4.   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 (CO_2), methane (CH_4), or nitrous oxide (N_2O). The processes addressed in this chapter include iron and steel production, cement production, ammonia manufacture and urea application, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and use, titanium dioxide production, phosphoric acid production, ferroalloy production, CO_2 consumption, aluminum production, petrochemical production, silicon carbide production, nitric acid production, and adipic acid production (see Figure 4-1).

Figure 4-1: 2002 Industrial Processes Chapter Greenhouse Gas Sources

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 (SF_6). 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. In addition, many of these gases have high global warming potentials, and sulfur hexafluoride is the most potent greenhouse gas the IPCC has evaluated. Usage of HFCs for the substitution of ozone depleting substances is growing rapidly, as they are the primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to ODS substitutes, HFCs, PFCs, SF_6, 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.

In 2002, industrial processes generated emissions of 310.7 Tg CO_2 Eq., or 4.5 percent of total U.S. greenhouse gas emissions. Carbon dioxide emissions from all industrial processes were 147.3 Tg CO_2 Eq. (147,308 Gg) in 2002. This amount accounted for only 2.5 percent of national CO_2 emissions. Methane emissions from petrochemical, silicon carbide, and iron and steel production resulted in emissions of approximately 2.5 Tg CO_2 Eq. (120 Gg) in 2002, which was 0.4 percent of U.S. CH_4 emissions. Nitrous oxide emissions from adipic acid and nitric acid production were 22.6 Tg CO_2 Eq. (73 Gg) in 2002, or 5.4 percent of total U.S. N_2O emissions. In 2002, combined emissions of HFCs, PFCs and SF_6 totaled 138.2 Tg CO_2 Eq. Overall, emissions from industrial processes increased by 4.5 percent from 1990 to 2002 despite decreases in emissions from several industrial processes, such as iron and steel, electrical transmission and distribution, HCFC-22 production, and aluminum production. The increase in overall emissions was driven by a rise in the emissions originating from cement manufacture and, primarily, the emissions from the use of substitutes for ozone depleting substances.

Table 4-1 summarizes emissions for the Industrial Processes chapter in units of teragrams of CO_2 equivalent (Tg CO_2 Eq.), while unweighted native gas emissions in gigagrams (Gg) are provided in Table 4-2.

Table 4-1: Emissions from Industrial Processes (Tg CO_2 Eq.)

Gas/Source	1990		1996	1997	1998	1999	2000	2001	2002
CO_2	170.9		162.8	168.0	166.4	162.9	161.7	148.8	147.3
Iron and Steel Production	85.4		68.3	71.9	67.4	64.4	65.7	59.1	54.4
Cement Manufacture	33.3		37.1	38.3	39.2	40.0	41.2	41.4	42.9
Ammonia Manufacture & Urea Application	19.3		20.3	20.7	21.9	20.6	19.6	16.2	17.7
Lime Manufacture	11.2		13.5	13.7	13.9	13.5	13.3	12.8	12.3
Limestone and Dolomite Use	5.5		7.8	7.2	7.4	8.1	6.0	5.7	5.8
Aluminum Production	6.3		5.6	5.6	5.8	5.9	5.7	4.1	4.2
Soda Ash Manufacture and Consumption	4.1		4.2	4.4	4.3	4.2	4.2	4.1	4.1

	1990		1996	1997	1998	1999	2000	2001	2002
Titanium Dioxide Production	1.3		1.7	1.8	1.8	1.9	1.9	1.9	2.0
Phosphoric Acid Production	1.5		1.6	1.5	1.6	1.5	1.4	1.3	1.3
Carbon Dioxide Consumption	0.9		0.8	0.8	0.9	0.9	1.0	0.8	1.3
Ferroalloy Production	2.0		2.0	2.0	2.0	2.0	1.7	1.3	1.2
CH_4	**2.5**		**2.9**	**2.9**	**2.9**	**2.9**	**2.9**	**2.5**	**2.5**
Petrochemical Production	1.2		1.6	1.6	1.7	1.7	1.7	1.4	1.5
Iron and Steel Production	1.3		1.3	1.3	1.2	1.2	1.2	1.1	1.0
Silicon Carbide Production	+		+	+	+	+	+	+	+
N_2O	**33.0**		**37.7**	**31.5**	**26.9**	**25.6**	**25.6**	**20.8**	**22.6**
Nitric Acid Production	17.8		20.7	21.2	20.9	20.1	19.6	15.9	16.7
Adipic Acid Production	15.2		17.0	10.3	6.0	5.5	6.0	4.9	5.9
HFCs, PFCs, and SF_6	**90.9**		**114.9**	**121.7**	**135.7**	**134.8**	**139.1**	**129.7**	**138.2**
Substitution of Ozone Depleting Substances	0.3		35.0	46.4	56.5	65.8	75.1	83.4	91.7
HCFC-22 Production	35.0		31.1	30.0	40.2	30.4	29.8	19.8	19.8
Electrical Transmission and Distribution	29.2		24.3	21.7	17.1	16.4	15.9	15.6	14.8
Aluminum Production	18.1		12.5	11.0	9.0	8.9	8.9	4.0	5.2
Semiconductor Manufacture	2.9		5.5	6.3	7.1	7.2	6.3	4.5	4.4
Magnesium Production and Processing	5.4		6.5	6.3	5.8	6.0	3.2	2.5	2.4
Total	**297.4**		**318.3**	**324.1**	**331.9**	**326.2**	**329.3**	**301.9**	**310.7**

+ Does not exceed 0.05 Tg CO_2 Eq.

Note: Totals may not sum due to independent rounding.

Table 4-2: Emissions from Industrial Processes (Gg)

Gas/Source	1990		1996	1997	1998	1999	2000	2001	2002
CO_2	**170,934**		**162,760**	**167,996**	**166,446**	**162,887**	**161,660**	**148,797**	**147,308**
Iron and Steel Production	85,414		68,324	71,864	67,429	64,376	65,693	59,074	54,411
Cement Manufacture	33,278		37,079	38,323	39,218	39,991	41,190	41,357	42,898
Ammonia Manufacture & Urea Application	19,306		20,282	20,650	21,934	20,615	19,587	16,250	17,652
Lime Manufacture	11,238		13,495	13,685	13,914	13,466	13,315	12,823	12,304
Limestone and Dolomite Use	5,533		7,817	7,242	7,449	8,057	5,959	5,733	5,836
Aluminum Production	6,315		5,580	5,621	5,792	5,895	5,723	4,114	4,223
Soda Ash Manufacture and Consumption	4,141		4,239	4,354	4,325	4,217	4,181	4,147	4,139
Titanium Dioxide Production	1,308		1,657	1,836	1,819	1,853	1,918	1,857	1,997
Phosphoric Acid Production	1,529		1,551	1,544	1,593	1,539	1,382	1,264	1,339
Carbon Dioxide Consumption	892		783	838	946	881	993	849	1,272
Ferroalloy Production	1,980		1,954	2,038	2,027	1,996	1,719	1,329	1,237
CH_4	**120**		**137**	**139**	**138**	**138**	**138**	**119**	**120**
Petrochemical Production	56		76	78	80	81	80	68	72
Iron and Steel Production	63		60	60	57	56	57	51	47
Silicon Carbide Production	1		1	1	1	1	1	+	+
N_2O	**107**		**122**	**102**	**87**	**83**	**83**	**67**	**73**
Nitric Acid Production	58		67	68	67	65	63	51	54
Adipic Acid Production	49		55	33	19	18	19	16	19
HFCs, PFCs, and SF_6	**M**		**M**	**M**	**M**	**M**	**M**	**M**	**M**
Substitution of Ozone Depleting Substances	M		M	M	M	M	M	M	M
HCFC-22 Production[a]	3		3	3	3	3	3	2	2
Electrical Transmission and Distribution[b]	1		1	1	1	1	1	1	1
Aluminum Production	M		M	M	M	M	M	M	M
Semiconductor Manufacture	M		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] SF_6 emitted
Note: Totals may not sum due to independent rounding.

In order to ensure the quality of the emission estimates from industrial processes, the IPCC QA/QC procedures were implemented by means of the *Quality Assurance/Quality Control and Uncertainty Management Plan for the U.S. Greenhouse Gas Inventory: Procedures Manual for QA/QC and Uncertainty Analysis* ("QA/QC plan"). This plan encompasses Tier 1 and Tier 2 procedures, and recommends that all Tier 1 procedures be performed annually, while Tier 2 procedures are performed when there are major shifts in the methodology. Tier 1 addresses annual procedures and checks to be used when gathering, maintaining, handling, documenting, checking and archiving the data, supporting documents, and files associated with the Industrial Processes section of the U.S. Inventory. Tier 2 procedures and checks specifically focus on the emission factor and activity data sources and methodology used for estimating emissions from Industrial Processes for the U.S. Inventory. Tier 1 procedures and checks have been performed on all industrial process sources; where Tier 2 procedures or checks were performed for a source, they will be described within the QA/QC and Verification Discussion of that source description. In addition to the national QA/QC plan, a more detailed plan was developed specifically for the CO_2 and CH_4 industrial processes sources. This plan was based on the U.S. strategy, but was tailored to include specific procedures recommended for these sources.

The general method employed to estimate emissions for industrial processes, as recommended by the Intergovernmental Panel on Climate Change (IPCC), involves multiplying production data (or activity data) for each process by an emission factor per unit of production. The uncertainty of the emission estimates is therefore generally a function of a combination of the uncertainties surrounding the production and emission factor variables. Uncertainty of activity data and the associated probability density functions for industrial processes CO_2 sources were estimated based on expert assessment of available qualitative information. Uncertainty estimates and probability density functions for the emission factors used to calculate emissions from this source were devised based on IPCC recommendations.

The uncertainty of activity data, which is obtained through a survey of manufacturers conducted by various organizations (specified within each source), is a function of the reliability of plant-level production data and is influenced by the completeness of the survey response. 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; therefore, they may not represent U.S. national averages. Additional assumptions are described within each source.

