly from the plant.

The emission factor was based on experiments (Thiemens and Trogler 1991) that attempt to replicate the industrial process and, thereby, measure the reaction stoichiometry for N₂O production in the preparation of adipic acid. However, the extent to which the lab results are representative of actual industrial emission rates is not known.

Nitric Acid Production

Nitric acid (HNO₃) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N₂O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for NO and NO₂, (i.e., NO_x). As such the industry uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NO_x, NSCR systems are also very affective at destroying N₂O. However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Currently, it is estimated that approximately 20 percent of

Table 3-31: N₂O Emissions from Nitric Acid Production

Year	Tg CO ₂ Eq.	Gg
1990	17.8	58
1995	19.9	64
1996	20.7	67
1997	21.2	68
1998	20.9	67
1999	20.1	65
2000	19.8	64

nitric acid plants use NSCR (Choe, et al. 1993). The remaining 80 percent use SCR or extended absorption, neither of which is known to reduce N₂O emissions.

Nitrous oxide emissions from this source were estimated at 19.8 Tg CO₂ Eq. (64 Gg) in 2000 (see Table 3-31). Emissions from nitric acid production have increased 11 percent since 1990.

Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of N₂O emitted per unit of nitric acid produced. The emissions factor was determined as a weighted average of 2 kg for plants using non-selective catalytic reduction (NSCR) systems and 9.5 kg for plants not equipped with NSCR (Reimer et al. 1992). An estimated 20 percent of HNO₃ plants in the United States were equipped with NSCR (Choe, et al. 1993). In the process of destroying NO_x, NSCR systems also destroy 80 to 90 percent of the N₂O. Hence, the emission factor is equal to $(9.5 \times 0.80) + (2 \times 0.20) = 8 \text{ kg N}_2\text{O} / \text{metric ton HNO}_3$.

Data Sources

Nitric acid production data for 1990 through 2000 (see Table 3-32) were obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2001). The emission factor range was taken from Reimer et al. (1992).

Table 3-32: Nitric Acid Production

Year	Thousand Metric Tons
1990	7,196
1991	7,191
1992	7,381
1993	7,488
1994	7,905
1995	8,020
1996	8,351
1997	8,557
1998	8,423
1999	8,115
2000	7,981

Uncertainty

In general, the nitric acid industry is not well categorized. A significant degree of uncertainty exists in nitric acid production figures because nitric acid plants are often part of larger production facilities, such as fertilizer or explosives manufacturing. As a result, only a small volume of nitric acid is sold on the market making production quantities difficult to track. Emission factors are also difficult to determine because of the large number of plants using many different technologies. Based on expert judgment, it is estimated that the N₂O destruction factor for NSCR nitric acid facilities is associated with an uncertainty of approximately ± 10 percent.

Substitution of Ozone Depleting Substances

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used primarily as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the *Montreal Protocol* and the Clean Air Act Amendments of 1990.¹⁵ Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, unlike ODSs, are not harmful to the stratospheric ozone layer, they are potent greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 3-33 and Table 3-34.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air conditioners and in refrigerant blends such as R-404A.¹⁶

Table 3-33: Emissions of HFCs and PFCs from ODS Substitution (Tg CO₂ Eq.)

Gas	1990	1995	1996	1997	1998	1999	2000
HFC-23	+	0.1	0.2	0.2	0.3	0.4	0.5
HFC-32	+	+	+	+	+	+	0.1
HFC-125	+	1.3	1.9	2.5	3.1	3.6	4.4
HFC-134a	0.7	15.9	21.1	26.2	30.0	33.9	37.6
HFC-143a	+	0.4	0.8	1.3	1.9	2.6	3.4
HFC-236fa	+	+	+	0.1	0.8	1.3	1.9
CF ₄	+	+	+	+	+	+	+
Others*	0.2	4.1	6.7	7.7	8.8	9.4	10.0
Total	0.9	21.8	30.6	38.0	44.9	51.3	57.8

+ Does not exceed 0.05 Tg CO₂ Eq.

* Others include HFC-152a, HFC-227ea, HFC-4310mee, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon C₆F₁₄.

Note: Totals may not sum due to independent rounding.

¹⁵ [42 U.S.C § 7671, CAA § 601]

¹⁶ R-404 contains HFC-125, HFC-143a, and HFC-134a.