The uncertainty analysis performed to quantify uncertainties associated with the 2002 inventory estimates from industrial processes is only the beginning of a multi-year process for developing credible quantitative uncertainty estimates for these source categories using the IPCC Tier 2 approach. It is expected that in subsequent years, the type and the characteristics of the actual probability density functions underlying the input variables will be identified and better characterized (resulting in development of more reliable inputs for the model, including accurate characterization of correlation between variables), based on expert elicitations obtained through implementation of elicitation protocols. Accordingly, the quantitative uncertainty estimates reported in this section should be considered as preliminary and illustrative. The interconnectivity among data used for estimating emissions for different sources can influence the uncertainty analysis of each individual source. While this preliminary uncertainty analysis recognizes very significant connections among sources, a more comprehensive approach that accounts for all linkages will be identified as the uncertainty analysis moves forward.

4.1.   Iron and Steel Production (IPCC Source Category 2C1)

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO_2 and CH_4. 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 coking coal as a raw material. Iron may be introduced into the blast furnace in the form of raw iron ore, pellets, briquettes, or sinter. Pig iron is used as a raw material in the production of steel (containing about 0.4 percent carbon by weight). Pig iron is also used as a raw material in the production of iron products in foundries. The pig iron production process produces CO_2 emissions and fugitive CH_4 emissions.

The production of metallurgical coke from coking coal and the consumption of the metallurgical coke used as a reducing agent in the blast furnace are considered in the inventory to be non-energy (industrial) processes, not energy (combustion) processes. Coal coke is produced by heating coking coal in a coke oven in a low-oxygen environment. The process drives off the volatile components of the coking coal and produces coal coke. Coke oven gas and coal tar are carbon by-products of the coke manufacturing process. Coke oven gas is generally burned as a fuel within the steel mill. Coal tar is used as a raw material to produce anodes used for primary aluminum production and other electrolytic processes, and also used in the production of other coal tar products. The coke production process produces CO_2 emissions and fugitive CH_4 emissions.

Sintering is a thermal process by which fine iron-bearing particles, such as air emission control system dust, are baked, which causes the material to agglomerate into roughly one-inch pellets that are then recharged into the blast furnace for pig iron production. Iron ore particles may also be formed into larger pellets or briquettes by mechanical means, and then agglomerated by heating prior to being charged into the blast furnace. The sintering process produces CO_2 emissions and fugitive CH_4 emissions.

The metallurgical coke is a reducing agent in the blast furnace. 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 CO_2 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 CO_2 and CH_4 from iron and steel production in 2002 were 54.4 Tg CO_2 Eq. (54,411 Gg) and 1.0 Tg CO_2 Eq. (47.4 Gg), respectively (see Table 4-3 and Table 4-4). Emissions have fluctuated significantly from 1990 to 2002 due to changes in domestic economic conditions and changes in product imports and exports. For the past several years, domestic production of pig iron, sinter, and coal coke has declined. Despite recovering somewhat in 2000, domestic pig iron production, coke, and sinter production fell in 2001 and again in 2002. Pig iron production in 2002 was 16 percent lower than in 2000 and 21 percent below 1995 levels. Coke production in 2002 was 15 percent lower than in 2001 and 42 percent below 1990 levels. A slowdown in the domestic and worldwide economy and the availability of low-priced imports limit growth in domestic production (USGS 2002).

Table 4-3: CO_2 and CH_4 Emissions from Iron and Steel Production (Tg CO_2 Eq.)

Year	1990		1996	1997	1998	1999	2000	2001	2002
CO_2	85.4		68.3	71.9	67.4	64.4	65.7	59.1	54.4
CH_4	1.3		1.3	1.3	1.2	1.2	1.2	1.1	1.0
Total	**86.7**		**69.6**	**73.1**	**68.6**	**65.5**	**66.9**	**60.1**	**55.4**

Table 4-4: CO_2 and CH_4 Emissions from Iron and Steel Production (Gg)

Year	1990		1996	1997	1998	1999	2000	2001	2002
CO_2	85,414		68,324	71,864	67,429	64,376	65,693	59,074	54,411
CH_4	62.9		60.4	59.6	57.2	55.8	57.5	50.8	47.4

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 6.4.

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 CO_2 were calculated by multiplying the annual production of steel in electric arc furnaces by an emission factor (4.4 kg CO_2/ton steel$_{EAF}$). It was assumed that the carbon anodes used in the production of steel in electric arc furnaces 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 have already been accounted for earlier in the iron and steel emissions calculation as part of the coking process, the emission factor was reduced by 20 percent to avoid double counting. Additionally, emissions from the coal tar pitch component of carbon anodes consumed during the production of aluminum, which are accounted for in the aluminum production section of this chapter, have been subtracted from the total coal tar emissions that were calculated above.

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 by-weight carbon content of 4 percent.

The production processes for coal coke, sinter, and pig iron result in fugitive emissions of CH_4, which are emitted via leaks in the production equipment rather than through the emission stacks or vents of the production plants. The fugitive emissions were calculated by applying emission factors taken from the *1995 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1995) (see Table 4-5) to annual domestic production data for coal coke, sinter, and pig iron.

Table 4-5: CH_4 Emission Factors for Coal Coke, Sinter, and Pig Iron Production

Material Produced	g CH_4/kg produced
Coal Coke	0.5
Pig Iron	0.9
Sinter	0.5

Source: IPCC/UNEP/OECD/IEA 1995

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 the Energy Information Administration (EIA), *Quarterly Coal Report* January-Dec 2002 (EIA 2003); *U.S. Coal Domestic and International Issues* (EIA 2001); *Mineral Yearbook: Iron and Steel* (USGS 2002a, 2001a, 2000a, 1999, 1997, 1995a, 1993) and the American Iron and Steel Institute (AISI), *Annual Statistical Report* (AISI 2002, 2000). Scrap steel and imported pig iron consumption data for 1990 through 2002 were obtained from *Annual Statistical Reports* (AISI 2002, 2001, 1995). Crude steel production, as well as pig iron use for purposes other than steel production, was also obtained from *Annual Statistical Reports* (AISI 2002, 2001, 1996). Carbon content percentages for pig iron and crude steel and the CO_2 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 2002 were obtained from *Mineral Industry Surveys: Aluminum Annual Report* (USGS 2002, 2001b, 2000b, 1998, 1995b). Annual consumption of iron ore used in sinter production for 1990 through 2002 were obtained from the USGS Iron Ore yearbook (USGS 2002b, 2001b, 2000b, 1999b, 1998b, 1997b, 1996b, 1995b, 1994b). The CO_2 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).

Table 4-6: Production and Consumption Data for the Calculation of CO_2 and CH_4 Emissions from Iron and Steel Production (Thousand Metric Tons)

Gas/Activity Data	1990	1996	1997	1998	1999	2000	2001	2002
CO_2								
Coal Consumption at Coke Plants	35,289	28,763	27,400	25,573	25,499	26,253	23,655	20,445
Coke Consumption for Pig Iron	24,946	20,600	22,100	19,800	18,700	19,215	17,129	15,850
Domestic Pig Iron Production for Steel	49,061	48,958	48,676	47,470	45,677	47,399	41,740	39,600
Basic Oxygen Furnace Steel Production	56,227	54,824	55,386	54,146	52,364	53,964	47,359	45,463
Electric Arc Furnace Steel Production	33,517	40,711	43,098	44,513	45,063	47,859	42,743	46,124
CH_4								
Coke Production	25,054	20,933	20,063	18,181	18,240	18,877	17,190	14,605
Iron Ore Consumption for Sinter	12,504	11,778	11,426	10,791	11,072	10,784	9,234	8,876
Domestic Pig Iron Production for Steel	49,061	48,958	48,676	47,470	45,677	47,399	41,740	39,600

Uncertainty

The time series data for production of coal coke, sinter, pig iron, steel, and aluminum and import and export data upon which the calculations are based are considered to be consistent for the entire time series. The estimates of CO_2 emissions from production and utilization of coke are based on energy consumption data, average carbon contents, and the fraction of carbon oxidized. These data and factors produce a relatively accurate estimate of CO_2 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 CO_2 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 CO_2 emission factors for each technology type. Consistent with the assumptions used in the Aluminum Production source, 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 CO_2/ton steel (IPCC 2000). For this analysis, the upper bound value was used.

For the purposes of the CH_4 calculation it is assumed that none of the CH_4 is captured in stacks or vents and that all of the CH_4 escapes as fugitive emissions. Additionally, the CO_2 emissions calculation is not corrected by subtracting the carbon content of the CH_4, which means there may be a slight double counting of carbon as both CO_2 and CH_4.

The preliminary results of the quantitative uncertainty analysis (see Table 4-7) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions from this source is within the range of approximately 22.7 to 97.1 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 58 percent below and 78 percent above the emission estimate of 54.4 Tg CO_2 Eq.).

For CH_4 emissions from iron and steel, the preliminary results of the quantitative uncertainty analysis (see Table 4-7) indicate that 19 out of 20 times (i.e., there is 95 percent probability), the actual estimate in 2002 is likely to be within the range of 0.6 Tg CO_2 Eq. to 1.4 Tg CO_2 Eq. (or that the actual CH_4 emissions are likely to fall within the range of approximately 39 percent below and 39 percent above the emission estimate of 1.0 Tg CO_2 Eq.).

Table 4-7: Quantitative Uncertainty Estimates for CO_2 and CH_4 Emissions from Iron and Steel Production (Tg. CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Iron and Steel	CO_2	54.4	22.7	97.1	-58%	+78%
Iron and Steel	CH_4	1.0	0.6	1.4	-39%	+39%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Recalculations Discussion

Methane emissions from iron and steel production have been added to this source for the entire time series. These calculations are based on the methodology and emission factors in the 1995 IPCC Guidelines. Methane emission factors for pig iron production and sinter production do not appear in the 1996 IPCC Guidelines, therefore these emissions have not previously been included in the inventory calculations. They were added this year based on a recommendation from the UNFCCC upon review of the 2001 U.S. Inventory.

4.2. *Cement Manufacture (IPCC Source Category 2A1)*

Cement manufacture is an energy and raw material intensive process that results in the generation of CO_2 from both the energy consumed in making the cement and the chemical process itself.[1] Cement production has accounted for about 2.4 percent of total global industrial and energy-related CO_2 emissions, and the United States is the world's third largest cement producer (IPCC 1996). 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 CO_2 emissions in the United States.

During the cement production process, calcium carbonate ($CaCO_3$) is heated in a cement kiln at a temperature of about 1,300^{o}C (2,400^{o}F) to form lime (i.e., calcium oxide or CaO) and CO_2. 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 CO_2 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 CO_2 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 2002, U.S. clinker production—including Puerto Rico—totaled 81,294 thousand metric tons, and U.S. masonry cement production was estimated to be 4,400 thousand metric tons (USGS 2002). The resulting emissions of CO_2 from 2002 cement production were estimated to be 42.9 Tg CO_2 Eq. (42,898 Gg) (see Table 4-8). Emissions from masonry production from clinker raw material were estimated to be 0.1 Tg CO_2 Eq. (99 Gg) in 2002, but again are accounted for under Lime Manufacture.

Table 4-8: CO_2 Emissions from Cement Production*

Year	Tg CO_2 Eq.	Gg
1990	33.3	33,278

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[1] The CO_2 emissions related to the consumption of energy for cement manufacture are accounted for under CO_2 from Fossil Fuel Combustion in the Energy chapter.

1996	37.1	37,079
1997	38.3	38,323
1998	39.2	39,218
1999	40.0	39,991
2000	41.2	41,190
2001	41.4	41,357
2002	42.9	42,898

* Totals exclude CO_2 emissions from making masonry cement from clinker, which 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 2002, emissions increased by 29 percent. 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 CO_2 and lime with the CO_2 released to the atmosphere. The quantity of the CO_2 emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of $CaCO_3$ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO_2:

$$CaCO_3 + heat \rightarrow CaO + CO_2$$
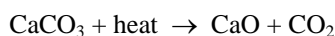
Carbon dioxide emissions were estimated by applying an emission factor, in tons of CO_2 released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 64.6 percent (IPCC 2000) and a constant reflecting the mass of CO_2 released per unit of lime. This calculation yields an emission factor of 0.507 tons of CO_2 per ton of clinker produced, which was determined as follows:

$$EF_{Clinker} = 0.646 \; CaO \times \left[\frac{44.01 \; g/mole \, CO_2}{56.08 \; g/mole \, CaO} \right] = 0.507 \; tons \; CO_2/ton \, clinker$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust. The emissions attributable to the calcinated portion of the cement kiln dust are not accounted for by the clinker emission factor. The IPCC recommends that these additional cement kiln dust CO_2 emissions should be estimated as 2 percent of the CO_2 emissions calculated from clinker production. Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to cement kiln dust (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 2.86 percent by the molecular weight ratio of CO_2 to CaO (0.785) to yield 0.0224 metric tons of additional CO_2 emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO_2 emissions from the additional lime added during masonry cement production are accounted for in the section on CO_2 emissions from Lime Manufacture. Thus, the activity data for masonry cement

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production are shown in this chapter for informational purposes only, and are not included in the cement emission totals.

The activity data for clinker and masonry cement production (see Table 4-9) were obtained from U.S. Geological Survey (USGS 1992, 1995a, 1995b, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

Table 4-9: 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	79,656	4,332
2001	79,979	4,450
2002	81,294	4,400

Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker and in the percentage of cement kiln dust recycled inside the clinker kiln. There is also an uncertainty in the amount of lime added to masonry cement, but it is accounted for under Lime Manufacture. The lime content of clinker varies from 64 to 66 percent. Cement kiln dust loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of CO_2 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 CO_2 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 CO_2 reabsorbed is thought to be minimal, it was not estimated.

The preliminary results of the quantitative uncertainty analysis (see Table 4-10) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions from this source is within the range of approximately 37.2 to 48.6 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 13 percent below and 13 percent above the emission estimate of 42.9 Tg CO_2 Eq.).

Table 4-10: Quantitative Uncertainty Estimates for CO_2 Emissions from Cement Manufacture (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Cement Manufacture	CO_2	42.9	37.2	48.6	-13%	+13%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval
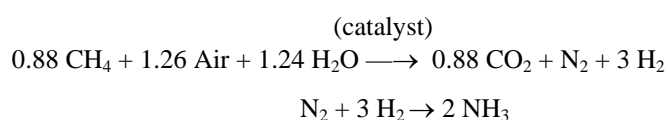
4.3.   Ammonia Manufacture and Urea Application (IPCC Source Category 2B1)

Emissions of CO_2 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 CO_2 and hydrogen (H_2), the latter of which is used in the production of ammonia. The brine electrolysis process does not lead to CO_2 emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH_4 to CO_2, carbon monoxide (CO), and H_2 in the presence of a catalyst. Only 30 to 40 percent of the CH_4 feedstock to the primary reformer is converted to CO and CO_2. The secondary reforming step converts the remaining CH_4 feedstock to CO and CO_2. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO_2 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 CO_2 is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO_2 is released.

The conversion process for conventional steam reforming of CH_4, including primary and secondary reforming and the shift conversion processes, is approximately as follows:

$$\text{(catalyst)}$$
$$0.88\ CH_4 + 1.26\ Air + 1.24\ H_2O \longrightarrow 0.88\ CO_2 + N_2 + 3\ H_2$$

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

Not all of the CO_2 produced in the production of ammonia is emitted directly to the atmosphere. Both ammonia and carbon dioxide are used as raw materials in the production of urea [$CO(NH_2)_2$], which is another type of nitrogenous fertilizer that contains carbon as well as nitrogen. The chemical reaction that produces urea is:

$$2\ NH_3 + CO_2 \rightarrow NH_2COONH_4 \rightarrow CO(NH_2)_2 + H_2O$$

The carbon in the urea that is produced and assumed to be subsequently applied to agricultural land as a nitrogenous fertilizer is ultimately released into the environment as CO_2; therefore, the CO_2 produced by ammonia production and subsequently used in the production of urea does not change overall CO_2 emissions. However, the CO_2 emissions are allocated to the ammonia and urea production processes in accordance to the amount of ammonia and urea produced.

Net emissions of CO_2 from ammonia production in 2002 were 9.6 Tg CO_2 Eq. (9,642 Gg). Carbon dioxide emissions from this source are summarized in Table 4-11. Emissions of CO_2 from urea application in 2002 totaled 8.0 Tg CO_2 Eq. (8,010 Gg). Carbon dioxide emissions from this source are summarized in Table 4-12.

Table 4-11: CO_2 Emissions from Ammonia Manufacture

Year	Tg CO_2 Eq.	Gg
1990	12.6	12,553
1996	13.8	13,825
1997	14.0	14,028
1998	14.2	14,215
1999	12.9	12,948
2000	12.1	12,100
2001	8.9	8,852
2002	9.6	9,642

Table 4-12: CO_2 Emissions from Urea Application

Year	Tg CO_2 Eq.	Gg
1990	6.8	6,753
1996	6.5	6,457

1997	6.6	6,622
1998	7.7	7,719
1999	7.7	7,667
2000	7.5	7,488
2001	7.4	7,398
2002	8.0	8,010

Methodology

The calculation methodology for non-combustion CO_2 emissions from production of nitrogenous fertilizers is based on a CO_2 emission factor published by the European Fertilizer Manufacturers Association (EFMA). The CO_2 emission factor (1.2 tons CO_2/ton NH_3) is applied to the total annual domestic ammonia production. Emissions of CO_2 from ammonia production are then adjusted to account for the use of some of the CO_2 produced from ammonia production as a raw material in the production of urea. For each ton of urea produced, 8.8 of every 12 tons of CO_2 are consumed and 6.8 of every 12 tons of ammonia are consumed. The CO_2 emissions reported for ammonia production are therefore reduced by a factor of 0.73 multiplied by total annual domestic urea production, and that amount of CO_2 emissions is allocated to urea fertilizer application. Total CO_2 emissions resulting from nitrogenous fertilizer production do not change as a result of this calculation, but some of the CO_2 emissions are attributed to ammonia production and some of the CO_2 emissions are attributed to urea application.

The calculation of the total non-combustion CO_2 emissions from nitrogenous fertilizers accounts for CO_2 emissions from the application of imported and domestically produced urea. For each ton of imported urea applied, 0.73 tons of CO_2 are emitted to the atmosphere. The amount of imported urea applied is calculated based on the net of urea imports and exports.

All ammonia production and subsequent urea production was assumed to be from the same process—conventional catalytic reforming of natural gas feedstock. Further, ammonia and urea are assumed to be manufactured in the same manufacturing complex, as both the raw materials needed for urea production are produced by the ammonia production process.

The emission factor of 1.2 ton CO_2/ton NH_3 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 CO_2/ton NH_3, with 1.2 ton CO_2/ton NH_3 as a typical value. The EFMA reference also indicates that more than 99 percent of the CH_4 feedstock to the catalytic reforming process is ultimately converted to CO_2. Ammonia and urea production data (see Table 4-13 and Table 4-14, respectively) were obtained from the Census Bureau of the U.S. Department of Commerce (U.S. Census Bureau 1991, 1992, 1993, 1994, 1998, 1999, 2000, 2001a, 2001b, 2002a, 2002b, 2002c, 2003) as reported in *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports. Import and export data were obtained from the U.S. Census Bureau *Current Industrial Reports Fertilizer Materials and Related Products* annual reports (U.S. Census Bureau) for 1997 through 2002, The Fertilizer Institute (TFI 2002) for 1993 through 1996, and the United States International Trade Commission Interactive Tariff and Trade DataWeb (U.S. ITC 2002) for 1990 through 1992.