Table 3-34: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990	1995	1996	1997	1998	1999	2000
HFC-23	+	8	14	20	28	36	45
HFC-32	+	+	3	7	11	17	94
HFC-125	+	478	675	889	1,116	1,289	1,559
HFC-134a	564	12,232	16,211	20,166	23,089	26,095	28,906
HFC-143a	+	111	209	334	488	676	903
HFC-236fa	+	+	+	15	120	213	296
CF ₄	+	+	+	+	+	1	1
Others*	M	M	M	M	M	M	M

M (Mixture of Gases)

+ Does not exceed 0.5 Mg

* Others include HFC-152a, HFC-227ea, HFC-4310mee and PFC/PFPEs, which are a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

In 1993, the use of HFCs in foam production and as an aerosol propellant began, and in 1994 these compounds also found applications as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes has been increasing from small amounts in 1990 to 57.8 Tg CO₂ Eq. in 2000. This increase was in large part the result of efforts to phase out CFCs and other ODSs in the United States. In the short term, this trend is expected to continue, and will likely accelerate in the next decade as HCFCs, which are interim substitutes in many applications, are themselves phased-out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*. Improvements in the technologies associated with the use of these gases and the introduction of alternative gases and technologies, however, may help to offset this anticipated increase in emissions.

Methodology and Data Sources

A detailed vintaging model of ODS-containing equipment and products was used to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual “vintages” of new

equipment that enter service in each end-use. This vintaging model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 40 different end-uses, the model produces estimates of annual use and emissions of each compound. Further information on the Vintaging Model is contained in Annex J.

Uncertainty

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the Vintaging Model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though the model is more comprehensive than the IPCC default methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

Table 3-35: CO₂ Emissions from Aluminum Production

Year	Tg CO ₂ Eq.	Gg
1990	6.3	6,315
1995	5.3	5,265
1996	5.6	5,580
1997	5.6	5,621
1998	5.8	5,792
1999	5.9	5,895
2000	5.4	5,410

Aluminum Production

Aluminum is a light-weight, malleable, and corrosion resistant metal that is used in many manufactured products including aircraft, automobiles, bicycles, and kitchen utensils. In 2000, the United States was the largest producer of primary aluminum, with 15 percent of the world total (USGS 2001). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of several greenhouse gases including carbon dioxide (CO₂) and two perfluorocarbons (PFCs): perfluoromethane (CF₄) and perfluoroethane (C₂F₆).

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al₂O₃) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na₃AlF₆). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, some of this carbon is oxidized and released to the atmosphere as CO₂.

Process emissions of CO₂ from aluminum production were estimated at 5.4 Tg CO₂ Eq. (5,410 Gg) in 2000 (see Table 3-35). The carbon anodes consumed during aluminum production consist of petroleum coke and, to a minor extent,

Table 3-36: PFC Emissions from Aluminum Production (Tg CO₂ Eq.)

Year	CF ₄	C ₂ F ₆	Total
1990	15.8	2.3	18.1
1995	10.5	1.3	11.8
1996	11.1	1.4	12.5
1997	9.8	1.2	11.0
1998	8.1	0.9	9.0
1999	8.0	0.9	8.9
2000	7.1	0.8	7.9

Note: Totals may not sum due to independent rounding.

coal tar pitch. The petroleum coke portion of the total CO₂ process emissions from aluminum production is considered to be a non-energy use of petroleum coke, and is accounted for in the Industrial Processes chapter and not with Fossil Fuel Combustion emissions in the Energy chapter. Similarly, the coal tar pitch portion of these CO₂ process emissions is subtracted from the Iron and Steel section—where it would otherwise be counted—to avoid double-counting.

In addition to CO₂ emissions, the aluminum production industry is also the largest source of PFC emissions in the United States. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed “anode effects.” These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF₄ and C₂F₆. In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. The more frequent and long-lasting the anode effects, the greater the emissions.

Primary aluminum production-related emissions of PFCs are estimated to have declined 56 percent since 1990. Since 1990, emissions of CF₄ and C₂F₆ have declined 55 and 64 percent, respectively, to 7.1 Tg CO₂ Eq. of CF₄ (1.10 Gg CF₄) and 0.8 Tg CO₂ Eq. of C₂F₆ (0.1 Gg C₂F₆) in 2000, as shown in Table 3-36 and Table 3-37. This decline was due to both reductions in domestic aluminum production and actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects.

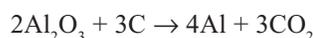
Table 3-37: PFC Emissions from Aluminum Production (Gg)

Year	CF ₄	C ₂ F ₆
1990	2.4	0.2
1995	1.6	0.1
1996	1.7	0.1
1997	1.5	0.1
1998	1.2	0.1
1999	1.2	0.1
2000	1.1	0.1

U.S. primary aluminum production for 2000—totaling 3,468 thousand metric tons—decreased slightly from 1999.¹⁷ This decrease is attributed to the curtailment of production at several U.S. smelters, due to high electric power costs in various regions of the country. The transportation industry remained the largest domestic consumer of aluminum, accounting for about 37 percent (USGS 2001).