Table 4-13: Ammonia Production

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	14,342
2001	11,092
2002	12,336

Table 4-14: Urea Production

Year	Thousand Metric Tons
1990	8,124
1991	7,373
1992	8,142
1993	7,557
1994	7,584
1995	7,363
1996	7,755
1997	7,430
1998	8,042
1999	8,080
2000	6,969
2001	6,080
2002	7,038

Table 4-15: Urea Net Imports

Year	Thousand Metric Tons
1990	1,086
1991	648
1992	656
1993	2,305
1994	2,249
1995	2,055
1996	1,051
1997	1,600
1998	2,483
1999	2,374
2000	3,241
2001	4,008
2002	3,885

Uncertainty

A factor of the uncertainty in this calculation is 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 CO_2/ton NH_3, with 1.2 ton CO_2/ton NH_3 reported as a typical value. The actual emission factor depends upon the amount of air used in the ammonia production process, with 1.15 ton CO_2/ton NH_3 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 CO_2 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 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, as CO_2 emissions from fuel use and non-energy use are calculated separately.[2]

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 CO_2/ton NH_3, which appears to be below the stoichiometric minimum that is achievable for the conventional steam reforming process. The EIA data for natural gas consumption for the years 1994 and 1998 correspond more closely to the CO_2 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 CO_2/ton NH_3, corresponding to CO_2 emissions estimates that are approximately 1.5 Tg CO_2 Eq. below the estimates calculated using the EFMA emission factor of 1.2 ton CO_2/ton NH_3. 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 CO_2 emissions from ammonia production, rather than EIA data.

All ammonia production and subsequent urea production was assumed to be from the same process—conventional catalytic reforming of natural gas feedstock. However, actual emissions may differ because processes other than catalytic steam reformation and feedstocks other than natural gas may have been used for ammonia production. Urea is also used for other purposes than as a nitrogenous fertilizer. It was assumed that 100 percent of the urea production and net imports are used as fertilizer or in otherwise emissive uses. It is also assumed that ammonia and urea are produced at collocated plants from the same natural gas raw material.

The preliminary results of the quantitative uncertainty analysis (see Table 4-16) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from Ammonia Manufacture is within the range of approximately 8.0 to 11.3 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 17 percent below and 17 percent above the emission estimate of 9.6 Tg CO_2 Eq.). For Urea Application, the total greenhouse gas emissions estimate is within the range of approximately 7.4 to 8.7 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 8 percent below and 8 percent above the emission estimate of 8.0 Tg CO_2 Eq.).

Table 4-16: Quantitative Uncertainty Estimates for CO_2 Emissions from Ammonia Manufacture and Urea Application (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ammonia	CO_2	9.6	8.0	11.3	-17%	+17%

[2] It appears that the IPCC emission factor for ammonia production of 1.5 ton CO_2 per ton ammonia may include both CO_2 emissions from the natural gas feedstock to the process and some CO_2 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 tons CO_2 per ton ammonia, respectively) and it is likely that if one value does not include fuel use, the other value also does not. For the conventional steam reforming process, however, the EFMA reports an emission factor range for feedstock CO_2 of 1.15 to 1.30 ton per ton (with a typical value of 1.2 ton per ton) and an emission factor for fuel CO_2 of 0.5 tons per ton. This corresponds to a total CO_2 emission factor for the ammonia production process, including both feedstock CO_2 and process heat CO_2, of 1.7 ton per ton, which is closer to the emission factors reported in the IPCC 1996 Reference Guidelines than to the feedstock-only CO_2 emission factor of 1.2 ton CO_2 per ton ammonia reported by the EFMA. Because it appears that the emission factors cited in the IPCC Guidelines may actually include natural gas used as fuel, we use the 1.2 tons/ton emission factor developed by the EFMA.

| Urea | CO_2 | 8.0 | 7.4 | 8.7 | -8% | +8% |

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Recalculations Discussion

Ammonia and Urea emissions for 2001 were adjusted to reflect revised production information from the U.S. Census Bureau (U.S. Census Bureau 2003). Revised 2001 ammonia and urea production data both decreased by two percent. These changes resulted in a two percent decrease in CO_2 emissions from ammonia manufacture and a one percent decrease in CO_2 emissions from urea application.

4.4.   Lime Manufacture (IPCC Source Category 2A2)

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) systems at coal-fired electric power plants, construction, 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 ($CaCO_3$)—is roasted at high temperatures in a kiln to produce CaO and CO_2. The CO_2 is given off as a gas and is normally emitted to the atmosphere. Some of the CO_2 generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC)[3] production. It is also important to note that, for certain applications, lime reabsorbs CO_2 during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 17,951 thousand metric tons in 2002 (USGS 2003). This resulted in estimated CO_2 emissions of 12.3 Tg CO_2 Eq. (12,304 Gg) (see Table 4-17 and Table 4-18).

Table 4-17: Net CO_2 Emissions from Lime Manufacture

Year	Tg CO_2 Eq.
1990	11.2
1996	13.5
1997	13.7
1998	13.9
1999	13.5
2000	13.3
2001	12.8
2002	12.3

Table 4-18: CO_2 Emissions from Lime Manufacture (Gg)

Year	Potential	Recovered*	Net Emissions
1990	11,730	(493)	11,238
1996	14,347	(852)	13,495
1997	14,649	(964)	13,685

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

1998	14,975	(1,061)	13,914
1999	14,655	(1,188)	13,466
2000	14,548	(1,233)	13,315
2001	13,941	(1,118)	12,823
2002	13,355	(1,051)	12,304

* 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 four end-use categories as follows: metallurgical uses, 35 percent; environmental uses, 28 percent; chemical and industrial uses, 24 percent, construction uses, 12 percent; and refractory dolomite, one percent. In the construction sector, hydrated lime is still used to improve durability in plaster, stucco, and mortars. The use of hydrated lime for traditional building decreased by about 5 percent in 2002 (USGS 2003).

Lime production in 2002 declined five percent from 2001, the fourth consecutive drop in annual production. Overall, from 1990 to 2002, lime production has increased by 13 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization technologies. In 1993, EPA completed regulations under the Clean Air Act capping sulfur dioxide (SO_2) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the flue gas desulfurization end-use to expand significantly over the years. Phase II of the Clean Air Act Amendments, which went into effect on January 1, 2000, remains the driving force behind the growth in the flue gas desulfurization market (USGS 2003).

Methodology

During the calcination stage of lime manufacture, CO_2 is given 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 CO_2 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: $[(44.01 \text{ g/mole } CO_2) \div (56.08 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.75 \text{ g } CO_2/\text{g lime}$

For dolomitic lime: $[(88.02 \text{ g/mole } CO_2) \div (96.39 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.87 \text{ g } CO_2/\text{g lime}$

Production is adjusted to remove the mass of chemically combined water found in hydrated lime, 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 17,951 thousand metric tons in 2002 (USGS 2003), resulting in potential CO_2 emissions of 13.4 Tg CO_2 Eq. Some of the CO_2 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 1,762 thousand metric tons in 2002. It was assumed that approximately 80 percent of the CO_2 involved in sugar refining and PCC was recovered, resulting in actual CO_2 emissions of 12.3 Tg CO_2 Eq.

The activity data for lime manufacture and lime consumption by sugar refining and PCC production for 1990 through 2002 (see Table 4-19) were obtained from USGS (1992, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003). Hydrated lime production is reported separately in Table 4-20. 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 (high-calcium and dolomitic) was not provided prior to 1997, total lime production for 1990 through 1996 was allocated according to the 1997 distribution. For sugar refining and PCC, it was assumed that 100 percent of lime manufacture and consumption was high-calcium, based on communication with the National Lime Association (Males 2003).

Table 4-19: Lime Production and Lime Use for Sugar Refining and PCC (Thousand Metric Tons)

Year	High-Calcium Production[a]	Dolomite Production[a,b]	Use for Sugar Refining and PCC
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	15,850	3,621	2,067
2001	15,630	3,227	1,874
2002	14,900	3,051	1,762

[a] Includes hydrated lime.
[b] Includes dead-burned dolomite.

Table 4-20: Hydrated Lime Production (Thousand Metric Tons)

Year	High-Calcium Hydrate	Dolomitic Hydrate
1990	1,781	319
1991	1,841	329
1992	1,892	338
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
2001	2,030	447
2002	1,500	431

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 CO_2 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, CO_2 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 reacts with CO_2; whereas most of the lime used in steel making 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 CO_2 that is reabsorbed.[4] As more information becomes available, this emission estimate will be adjusted accordingly.

In some cases, lime is generated from calcium carbonate by-products at pulp mills and water treatment plants.[5] The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the pulping industry, mostly using the Kraft (sulfate) pulping process, lime is consumed in order to causticize a process liquor (green liquor) composed of sodium carbonate and sodium sulfide. The green liquor results from the dilution of the smelt created by combustion of the black liquor where biogenic carbon is present from the wood. Kraft mills recover the calcium carbonate "mud" after the causticizing operation and most sulfate mills recover the waste calcium carbonate after the causticizing operation and calcine it back into lime—thereby generating CO_2—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO_2 emitted during this process is mostly 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.

The preliminary results of the quantitative uncertainty analysis (see Table 4-21) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 11.2 to 13.3 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 9 percent below and 8 percent above the emission estimate of 12.3 Tg CO_2 Eq.).

Table 4-21: Quantitative Uncertainty Estimates for CO_2 Emissions from Lime Manufacture (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lime Manufacture	CO_2	12.3	11.2	13.3	-9%	+8%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Recalculations Discussion

The 2001 production data of high calcium quicklime and the 2001 CO_2 recovery from sugar refining were revised in the 2002 Minerals Yearbook (USGS 2003). These changes resulted in a 0.3 percent decrease in 2001 net CO_2 emissions from lime manufacture.

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[4] Representatives of the National Lime Association estimate that CO_2 reabsorption that occurs from the use of lime may offset as much as a quarter of the CO_2 emissions from calcination (Males 2003).

[5] Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO_2. 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) [$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$], not calcium carbonate [$CaCO_3$]. Thus, the calcium hydroxide is heated in the kiln to simply expel the water [$Ca(OH)_2 + heat \rightarrow CaO + H_2O$] and no CO_2 is released.

4.5. Limestone and Dolomite Use (IPCC Source Category 2A3)

Limestone ($CaCO_3$) and dolomite ($CaCO_3MgCO_3$)[6] 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 CO_2 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 systems for utility and industrial plants, or as a raw material in glass manufacturing and magnesium production.

In 2002, approximately 10,820 thousand metric tons of limestone and 2,252 thousand metric tons of dolomite were consumed for these applications. Overall, usage of limestone and dolomite resulted in aggregate CO_2 emissions of 5.8 Tg CO_2 Eq. (5,836 Gg) (see Table 4-22 and Table 4-23). Emissions in 2002 increased 2 percent from the previous year and have increased 5 percent overall from 1990 through 2002.

Table 4-22: CO_2 Emissions from Limestone & Dolomite Use (Tg CO_2 Eq.)

Activity	1990		1996	1997	1998	1999	2000	2001	2002
Flux Stone	3.0		4.2	5.0	5.1	6.0	2.8	2.5	2.4
Glass Making	0.2		0.4	0.3	0.2	0	0.4	0.1	0.1
FGD	1.4		2.0	1.4	1.2	1.2	1.8	2.6	2.8
Magnesium Production	0.1		0.1	0.1	0.1	0.1	0.1	0.1	+
Other Miscellaneous Uses	0.8		1.1	0.4	0.9	0.7	0.9	0.5	0.6
Total	**5.5**		**7.8**	**7.2**	**7.4**	**8.1**	**6.0**	**5.7**	**5.8**

Notes: Totals may not sum due to independent rounding. Other miscellaneous uses include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Table 4-23: CO_2 Emissions from Limestone & Dolomite Use (Gg)

Activity	1990		1996	1997	1998	1999	2000	2001	2002
Flux Stone	**2,999**		**4,236**	**5,023**	**5,132**	**6,030**	**2,829**	**2,514**	**2,405**
Limestone	2,554		3,328	3,963	4,297	4,265	1,810	1,640	1,330
Dolomite	446		908	1,060	835	1,765	1,020	874	1,075
Glass Making	**217**		**415**	**319**	**157**	**0**	**368**	**113**	**110**
Limestone	189		294	319	65	0	368	113	110
Dolomite	28		121	0	91	0	0	0	0
FGD	**1,433**		**1,991**	**1,426**	**1,230**	**1,240**	**1,773**	**2,551**	**2,766**
Magnesium Production	**64**		**73**	**73**	**73**	**73**	**73**	**53**	**0**
Other Miscellaneous Uses	**819**		**1,101**	**401**	**858**	**713**	**915**	**501**	**555**
Total	**5,533**		**7,817**	**7,242**	**7,449**	**8,057**	**5,959**	**5,733**	**5,836**

Notes: Totals may not sum due to independent rounding. Other miscellaneous uses include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Methodology

Carbon dioxide emissions were calculated by multiplying the quantity of limestone or dolomite consumed by the average carbon content, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). This assumes that all carbon is oxidized and released. This methodology was used for flux stone,

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

glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining and then converting to CO_2 using a molecular weight ratio.

Traditionally, the production of magnesium metal was the only other use of limestone and dolomite that produced CO_2 emissions. At the start of 2001, there were two magnesium production plants operating in the United States and they used different production methods. One plant produced magnesium metal using a dolomitic process that resulted in the release of CO_2 emissions, while the other plant produced magnesium from magnesium chloride using a CO_2-emissions-free process called electrolytic reduction. However, the plant utilizing the dolomitic process ceased its operations prior to the end of 2001, so the 2002 emissions from limestone and dolomite use contain zero emissions from this particular sub-use.

Consumption data for 1990 through 2002 of limestone and dolomite used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining (see Table 4-24) were obtained from personal communication with Valentine Tepordei of the USGS regarding data in the *Minerals Yearbook: Crushed Stone Annual Report* (Tepordei 2002 and USGS 1993, 1995a, 1995b, 1996a, 1997a, 1998a, 1999a, 2000a, 2001a, 2002). The production capacity data for 1990 through 2002 of dolomitic magnesium metal (see Table 4-25) also came from the USGS (1995c, 1996b, 1997b, 1998b, 1999b, 2000b, 2001b, 2002). During 1990 and 1992, the USGS did not conduct a detailed survey of limestone and dolomite consumption by end-use. Consumption figures for 1990 were estimated by applying the 1991 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to the 1990 total use figure. Similarly, the 1992 consumption figures were approximated by applying an average of the 1991 and 1993 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to the 1992 total figure.

Additionally, each year the USGS withholds certain limestone and dolomite end-uses due to confidentiality agreements regarding company proprietary data. For the purposes of this analysis, emissive end-uses that contained withheld data were estimated using one of the following techniques: (1) the value for all the withheld data points for limestone or dolomite use was distributed evenly to all withheld end-uses; (2) the average percent of total limestone or dolomite for the withheld end-use in the preceding and succeeding years; or (3) the average fraction of total limestone or dolomite for the end-use over the entire time period.

Finally, 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 for emissive end uses. 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.[7]

Table 4-24: Limestone and Dolomite Consumption (Thousand Metric Tons)

Activity	1990		1996	1997	1998	1999	2000	2001	2002
Flux Stone	**6,738**		**9,466**	**11,226**	**11,514**	**13,390**	**6,248**	**5,558**	**5,275**
Limestone	5,804		7,564	9,007	9,767	9,694	4,113	3,727	3,023
Dolomite	933		1,902	2,219	1,748	3,696	2,135	1,831	2,252
Glass Making	**489**		**922**	**725**	**340**	**0**	**836**	**258**	**250**
Limestone	430		669	725	149	0	836	258	250
Dolomite	59		253	0	191	0	0	0	0
FGD	**3,258**		**4,523**	**3,242**	**2,795**	**2,819**	**4,030**	**5,798**	**6,286**
Other Miscellaneous Uses	**1,835**		**2,481**	**898**	**1,933**	**1,620**	**2,080**	**1,138**	**1,261**
Total	**12,319**		**17,392**	**16,091**	**16,582**	**17,830**	**13,194**	**12,751**	**13,072**

Note: "Other miscellaneous uses" includes chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

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[7] This approach was recommended by USGS.

Table 4-25: 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
2002	0

Note: Production capacity for 2002 amounts to zero because the last U.S. production plant employing the dolomitic process shut down mid-2001 (USGS 2002).

Uncertainty

Uncertainties in this estimate are due, in part, to variations in the chemical composition of limestone. In addition to calcium carbonate, 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. Additionally, there is significant inherent uncertainty associated with estimating withheld data points for specific end uses of limestone and dolomite. Lastly, the uncertainty of the estimates for limestone used in glass making is especially high. Large fluctuations in reported consumption exist, reflecting year-to-year changes in the number of survey responders. 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 a small percent of consumption, its contribution to the overall emissions estimate is low.

The preliminary results of the quantitative uncertainty analysis (see Table 4-26) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 4.9 to 6.9 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 17 percent below and 18 percent above the emission estimate of 5.8 Tg CO_2 Eq.).

Table 4-26: Quantitative Uncertainty Estimates for CO_2 Emissions from Limestone and Dolomite Use (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Limestone and Dolomite Use	CO_2	5.8	4.9	6.9	-17%	+18%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Recalculations Discussion

The recalculation of limestone and dolomite consisted of a correction in the way unspecified data, both reported and estimated, was apportioned to the various emissive uses. This change resulted in an average annual increase of 0.2 Tg CO_2 Eq. (3 percent) in CO_2 emissions from 1990 through 2001.

4.6.   Soda Ash Manufacture and Consumption (IPCC Source Category 2A4)

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 three states produce natural soda ash: Wyoming, California, and Colorado. Of these three states, only net emissions of CO_2 from Wyoming were calculated. This difference is a result of the production processes employed in each state.[8] During the production process used in Wyoming, trona ore is treated to produce soda ash. Carbon dioxide is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. The one Colorado facility produces soda ash using nahcolite, a different production process than is used in Wyoming, and emissions from this process will be included in future inventories. In addition, CO_2 may also be released when soda ash is consumed.

In 2002, CO_2 emissions from the manufacture of soda ash from trona were approximately 1.5 Tg CO_2 Eq. (1,470 Gg). Soda ash consumption in the United States generated 2.7 Tg CO_2 Eq. (2,668 Gg) in 2002. Total emissions from soda ash in 2002 were 4.1 Tg CO_2 Eq. (4,139 Gg) (see Table 4-27 and Table 4-28). Emissions have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 2002 decreased by less than 1 percent from the previous year, and have increased overall by less than 1 percent since 1990.

Table 4-27: CO_2 Emissions from Soda Ash Manufacture and Consumption

Year	Tg CO₂ Eq.
1990	4.1
1996	4.2
1997	4.4
1998	4.3
1999	4.2
2000	4.2
2001	4.1
2002	4.1

Table 4-28: CO_2 Emissions from Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture	Consumption	Total

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[8] 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.

1990	1,431	2,710	4,141
1996	1,587	2,652	4,239
1997	1,665	2,689	4,354
1998	1,607	2,718	4,325
1999	1,548	2,668	4,217
2000	1,529	2,652	4,181
2001	1,500	2,648	4,147
2002	1,470	2,668	4,139

Note: Totals may not sum due to independent rounding.

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 2002 was glass making, 48 percent; chemical production, 26 percent; soap and detergent manufacturing, 11 percent; distributors, five percent; flue gas desulfurization, pulp and paper production, water treatment, two percent each; and miscellaneous, four percent (USGS 2003).

The domestic 2002 market for soda ash was nearly identical to that of 2001: a decline in the first period partially offset by an increase in exports. Although the United States continues to be the major supplier of world soda ash, China's soda ash manufacturing capacity is rapidly increasing. This will likely cause greater competition in Asian markets in the future. The world market for soda ash is expected to grow 1.5 to 2 percent annually (USGS 2003).

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:

$$2(Na_3H(CO_3)_2 \cdot 2H_2O) \rightarrow 3Na_2CO_3 + 5H_2O + CO_2$$
$$\text{[trona]} \qquad \qquad \text{[soda ash]}$$

Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO_2. Thus, the 15.1 million metric tons of trona mined in 2002 for soda ash production (USGS 2003) resulted in CO_2 emissions of approximately 1.5 Tg CO_2 Eq. (1,470 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 CO_2 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 CO_2) are released for every metric ton of soda ash consumed.

The activity data for trona production and soda ash consumption (see Table 4-29) were taken from USGS (1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003). 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.