Methodology

Carbon dioxide is generated during alumina reduction to aluminum metal following the reaction below:



The CO₂ emission factor employed was estimated from the production of primary aluminum metal and the carbon consumed by the process. Emissions vary depending on the specific technology used by each plant (e.g., Prebake or Soderberg). The *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) provide CO₂ emission factors for each technology type. During alumina reduction in a prebake anode cell process, approximately 1.5 metric tons of CO₂ are emitted for each metric ton of aluminum produced (IPCC/UNEP/OECD/IEA 1997). Similarly, during alumina reduction in a Soderberg cell process, approximately 1.8 metric tons of CO₂ are emitted per metric ton of aluminum produced (IPCC/UNEP/OECD/IEA 1997). Based on information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program, it was assumed that production was split 80 percent prebake and 20 percent Soderberg for the whole time series.

PFC emissions from aluminum production were estimated using a per unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

$$\text{PFC (CF}_4 \text{ or C}_2\text{F}_6\text{) kg/metric ton Al} = S \times \text{Anode Effect Minutes/Cell-Day}$$

where,

S = Slope coefficient

$$\text{Anode Effect Minutes/Cell-Day} = \text{Anode Effect Frequency} \times \text{Anode Effect Duration}$$

The slope coefficient was established for each smelter based on field measurements, where available, or default coefficients by technology-type, based on field measurements. Once established, the slope coefficient was used along with smelter anode effect data, collected by aluminum companies and reported to the VAIP, to estimate emissions factors over time. Where smelter-specific anode effect data were not available, industry averages were used. Emissions factors were multiplied by annual production to estimate annual emissions at the smelter level. Emissions were then aggregated across smelters to estimate national emissions. The methodology used to estimate emissions is consistent with the methodologies recommended by the *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2000).

Data Sources

Primary aluminum production data for 2000 (see Table 3-38) were obtained by using information from VAIP program submittals and from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 2001). The 2000 data from the USGS were adjusted based on the VAIP submittals. Primary aluminum production data for 1990 through 1999 (see Table 3-38) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000). The USGS requested data from the 12 domestic producers, all of whom responded. The CO₂ emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Emission estimates of PFCs

¹⁷ Comparing a subset of smelter specific production data from EPA's Voluntary Aluminum Industrial Partnership (VAIP) program and the USGS *Mineral Industry Surveys: Aluminum Annual Report* (USGS 2001), it was observed that the VAIP program data was approximately 200 thousand metric tons less than the USGS production total. The data from VAIP were believed to provide a more accurate estimate of U.S. aluminum production and therefore were used to calculate emissions.

Table 3-38: Production of Primary Aluminum

Year	Thousand Metric Tons
1990	4,048
1991	4,121
1992	4,042
1993	3,695
1994	3,299
1995	3,375
1996	3,577
1997	3,603
1998	3,713
1999	3,779
2000	3,468

were provided by aluminum smelters participating in the VAIP program. Where smelter-specific slope coefficients were not available, technology-specific coefficients were drawn from the IPCC's *Good Practice Guidance* (IPCC 2000). Information on the average frequency and duration of anode effects was taken from the International Aluminum Institute's anode effect survey (IAI 2000).

Uncertainty

Carbon dioxide emissions vary depending on the specific technology used by each plant. A more accurate method would be to calculate CO₂ emissions based upon the amount of carbon—in the form of petroleum coke or tar pitch—consumed by the process; however, this type of information was not available.

For PFC emission estimates, the uncertainty in the aluminum production data is relatively low (roughly ± 1 to 2 percent) compared to the uncertainty in the emissions factors (roughly ± 10 to 50 percent). Uncertainty in the emissions factors arises from the lack of comprehensive data for both the slope coefficients and anode effect data. Currently, insufficient measurement data exist to quantify a relationship between PFC emissions and anode effect minutes for all smelters. Future inventories will incorporate additional data reported by aluminum smelters and ongoing research into PFC emissions from aluminum production.

Occasionally, sulfur hexafluoride (SF₆) is also used by the aluminum industry as a cover gas or a fluxing and degassing agent in experimental and specialized casting operations. In its application as a cover gas, SF₆ is mixed with nitrogen or carbon dioxide and injected above the surface of molten aluminum; as a fluxing and degassing agent, SF₆ is mixed with argon, nitrogen, and/or chlorine and blown through molten aluminum. These practices are not employed extensively by primary aluminum producers and are believed to be isolated to secondary casting firms. The aluminum industry in the United States and Canada was estimated to use 230 Mg of SF₆ per year (Maiss and Brenninkmeijer 1998); however, this estimate is highly uncertain.

Historically, SF₆ from aluminum activities has been omitted from estimates of global SF₆ emissions, with the caveat that any emissions would be insignificant (Ko et al. 1993, Victor and MacDonald 1998). Emissions are believed to be insignificant, given that the concentration of SF₆ in the mixtures is small and a portion of the SF₆ is decomposed in the process (MacNeal et al. 1990, Gariepy and Dube 1992, Ko et al. 1993, Ten Eyck and Lukens 1996, Zurecki 1996).

Emissions of SF₆ from aluminum fluxing and degassing have not been estimated. Uncertainties exist as to the quantity of SF₆ used by the aluminum industry and its rate of destruction in its uses as a degassing agent or cover gas.

¹⁸ As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

Table 3-39: HFC-23 Emissions from HCFC-22 Production

Year	Tg CO ₂ Eq.	Gg
1990	35.0	3.0
1995	27.0	2.3
1996	31.1	2.7
1997	30.0	2.6
1998	40.2	3.4
1999	30.4	2.6
2000	29.8	2.6

HCFC-22 Production

Trifluoromethane (HFC-23 or CHF₃) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Since 1990, production and use of HCFC-22 has increased significantly as it has replaced chlorofluorocarbons (CFCs) in many applications. Because HCFC-22 depletes stratospheric ozone, its production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.¹⁸ Feedstock production, however, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl₃) and hydrogen fluoride (HF) in the presence of a catalyst, SbCl₅. The reaction of the catalyst and HF produces SbCl_xF_y, (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 (CHCl₂F), HCFC-22 (CHClF₂), HFC-23 (CHF₃), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. The HCl is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 is generally vented to the atmosphere as an unwanted by-product, or may be captured for use in a limited number of applications.

Table 3-40: HCFC-22 Production

Year	Gg
1990	138.9
1991	142.7
1992	149.6
1993	132.4
1994	146.8
1995	154.7
1996	166.1
1997	164.5
1998	182.8
1999	165.5
2000	186.9

Emissions of HFC-23 in 2000 were estimated to be 29.8 Tg CO₂ Eq. (2.6 Gg). This quantity represents a 15 percent decrease from emissions in 1990 (see Table 3-39). Although HCFC-22 production has increased by 35 percent since 1990, the intensity of HFC-23 emissions (i.e., the amount of HFC-23 emitted per kilogram of HCFC-22 manufactured) has declined by 37 percent, lowering emissions.

In the future, production of HCFC-22 in the United States is expected to decline as non-feedstock HCFC production is phased-out. Feedstock production is anticipated to continue growing, mainly for manufacturing fluorinated polymers.

Methodology

The methodology employed for estimating emissions was based upon measurements of critical feed components at individual HCFC-22 production plants. Individual producers also measured HFC-23 concentrations in their output stream by gas chromatography. Using measurements of feed components and HFC-23 concentrations in output streams, the amount of HFC-23 generated was estimated. HFC-23 concentrations were determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Data Sources

Emission estimates were provided by the EPA's Global Programs Division in cooperation with the U.S. manufacturers of HCFC-22. Annual estimates of U.S. HCFC-22 production are presented in Table 3-40.

Uncertainty

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. It is believed that the emissions reported are roughly within 10 percent of the true value. This methodology accounted for the declining intensity of HFC-23 emissions over time. The use of a constant emission factor would not have allowed for such accounting. More simplistic emission estimates generally assume that HFC-23 emissions are between 2 and 4 percent of HCFC-22 production on a mass ratio basis.

Semiconductor Manufacture

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and chemical vapor deposition (CVD) processes. The gases most commonly employed are trifluoromethane (HFC-23), perfluoromethane (CF_4), perfluoroethane (C_2F_6), nitrogen trifluoride (NF_3), and sulfur hexafluoride (SF_6), although other compounds such as perfluoropropane (C_3F_8) and perfluorocyclobutane ($\text{c-C}_4\text{F}_8$) are also used. The exact combination of compounds is specific to the process employed.