Table 4-29: Soda Ash Manufacture and Consumption (Thousand Metric Tons)

Year	Manufacture*	Consumption
1990	14,700	6,530
1991	14,700	6,280
1992	14,900	6,320
1993	14,500	6,280
1994	14,600	6,260
1995	16,500	6,500
1996	16,300	6,390

1997	17,100	6,480
1998	16,500	6,550
1999	15,900	6,430
2000	15,700	6,390
2001	15,400	6,380
2002	15,100	6,430

* Soda ash manufactured from trona ore only.

Uncertainty

Emissions from soda ash manufacture are considered to have low associated uncertainty. Both the emission factor and activity data are reliable. However, emissions from soda ash 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, there is uncertainty surrounding the emission factors from the consumption of soda ash.

The preliminary results of the quantitative uncertainty analysis (see Table 4-30) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 3.8 to 4.4 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 7 percent below and 7 percent above the emission estimate of 4.1 Tg CO_2 Eq.).

Table 4-30: Quantitative Uncertainty Estimates for CO_2 Emissions from Soda Ash Manufacture and Consumption (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Soda Ash Manufacture and Consumption	CO_2	4.1	3.8	4.4	-7%	+7%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Planned Improvements

Emissions from soda ash production in Colorado, which is produced using the nahcolite production process, will be investigated for inclusion in future inventories.

4.7. Titanium Dioxide Production (IPCC Source Category 2B5)

Titanium dioxide (TiO_2) 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 TiO_2 is also used as a pigment in the manufacture of white paper, foods, and other products. There are two processes for making TiO_2, the chloride process and the sulfate process. Carbon dioxide is emitted from the chloride process, which uses petroleum coke and chlorine as raw materials and emits process-related CO_2. The sulfate process does not use petroleum coke or other forms of carbon as a raw material and does not emit CO_2. In 2002, approximately 97 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:

$$2\ FeTiO_3 + 7\ Cl_2 + 3\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 3\ CO_2$$

$$2\ TiCl_4 + 2\ O_2 \rightarrow 2\ TiO_2 + 4\ Cl_2$$
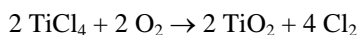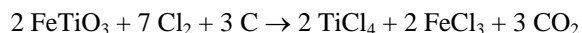
The carbon in the first chemical reaction is provided by petroleum coke, which is oxidized in the presence of the chlorine and $FeTiO_3$ (the Ti-containing ore) to form CO_2. The majority of U.S. TiO_2 was produced in the United

States through the chloride process, and a special grade of petroleum coke is manufactured specifically for this purpose. Emissions of CO_2 from titanium dioxide production in 2002 were 2.0 Tg CO_2 Eq. (1,997 Gg), an increase of 8 percent from the previous year and 53 percent from 1990 due to increasing production within the industry (see Table 4-31).

Table 4-31: CO_2 Emissions from Titanium Dioxide

Year	Tg CO_2 Eq.	Gg
1990	1.3	1,308
1996	1.7	1,657
1997	1.8	1,836
1998	1.8	1,819
1999	1.9	1,853
2000	1.9	1,918
2001	1.9	1,857
2002	2.0	1,997

Methodology

Emissions of CO_2 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 97 percent of the total production in 2002 was produced using the chloride process. An emission factor of 0.4 metric tons C/metric ton TiO_2 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.

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 2002 (see Table 4-32) 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, 2001, 2002, 2003). Data for the percentage of the total titanium dioxide production capacity that is chloride process for 1994 through 2002 were also taken from the USGS *Minerals Yearbook*. Percentage chloride process data were not available for 1990 through 1993, and data from the 1994 USGS *Minerals Yearbook* were used for these years. Because a sulfate-process plant closed in September 2001, the chloride process percentage for 2001 was estimated based on a discussion with Joseph Gambogi, USGS Commodity Specialist (2002). By 2002, only one sulfate plant remained online in the United States. The composition data for petroleum coke were obtained from Onder and Bagdoyan (1993).

Table 4-32: 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	1,400,000
2001	1,330,000
2002	1,410,000

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 CO_2 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.

The preliminary results of the quantitative uncertainty analysis (see Table 4-33) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 1.6 to 2.4 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 21 percent below and 21 percent above the emission estimate of 2.0 Tg CO_2 Eq.).

Table 4-33: Quantitative Uncertainty Estimates for CO_2 Emissions from Titanium Dioxide Production (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO₂ Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Titanium Dioxide Production	CO₂	2.0	1.6	2.4	-21%	+21%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

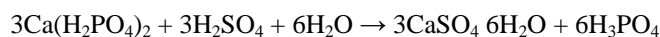## *4.8. Phosphoric Acid Production (IPCC Source Category 2A7)*

Phosphoric acid [H_3PO_4] is a basic raw material in the production of phosphate-based fertilizers. Phosphate rock is mined in Florida, North Carolina, Idaho, Utah, and other areas of the United States and is used primarily as a raw material for phosphoric acid production. The production of phosphoric acid from phosphate rock produces byproduct gypsum [$CaSO_4 \cdot 2H_2O$], referred to as phosphogypsum.

The composition of natural phosphate rock varies depending upon the location where it is mined. Natural phosphate rock mined in the United States generally contains inorganic carbon in the form of calcium carbonate (limestone) and also may contain organic carbon. The chemical composition of phosphate rock (francolite) mined in Florida is:

$$Ca_{10-x-y} \, Na_x \, Mg_y \, (PO_4)_{6-x}(CO_3)_x F_{2+0.4x}$$
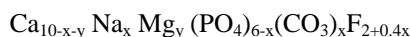
The calcium carbonate component of the phosphate rock is integral to the phosphate rock chemistry. Phosphate rock can also contain organic carbon that is physically incorporated into the mined rock but is not an integral component of the phosphate rock chemistry. Phosphoric acid production from natural phosphate rock is a source of CO_2 emissions. The source of the CO_2 emissions is the chemical reaction of the inorganic carbon (calcium carbonate) component of the phosphate rock.

The phosphoric acid production process involves chemical reaction of the calcium phosphate ($Ca_3(PO_4)_2$) component of the phosphate rock with sulfuric acid (H_2SO_4) and recirculated phosphoric acid (H_3PO_4) (EFMA 1997). The primary chemical reactions for the production of phosphoric acid from phosphate rock are:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

$$3Ca(H_2PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3CaSO_4\ 6H_2O + 6H_3PO_4$$

The limestone ($CaCO_3$) component of the phosphate rock reacts with the sulfuric acid in the phosphoric acid production process to produce calcium sulfate (phosphogypsum) and carbon dioxide. The chemical reaction for the limestone–sulfuric acid reaction is:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4\ 2H_2O + CO_2$$
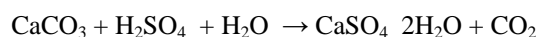
Total marketable phosphate rock production in 2002 was 37.4 million metric tons. Approximately 86 percent of domestic phosphate rock production was mined in Florida and North Carolina, with the remaining 14 percent of production being mined in Idaho and Utah. Florida alone represented more than 75 percent of domestic production. In addition, 2.7 million metric tons of crude phosphate rock was imported for consumption in 2002. Marketable phosphate rock production, including domestic production and imports for consumption, increased by approximately 6 percent between 2001 and 2002. However, over the 1990 to 2002 period, production decreased by 15 percent. The 35.3 million metric tons produced in 2001 was the lowest production level recorded since 1965 and was driven by a worldwide decrease in demand for phosphate fertilizers. Domestic consumption is anticipated to increase over the next several years as planted acreage and associated phosphate fertilizer application increase (USGS, 2002). Total CO_2 emissions from phosphoric acid production were 1.3 Tg CO_2 Eq. (1,339 Gg) in 2002 (see Table 4-34).

Table 4-34: CO_2 Emissions from Phosphoric Acid Production

Year	Tg CO_2 Eq.	Gg
1990	1.5	1,529
1996	1.6	1,551
1997	1.5	1,544
1998	1.6	1,593
1999	1.5	1,539
2000	1.4	1,382
2001	1.3	1,264
2002	1.3	1,339

Methodology

Carbon dioxide emissions from production of phosphoric acid from phosphate rock is calculated by multiplying the average amount of calcium carbonate contained in the natural phosphate rock by the amount of phosphate rock that is used annually to produce phosphoric acid, accounting for domestic production and net imports for consumption.

The USGS reports in the Minerals Yearbook, Phosphate Rock, the aggregate amount of phosphate rock mined annually in Florida and North Carolina and the aggregate amount of phosphate rock mined annually in Idaho and Utah, and reports the annual amounts of phosphate rock exported and imported for consumption (see Table 4-35). Data for domestic production of phosphate rock, exports of phosphate rock, and imports of phosphate rock for

consumption for 1990 through 2002 were obtained from USGS Mineral Yearbook, Phosphate Rock (USGS 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003).

The carbonate content of phosphate rock varies depending upon where the material is mined. Composition data for domestically mined and imported phosphate rock were provided by the Florida Institute of Phosphate Research (FIPR 2003). Phosphate rock mined in Florida contains approximately 3.5 percent inorganic carbon (as CO_2), and phosphate rock imported from Morocco contains approximately 5 percent inorganic carbon (as CO_2). Calcined phosphate rock mined in North Carolina and Idaho contains approximately 1.5 percent and 1.0 percent inorganic carbon (as CO_2), respectively (see Table 4-36).

Carbonate content data for phosphate rock mined in Florida are used to calculate the CO_2 emissions from consumption of phosphate rock mined in Florida and North Carolina (85 percent of domestic production) and carbonate content data for phosphate rock mined in Morocco are used to calculate CO_2 emissions from consumption of imported phosphate rock. The CO_2 emissions calculation is based on the assumption that all of the domestic production of phosphate rock is used in uncalcined form. The USGS reported that one phosphate rock producer in Idaho is producing calcined phosphate rock, however, no production data were available for this single producer (USGS 2003). Carbonate content data for uncalcined phosphate rock mined in Idaho and Utah (14 percent of domestic production in 2002) were not available, and carbonate content was therefore estimated from the carbonate content data for calcined phosphate rock mined in Idaho.

The CO_2 emissions calculation methodology is based on the assumption that all of the inorganic carbon (calcium carbonate) content of the phosphate rock reacts to CO_2 in the phosphoric acid production process and is emitted with the stack gas. The methodology also assumes that none of the organic carbon content of the phosphate rock is converted to CO_2 and that all of the organic carbon content remains in the phosphoric acid product.