Plasma etching is performed to provide pathways for conducting material to connect individual circuit components in silicon wafers, using HFCs, PFCs, SF_6 and other gases in plasma form. The etching process uses plasma-generated fluorine atoms that react at the semiconductor surface according to prescribed patterns to selectively remove substrate material. A single semiconductor wafer may require as many as 100 distinct process steps that use these gases. Chemical vapor deposition chambers, used for depositing materials that will act as insulators and wires, are cleaned periodically using PFCs and other gases. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. However, due to the low destruction efficiency (i.e., high dissociation energy) of PFCs, a portion of the gas flowing into the chamber flows unreacted through the chamber and, unless emission abatement technologies are used, this portion is emitted into the atmosphere. In addition to emissions of unreacted gases, these compounds

can also be transformed in the plasma processes into a different HFC or PFC compound, which is then exhausted into the atmosphere. For example, when either CHF_3 or C_2F_6 is used in cleaning or etching, CF_4 is generated and emitted as a process by-product.

For 2000, in part, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 7.6 Tg CO_2 Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 3-41 and Table 3-42 below. The rapid growth of this industry and the increasing complexity of semiconductor products which use more PFCs in the production process have led to an increase in emissions of over 160 percent since 1990. However, the growth rate in emissions has slowed since 1997, and emissions declined between 1999 and 2000. This decline is due to the initial implementation of PFC emission reduction methods, such as process optimization.

Methodology

Emissions from semiconductor manufacturing were estimated using two sets of data. For 1990 through 1994, emission estimates were based on the historical consumption of silicon (i.e., square centimeters), the estimated average number of interconnecting layers in the chips produced, and an estimated per-layer emission factor. (The number of layers per chip, and hence the PFC emissions per square centimeter of silicon, increases as the line-width of the chip decreases.) The average number of layers per chip was based on industry estimates of silicon consumption by line-width and of the number of layers per line-width. The per-layer emission factor was based on the total annual emissions reported by participants in EPA's PFC Emission Reduction Partnership for the Semiconductor Industry in 1995 and later years. For the three years for which gas sales data were available (1992 to 1994), the estimates derived using this method are within 10 percent of the estimates derived using gas sales data and average values for emission factors and global warming potentials (GWPs).

For 1995 through 2000, total U.S. emissions were extrapolated from the total annual emissions reported by the participants in the PFC Emission Reduction Partnership for the Semiconductor Industry. The emissions from the participants were multiplied by the ratio of the total layer-

Table 3-41: PFC, HFC, and SF₆ Emissions from Semiconductor Manufacture (Tg CO₂ Eq.)

Year	1990	1995	1996	1997	1998	1999	2000
CF ₄	0.7	1.5	1.4	1.7	1.8	1.9	1.9
C ₂ F ₆	1.5	3.2	2.9	3.5	3.9	4.2	4.0
C ₃ F ₈	0.1	0.2	0.2	0.2	0.2	0.3	0.2
HFC-23	0.1	0.2	0.2	0.2	0.2	0.3	0.2
SF ₆	0.4	0.8	0.8	1.0	1.0	1.1	1.1
NF ₃ *	0.1	0.1	0.1	0.2	0.2	0.2	0.2
Total	2.9	6.1	5.6	6.7	7.4	7.9	7.6

Note: Totals may not sum due to independent rounding.

* NF₃ emissions are presented for informational purposes, using a GWP of 8,000, and are not included in totals.

Table 3-42: PFC, HFC, and SF₆ Emissions from Semiconductor Manufacture (Mg)

Year	1990	1995	1996	1997	1998	1999	2000
CF ₄	111	229	211	254	282	300	286
C ₂ F ₆	167	345	318	383	424	452	431
C ₃ F ₈	14	28	26	31	35	37	35
HFC-23	8	17	16	19	21	22	21
SF ₆	17	35	32	39	43	46	44
NF ₃	9	19	17	21	23	24	23

weighted capacity of all of the semiconductor plants in the United States and the total layer-weighted capacity of the plants operated by the participants. The layer-weighted capacity of a plant (or group of plants) consists of the silicon capacity of that plant multiplied by the number of layers used in the chips produced by that plant. This method assumes that participants and non-participants have similar capacity utilizations and per-layer emission factors.

From 1995 through 1999, the per-layer emission factor calculated for participants remained fairly constant and was assumed to be applicable to the non-participants. In 2000, the per-layer emission factor of participants declined significantly, presumably reflecting efforts to reduce PFC emissions. However, non-participants were assumed to emit PFCs at the historic per-layer rate during the year 2000. The 2000 U.S. emissions estimate was adjusted accordingly.