Table 4-35: Phosphate Rock Domestic Production, Exports, and Imports (Thousand Metric Tons)

Location/Year	1990		1996	1997	1998	1999	2000	2001	2002
U.S. Production									
FL & NC	42,494		38,100	36,604	38,000	35,900	31,900	28,100	29,800
ID & UT	7,306		5,460	5,496	5,640	5,540	5,470	4,730	4,920
Exports - FL & NC	6,240		1,570	335	378	272	299	9	39
Imports - Morocco	451		1,800	1,830	1,760	2,170	1,930	2,500	2,700
Total U.S. Consumption	**44,011**		**43,790**	**43,595**	**45,022**	**43,338**	**39,001**	**35,321**	**37,381**

Source: USGS, 2003, 2002, 2001, 2000, 1999, 1998, 1997, 1996, 1995.

Table 4-36: Chemical Composition of Phosphate Rock (percent by weight)

Composition	Central Florida	North Florida	North Carolina (calcined)	Idaho (calcined)	Morocco
Total Carbon (as C)	1.60	1.76	0.76	0.60	1.56
Inorganic Carbon (as C)	1.0	0.93	0.41	0.27	1.46
Organic Carbon (as C)	0.60	0.83	0.35	--	0.1
Inorganic Carbon (as CO_2)	3.67	3.43	1.50	1.0	5.0

Source: FIPR 2003

Uncertainty

Phosphate rock production data used in the emission calculations are developed by the USGS through monthly and semiannual voluntary surveys of the eleven companies that owned phosphate rock mines during 2002. The phosphate rock production data are not considered to be a significant source of uncertainty, because all eleven of the domestic phosphate rock producers are reporting their annual production to the USGS. Data for imports for consumption and exports of phosphate rock used in the emission calculation are based on international trade data collected by the U.S. Census Bureau. These U.S. government economic data are not considered to be a significant source of uncertainty.

In addition, the carbonate composition of domestic phosphate rock could potentially vary by ±1 percent (i.e., from 2.5 percent to 4.5 percent) based on the carbonate content data provided by the FIPR. An assumed increase of one percent in the carbonate content (i.e., from 3.5 percent to 4.5 percent) translates into an approximately 20 percent increase in the calculated CO_2 emissions from phosphoric acid production.

One source of potentially significant uncertainty in the calculation of CO_2 emissions from phosphoric acid production is the data for the carbonate composition of phosphate rock. The composition of phosphate rock varies depending upon where the material is mined, and may also vary over time. Only one set of data from the Florida Institute of Phosphate Research was available for the composition of phosphate rock mined domestically and imported, and data for uncalcined phosphate rock mined in North Carolina and Idaho were unavailable. Inorganic carbon content (as CO_2) of phosphate rock could vary ±1 percent from the data included in Table 4-36, resulting in a variation in CO_2 emissions of ±20 percent. Another source of uncertainty is the disposition of the organic carbon content of the phosphate rock. A representative of the FIPR indicated that in the phosphoric acid production process the organic carbon content of the mined phosphate rock generally remains in the phosphoric acid product, which is what produces the color of the phosphoric acid product (FIPR 2003a). Organic carbon is therefore not included in the calculation of CO_2 emissions from phosphoric acid production. However, if, for example, 50 percent of the organic carbon content of the phosphate rock were to be emitted as CO_2 in the phosphoric acid production process, the CO_2 emission estimate would increase by on the order of 50 percent.

A third source of uncertainty is the assumption that all domestically produced phosphate rock is used in phosphoric acid production and used without first being calcined. Calcination of the phosphate rock would result in conversion of some of the organic carbon in the phosphate rock into CO_2. However, according to the USGS, only one producer in Idaho is currently calcining phosphate rock, and no data were available concerning the annual production of this single producer (USGS 2003). Total production of phosphate rock in Utah and Idaho combined amounts to approximately 14 percent of total domestic production in 2002. If it is assumed that 100 percent of the reported domestic production of phosphate rock for Idaho and Utah was first calcined, and it is assumed that 50 percent of the organic carbon content of the total production for Idaho and Utah was converted to CO_2 in the calcination process, the CO_2 emission estimate would increase by on the order of 10 percent.

Finally, USGS indicated that 5 percent of domestically produced phosphate rock is used to manufacture elemental phosphorus and other phosphorus-based chemicals, rather than phosphoric acid (USGS 2003a). According to USGS, there is only one domestic producer of elemental phosphorus, in Idaho, and no data were available concerning the annual production of this single producer. Elemental phosphorus is produced by reducing phosphate rock with coal coke, and it therefore is anticipated that 100 percent of the carbonate content of the phosphate rock will be converted to CO_2 in the elemental phosphorus production process. The CO_2 emissions calculation also is based on the assumption that phosphate rock consumption other than for phosphoric acid production (approximately 5 percent of total phosphate rock consumption) also results in emission of 100 percent of the inorganic carbon content of the phosphate rock but none of the organic carbon content, as CO_2. If none of the inorganic carbon were to be emitted from these other processes, the CO_2 emissions estimate could decrease by on the order of 5 percent. If all of the organic carbon and inorganic carbon were to be emitted from these other processes the CO_2 emissions estimate could increase by on the order of 5 percent.

The preliminary results of the quantitative uncertainty analysis (see Table 4-37) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 1.0 to 1.7 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 26 percent below and 28 percent above the emission estimate of 1.3 Tg CO_2 Eq.).

Table 4-37: Quantitative Uncertainty Estimates for CO_2 Emissions from Phosphoric Acid Production (Tg CO_2 Eq. and Percent)

| Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Phosphoric Acid Production	CO_2	1.3	1.0	1.7	-26%	+28%

Recalculations Discussion

Carbon dioxide emissions from phosphoric acid production from phosphate rock are being reported for the first time in this report. Phosphoric acid production is being added as a result of ongoing research into sources of carbon dioxide emissions from mineral processing industries.

Planned Improvements

The estimate of CO_2 emissions from phosphoric acid production could be improved through collection of additional data. Additional data is being collected concerning the carbonate content of uncalcined phosphate rock mined in various locations in the United States and imported to improve the CO_2 emissions estimate. Additional research will also be conducted concerning the disposition of the organic carbon content of the phosphate rock in the phosphoric acid production process. Only a single producer of phosphate rock is calcining the product, and only a single producer is manufacturing elemental phosphorus. Annual production data for these single producers will probably remain unavailable.

4.9.   Ferroalloy Production (IPCC Source Category 2C2)

Carbon dioxide is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements such as 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 in the United States. Subsequently, government information disclosure rules prevent the publication of production data for these production facilities. Similar to emissions from the production of iron and steel, CO_2 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 to CO_2. A representative reaction equation for the production of 50 percent ferrosilicon is given below:

$$Fe_2O_3 + 2SiO_2 + 7C \rightarrow 2FeSi + 7CO$$
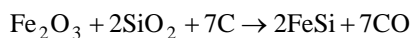
Emissions of CO_2 from ferroalloy production in 2002 were 1.2 Tg CO_2 Eq. (1,237 Gg) (see Table 4-38), a 7 percent reduction from the previous year and a 38 percent reduction since 1990.

Table 4-38: CO_2 Emissions from Ferroalloy Production

Year	Tg CO$_2$ Eq.	Gg
1990	2.0	1,980
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
2001	1.3	1,329
2002	1.2	1,237

Methodology

Emissions of CO_2 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 50 percent silicon ferrosilicon (2.35 tons CO_2/ton of alloy produced) was applied. Additionally, for ferrosilicon alloys containing 56 to 95 percent silicon, an emission factor for 75 percent silicon ferrosilicon (3.9 tons CO_2 per ton alloy produced) was applied. The emission factor for silicon metal was assumed to be 4.3 tons CO_2/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.

Ferroalloy production data for 1990 through 2002 (see Table 4-39) 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, 2001, 2002, 2003). Until 1999, the USGS reported production of ferrosilicon containing 25 to 55 percent silicon 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 4-39). The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

Table 4-39: 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	72,442
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
2001	167,000	89,000	137,000	NA
2002	156,000	98,600	113,000	NA

NA (Not Available)

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.[9] Emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, but may generate differing amounts of CO_2 per unit of ferroalloy produced compared to the use of petroleum coke. 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.

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

The preliminary results of the quantitative uncertainty analysis (see Table 4-40) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 1.1 to 1.4 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 9 percent below and 9 percent above the emission estimate of 1.2 Tg CO_2 Eq.).

Table 4-40: Quantitative Uncertainty Estimates for CO_2 Emissions from Ferroalloy Production (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ferroalloy Production	CO_2	1.2	1.1	1.4	-9%	+9%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

4.10. Carbon Dioxide Consumption (IPCC Source Category 2B5)

Carbon dioxide (CO_2) is used for a variety of applications, including food processing, chemical production, carbonated beverages, refrigeration, and enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the ground to increase reservoir pressure, and is considered for the purposes of this analysis to remain sequestered in the underground formations.[10] For the most part, however, CO_2 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 byproduct CO_2 generated during production processes may already be accounted for in the CO_2 emission estimates from fossil fuel consumption (either during combustion or from non-energy uses). For example, ammonia is primarily manufactured using natural gas as both a feedstock and energy source. Carbon dioxide emissions from natural gas combustion for ammonia production are accounted for in the Energy chapter under Fossil Fuel Combustion and, therefore, are not included here. Carbon dioxide emissions from natural gas used as feedstock for ammonia production are accounted for in this chapter under Ammonia Manufacture and, therefore, are also not included under Carbon Dioxide Consumption. Carbon dioxide is also produced as a byproduct of crude oil and natural gas production. This CO_2 may be emitted directly to the atmosphere, reinjected into underground formations, used for EOR, or sold for other commercial uses. Carbon dioxide separated from crude oil and natural gas has not been estimated.[11] Therefore, the only CO_2 consumption that is accounted for here is CO_2 produced from natural wells other than crude oil and natural gas wells.