Chemical-specific emission estimates were based data submitted for the year by participants, which were the first reports to provide emissions by chemical. It was assumed that emissions from non-participants and emissions from previous years were distributed among the chemicals in the same proportions as in these 2000 participant reports. This assumption is supported by chemical sales information from previous years and chemical-specific emission factors.

Participants estimate their emissions using a range of methods. For 2000, all participants used a method at least as accurate as the IPCC's method 2c, recommended in *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2000). The partners with relatively high emissions typically use the more accurate IPCC 2b or 2a methods, multiplying estimates of their PFC consumption by process-specific emission factors that they have either measured or obtained from tool suppliers.

Data Sources

Aggregate emissions estimates from the semiconductor manufacturers participating in the EPA's PFC Emission Reduction Partnership were used to develop these estimates. Estimates of the capacities and characteristics of plants operated by participants and non-participants were derived from the Semiconductor Equipment and Materials International (SEMI) *World Fab Watch* (formerly *International Fabs on Disk*) database (1996 to 2001). Estimates of silicon consumed by line-width from 1990 through 1994 were derived from information from VLSI Research (2000), and the number of layers per line-width was obtained from International SEMATECH's *International Technology Roadmap: 2000 Update*.

Table 3-43: SF₆ Emissions from Electrical Transmission and Distribution

Year	Tg CO ₂ Eq.	Gg
1990	31.2	1.3
1995	26.5	1.1
1996	26.8	1.1
1997	24.5	1.0
1998	20.1	0.8
1999	15.5	0.7
2000	14.4	0.6

Uncertainty

Emission estimates for this source category have improved, but are still relatively uncertain. Emissions vary depending upon the total amount of gas used and the tool and process employed. Much of this information is tracked by semiconductor manufacturers participating in the EPA's PFC Emission Reduction Partnership; however, there is some uncertainty associated with the data collected. In addition, not all semiconductor manufacturers track this information. Total U.S. emissions were extrapolated from the information submitted by the participants, introducing additional uncertainty.

Electrical Transmission and Distribution

The largest use for sulfur hexafluoride (SF₆), both domestically and internationally, is as an electrical insulator in equipment that transmits and distributes electricity (RAND 2000). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF₆ can escape from gas-insulated substations and switch gear through seals, especially from older equipment. The gas can also be released during equipment installation, servicing, and disposal. In the past, some electric utilities vented SF₆ to the atmosphere during servicing and disposal; however, increased awareness and the relatively high cost of the gas have reduced this practice.

Emissions of SF₆ from electrical transmission and distribution systems were estimated to be 14.4 Tg CO₂ Eq. (0.6 Gg) in 2000. This quantity represents a 54 percent decrease below the estimate for 1990 (see Table 3-43). This decrease, which is reflected in the atmospheric record, is believed to be a response to increases in the price of SF₆ and to growing awareness of the environmental impact of SF₆ emissions.

Methodology

The 2000 estimate of SF₆ emissions from electrical equipment, 14.4 Tg CO₂ Eq., is comprised of (1) estimated emissions of approximately 14.3 Tg CO₂ Eq. from U.S. electric power systems, and (2) estimated emissions of approximately 0.2 Tg CO₂ Eq. from U.S. electrical equipment manufacturers (original equipment manufacturers, or OEMs). The 2000 estimate of emissions from electric power systems is based on the reported 2000 emissions (5.1 Tg CO₂) of participating utilities in EPA's SF₆ Emissions Reduction Partnership for Electric Power Systems, which began in 1999. These emissions were scaled up to the national level using the results of a regression analysis that indicated that utilities' emissions are strongly correlated with their transmission miles. The 2000 emissions estimate for OEMs of 0.2 Tg CO₂ is based on statistics compiled by the National Electrical Manufacturers Association and a paper prepared under the auspices of the International Council on Large Electric Systems (CIGRE) in May 2001 (P. O'Connell, et al., Study Committee 23), which indicates that OEMs have a release rate of approximately 3 percent of the amount of SF₆ installed in new equipment. Emissions for 1999 were estimated similarly.

Because most participating utilities reported emissions only for 1999 and 2000, and only one reported emissions for more than three years, it was necessary to model "backcast" electric power system SF₆ emissions for the years 1990 through 1998. It was assumed that SF₆ purchases were strongly related to emissions. To estimate 1990 through 1998 emissions, aggregate world sales of SF₆ (RAND 2000) for each year from 1990 through 1999 were divided by the world sales from 1999. The result was a time series that gave each year's sales as a multiple of 1999 sales. Each year's normalized sales were then multiplied by the estimated U.S. emissions of SF₆ from electrical equipment in 1999, which

was estimated to be 15.5 Tg of CO₂ Eq., to estimate U.S. emissions of SF₆ from electrical equipment in that year. This yielded a time series that was related to statistics for both SF₆ emissions and SF₆ sales.

Data Sources

Emission estimates were provided by EPA's Global Programs Division in cooperation with companies that participate in the SF₆ Emissions Reduction Partnership for Electric Power Systems and with producers of SF₆.

Uncertainty

There is uncertainty involved in extrapolating emissions reported by participants to total U.S. emissions, and in extrapolating to estimate past emissions. The regression equations used to extrapolate U.S. emissions from participant reports have a variance (at the 95 percent confidence level) of +/- 2 Tg CO₂ for 1999 and +/- 2.5 Tg CO₂ for 2000. In addition, emission rates for utilities that were not participants, which accounted for approximately 75 percent of U.S. transmission miles, may differ from those that were participants. Global sales of SF₆ appear to closely reflect global emissions; global sales declined by 24 percent between 1995 and 1998, while atmospheric measurements indicate that world emissions of SF₆ declined by 27 percent during the same period. However, U.S. emission patterns may differ from global emission patterns.

Magnesium Production and Processing

The magnesium metal production and casting industry uses sulfur hexafluoride (SF₆) as a covergas to prevent the violent oxidation of molten magnesium in the presence of air. A dilute gaseous mixture of SF₆ with dry air and/or carbon dioxide is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A minute portion of the SF₆ reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. It is assumed that the amount of SF₆ reacting in magnesium production and processing is negligible and thus all SF₆ used is emitted into the

Table 3-44: SF₆ Emissions from Magnesium Production and Processing

Year	Tg CO ₂ Eq.	Gg
1990	5.5	0.2
1995	5.5	0.2
1996	5.5	0.2
1997	6.9	0.3
1998	6.2	0.3
1999	6.1	0.3
2000	4.0	0.2

atmosphere. Sulfur hexafluoride has been used in this application around the world for the last twenty years. It has largely replaced salt fluxes and sulfur dioxide (SO₂), which are more toxic and corrosive than SF₆.

The magnesium industry emitted 4.0 Tg CO₂ Eq. (0.17 Gg) of SF₆ in 2000 (see Table 3-44). There are no significant plans for expansion of primary magnesium production in the United States, but demand for magnesium metal by U.S. casting companies has grown as auto manufacturers design more lightweight magnesium parts into vehicle models. Foreign magnesium producers are expected to meet the growing U.S. demand for primary magnesium.

Methodology

U.S. magnesium metal production (primary and secondary) and consumption data from 1993 to 1999 were available from the U.S. Geological Survey (USGS).¹⁹ Emissions were estimated by multiplying average industry emission factors (kg SF₆/tonne Mg produced or processed) by the amount of metal produced or consumed in the six major processes that require SF₆ melt protection; 1) primary production, 2) secondary production, 3) die casting, 4) gravity casting, 5) wrought products and, 6) anodes. The emission factors were derived from participants in EPA's SF₆ Emission Reduction Partnership for the Magnesium Industry, technical publications (Gjestland and Magers 1996), and expert judgement. Participants represent 100 percent of U.S. primary production and approximately 60 percent of magnesium casting in the United States.

¹⁹ <http://minerals.usgs.gov/minerals/pubs/commodity/magnesium/index.html#mis>

Box 3-1: Potential Emission Estimates of HFCs, PFCs, and SF₆

Emissions of HFCs, PFCs and SF₆ from industrial processes can be estimated in two ways, either as potential emissions or as actual emissions. Emission estimates in this chapter are “actual emissions,” which are defined by the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC/UNEP/OECD/IEA 1997) as estimates that take into account the time lag between consumption and emissions. In contrast, “potential emissions” are defined to be equal to the amount of a chemical consumed in a country, minus the amount of a chemical recovered for destruction or export in the year of consideration. Potential emissions will generally be greater for a given year than actual emissions, since some amount of chemical consumed will be stored in products or equipment and will not be emitted to the atmosphere until a later date, if ever. Because all chemicals consumed will eventually be emitted into the atmosphere, in the long term the cumulative emission estimates using the two approaches should be equivalent unless the chemical is captured and destroyed. Although actual emissions are considered to be the more accurate estimation approach for a single year, estimates of potential emissions are provided for informational purposes.

Separate estimates of potential emissions were not made for industrial processes that fall into the following categories:

- *By-product emissions.* Some emissions do not result from the consumption or use of a chemical, but are the unintended by-products of another process. For such emissions, which include emissions of CF₄ and C₂F₆ from aluminum production and of HFC-23 from HCFC-22 production, the distinction between potential and actual emissions is not relevant.
- *Potential emissions that equal actual emissions.* For some sources, such as magnesium production and processing, it is assumed that there is no delay between consumption and emission and that no destruction of the chemical takes place. In this case, actual emissions equal potential emissions.
- *Emissions that are not easily defined.* In some processes, such as PFC emissions from semiconductor manufacture, the gases used in the process may be destroyed or transformed into other compounds, which may also be greenhouse gases. It is therefore not logical to estimate potential emissions based on consumption of the original chemical.

Table 3-45 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances and SF₆ emissions from semiconductor manufacturer, magnesium production and processing, and electrical transmission and distribution.²⁰ Potential emissions associated with the substitution for ozone depleting substances were calculated through a combination of the EPA's Vintaging Model and information provided by U.S. chemical manufacturers. For SF₆ from semiconductor manufacture, estimates were assumed to equal emissions divided by a 0.53 percent emission factor. The U.S. utility purchases of SF₆ for electrical equipment were backcasted based on world sales of SF₆ to utilities, this was added to the SF₆ Purchased by U.S. original equipment manufacturers (OEMs).

Table 3-45: 2000 Potential and Actual Emissions of HFCs, PFCs, and SF₆ from Selected Sources (Tg CO₂ Eq.)

Source	Potential	Actual
Substitution of Ozone Depleting Substances	203.4	57.8
Aluminum Production	-	7.9
HCFC-22 Production	-	29.8
Semiconductor Manufacture*	2.0	7.4
Magnesium Production and Processing	4.0	4.0
Electrical Transmission and Distribution	23.2	14.4

- Not applicable.

*Potential emissions only include SF₆, while actual emissions include SF₆ and PFCs.

²⁰ See Annex V for a discussion of sources of SF₆ emissions excluded from the actual emissions estimates in this report.

Table 3-46: NO_x, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990	1995	1996	1997	1998	1999	2000
NO_x	921	842	976	991	924	946	1184
Chemical & Allied Product Manufacturing	152	144	113	115	117	119	122
Metals Processing	88	89	75	80	80	80	83
Storage and Transport	3	5	14	15	15	15	15
Other Industrial Processes	343	362	397	417	424	422	442
Miscellaneous*	335	242	376	364	288	311	523
CO	9,502	5,291	7,171	8,776	5,557	10,763	19,469
Chemical & Allied Product Manufacturing	1,074	1,109	955	972	981	981	1,009
Metals Processing	2,395	2,159	1,455	1,550	1,544	1,518	1,574
Storage and Transport	69	22	64	64	65	65	67
Other Industrial Processes	487	566	509	528	535	543	562
Miscellaneous*	5,479	1,435	4,188	5,662	2,431	7,656	16,257
NMVOCs	3,110	3,622	3,110	3,578	3,145	3,883	4,232
Chemical & Allied Product Manufacturing	575	599	351	352	357	359	369
Metals Processing	111	113	66	71	71	69	72
Storage and Transport	1,356	1,499	1,169	1,204	1,204	1,129	1,111
Other Industrial Processes	364	409	383	397	402	420	435
Miscellaneous*	705	185	375	759	308	1,065	2,244

* Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, TSDFs (Transport, Storage, and Disposal Facilities under the Resource Conservation and Recovery Act), cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Agricultural Residue Burning source.

Note: Totals may not sum due to independent rounding.

Data Sources

Emission estimates were provided by EPA's Climate Protection Division in cooperation with the U.S. EPA SF₆ Emission Reduction Partnership for the Magnesium Industry and the USGS.

Uncertainty

There are a number of uncertainties in these estimates, including the assumption that SF₆ neither reacts nor decomposes during use. It is possible that the melt surface reactions and high temperatures associated with molten magnesium would cause some gas degradation. As is the case for other sources of SF₆ emissions, total SF₆ consumption data for magnesium production and processing in United States were not available. Sulfur hexafluoride may also be used as a covergas for the casting of molten aluminum with a high magnesium content; however, it is unknown to what extent this technique is used in the United States.

Industrial Sources of Ambient Air Pollutants

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of ambient air pollutants. Total emissions of nitrogen oxides (NO_x), carbon monoxide (CO), and nonmethane volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 2000 are reported in Table 3-46.

Methodology and Data Sources

The emission estimates for this source were taken directly from the EPA (2001). Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual categories from various agencies. Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

Uncertainty

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data.