There are two such facilities currently in operation, one in Mississippi and one in New Mexico, both of which produce CO_2 for use in EOR and for use in other commercial applications (e.g., chemical manufacturing). In 2002, CO_2 emissions from these two facilities not accounted for elsewhere were 1.3 Tg CO_2 Eq. (1,272 Gg) (see Table 4-41). This amount represents an increase of 50 percent from the previous year and an increase of 43 percent from emissions in 1990. This increase was due to an increase in the reported production for use in industrial applications from one facility.

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[10] It is unclear to what extent the CO_2 used for EOR will be re-released. For example, the CO_2 used for EOR may show up at the wellhead after a few years of injection (Hangebrauk et al. 1992). This CO_2, however, is typically recovered and re-injected into the well. More research is required to determine the amount of CO_2 that in fact escapes from EOR operations. For the purposes of this analysis, it is assumed that all of the CO_2 used in EOR remains sequestered.

[11] The United States is in the process of developing a methodology to account for CO_2 emissions from Natural Gas Systems and Petroleum Systems for inclusion in future Inventory submissions. For more information please see Annex 5.

Table 4-41: CO_2 Emissions from Carbon Dioxide Consumption

Year	Tg CO_2 Eq.	Gg
1990	0.9	892
1996	0.8	783
1997	0.8	838
1998	0.9	946
1999	0.9	881
2000	1.0	993
2001	0.8	849
2002	1.3	1,272

Methodology

Carbon dioxide emission estimates for 2001 and 2002 were based on production data for the two facilities currently producing CO_2 from natural wells. Some of the CO_2 produced by these facilities is used for EOR and some is used for other applications (e.g., chemical manufacturing). Carbon dioxide production from these two facilities that was used for EOR is assumed to remain sequestered and is not included in the CO_2 emissions totals. It is assumed that 100 percent of the CO_2 production used for end-use applications other than EOR is eventually released into the atmosphere.

Carbon dioxide production data for the fourth quarter of 2001 and fourth quarter of 2002 for the Jackson Dome, Mississippi facility, and the percentage of total production that was used in EOR and non-EOR applications, were obtained from the Annual Reports for Denbury Resources, the operator of the facility (Denbury Resources 2001; Denbury Resources 2002). Fourth quarter production data were annualized for the entire calendar years for 2001 and 2002. Carbon dioxide production data for the Bravo Dome, New Mexico facility were obtained from the New Mexico Bureau of Geology and Mineral Resources for the years 1990 through 2000 (Broadhead 2003). According to the New Mexico Bureau, the amount of carbon dioxide produced from Bravo Dome for use in non-EOR applications is less than one percent of total production. Production data for 2001 and 2002 were not available for Bravo Dome. Production for 2001 and 2002 for Bravo Dome is assumed to be the same as the production for the year 2000.

Denbury Resources acquired the Jackson Dome facility in 2001, and CO_2 production data for the facility are not available for years prior to 2001. Therefore for 1990 through 2000, CO_2 emissions from CO_2 consumption are estimated based on the total annual domestic commercial consumption of CO_2, as reported by the U.S. Census Bureau, multiplied by the percentage of the total domestic non-EOR consumption that was provided by the Jackson Dome and Bravo Dome facilities; the two facilities that were producing CO_2 from natural wells in 2001. The total domestic consumption of CO_2 as reported by the U.S. Census Bureau was about 11,414 thousand metric tons in 2001. The total non-EOR CO_2 produced from natural wells in 2001 was about 850 thousand metric tons, corresponding to 7.4 percent of the total domestic CO_2 consumption. This 7.4 percent factor was applied to the annual CO_2 consumption data for the years 1990 through 2000 as reported by the U.S. Census Bureau to estimate annual CO_2 emissions from consumption of CO_2 produced from natural wells. The remaining 92.6 percent of the total annual CO_2 consumption is assumed either to be accounted for in the CO_2 emission estimates from other categories (the most important being Fossil Fuel Combustion) or to be produced from biogenic sources (e.g., grain fermentation) that are not accounted for here.

Carbon dioxide consumption data (see Table 4-42) for years 1991 and 1992 were obtained from *Industry Report 1992*, provided by the U.S. Census Bureau. Consumption data are not available for 1990, and therefore CO_2 consumption data for 1990 is assumed to be equal to that for 1991. Consumption data for 1993 and 1994 were obtained from *U.S. Census Bureau Manufacturing Profile, 1994*. Consumption data for 1996 through 2002 were obtained from the U.S. Census Bureau's *Industry Report, 1996, 1998, 2000, 2002*.

Table 4-42: Carbon Dioxide Consumption

Year	Metric Tons
1990	11,997,726

1996	10,532,353
1997	11,268,219
1998	12,716,070
1999	11,843,386
2000	13,354,262
2001	11,413,889
2002	11,313,478

Uncertainty

Uncertainty exists in the assumed allocation of CO_2 produced from fossil fuel by-products and biogenic sources (92.6 percent) and CO_2 produced from natural wells (7.4 percent) for the years 1990 through 2000. The allocation for these years is assumed to be the same allocation as for 2001, the last year for which data are available to calculate the allocation. Uncertainty also exists with respect to the number of facilities that are currently producing CO_2 from natural wells and for which CO_2 emissions are not accounted for elsewhere. Research indicates that there are only two such facilities, however, additional facilities may exist that have not been identified. In addition, it is possible that CO_2 recovery exists in particular production and end-use sectors that are not accounted for elsewhere. Such recovery may or may not affect the overall estimate of CO_2 emissions from that sector depending upon the end use to which the recovered CO_2 is applied. For example, research has identified one ammonia production facility that is recovering CO_2 for use in EOR. Such CO_2 is assumed to remain sequestered. Recovery of CO_2 from ammonia production facilities for use in EOR is discussed in this chapter under Ammonia Production. Further research is required to determine whether CO_2 is being recovered from other facilities for application to end uses that are not accounted for elsewhere.

The preliminary results of the quantitative uncertainty analysis (see Table 4-43) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 1.1 to 1.4 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 10 percent below and 10 percent above the emission estimate of 1.3 Tg CO_2 Eq.).

Table 4-43: Quantitative Uncertainty Estimates for CO_2 Emissions from Carbon Dioxide Consumption (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO$_2$ Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO$_2$ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Carbon Dioxide Consumption	CO$_2$	1.3	1.1	1.4	-10%	+10%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Recalculations Discussion

The methodology used to calculate CO_2 consumption was revised because the underlying assumption upon which the previous methodology was based, that 20 percent of the CO_2 produced for domestic consumption was from "natural sources" is more than ten years out of date and conflicts with more recently available data. Research conducted indicates that there are only two facilities producing CO_2 from natural sources for domestic non-EOR consumption. The estimate of CO_2 emissions from CO_2 Consumption for the years 2001 and 2002 has been revised and is now based on actual production data for these two facilities.

For years prior to 2001, estimates have been updated and are now based on total annual domestic commercial consumption of CO_2, as reported by the U.S. Census Bureau, multiplied by the percentage of the total domestic non-EOR consumption that was provided by the two facilities producing CO_2 from natural wells in 2001 (7.4 percent.) The CO_2 consumption published by the U.S. Census Bureau is being used for the current methodology because the U.S. Census Bureau data are public, contain actual CO_2 consumption collected from CO_2 producers and consumers,

and cover all years except 1990. Additionally, the Census Bureau provides documentation that can be used as a basis for uncertainty analysis.

These changes in the methodology and data sources used to calculate CO_2 emissions from CO_2 consumption resulted in an average annual decrease of 0.2 Tg CO_2 Eq. (19 percent) from previous estimates.

A 2001 industry publication (Sim 2001) provides data to indicate that the assumption that 20 percent of domestic CO_2 consumption is derived from natural sources does not reflect current industry conditions. This reference provides a breakdown of both CO_2 production and consumption by industry sector for the year 2000. Sim (2001) indicates that 9.9 million short tons of CO_2 were produced in 2000 for industrial consumption. For the year 2000, 35 percent of the reported domestic production sold in industry was produced by the recovery of CO_2 from ammonia production. Carbon dioxide produced from refineries and from oil and gas wells each accounted for 21 percent of domestic CO_2 production. Carbon dioxide recovered from ethanol production accounted for 14 percent of domestic production, and CO_2 produced from cogeneration and other sources accounted for the remaining 9 percent of domestic production. Neither the CO_2 production data reported in Sim (2001) nor the production data published by the Census Bureau include all of the CO_2 produced from natural wells for use for EOR, which in 2000 was more than 22 million metric tons. Sim (2001) also indicates that for the year 2000, 70 percent of domestic CO_2 reported consumed in commerce (a total of 7.5 million short tons) was used for refrigeration or food production, including dry ice and beverage carbonation. Of the remaining reported consumption, 10 percent was used in manufacturing processes, 7 percent was used for oil recovery, and 13 percent was used in other applications. Neither the CO_2 consumption data reported by Sim (2001) nor the Census Bureau consumption data include all of the CO_2 used for enhanced oil recovery.

4.11. Petrochemical Production (IPCC Source Category 2B5)

Methane is released, in small amounts, 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 generated 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 CH_4 from petrochemical production in 2002 were 1.5 Tg CO_2 Eq. (72 Gg) (see Table 4-44), an increase of 6 percent from the previous year and 30 percent from 1990.

Table 4-44: CH_4 Emissions from Petrochemical Production

Year	Tg CO_2 Eq.	Gg
1990	1.2	56
1996	1.6	76
1997	1.6	78
1998	1.7	80
1999	1.7	81
2000	1.7	80

2001	1.4	68
2002	1.5	72

Methodology

Emissions of CH_4 were calculated by multiplying annual estimates of chemical production by an emission factor. The following factors were used: 11 kg CH_4/metric ton carbon black, 1 kg CH_4/metric ton ethylene, 0.4 kg CH_4/metric ton ethylene dichloride,[12] 4 kg CH_4/metric ton styrene, and 2 kg CH_4/metric ton methanol. These emission factors were based upon measured material balances. Although the production of other chemicals may also result in CH_4 emissions, there were not sufficient data to estimate their emissions.

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data for 1990 (see Table 4-45) were obtained from the Chemical Manufacturer's Association *Statistical Handbook* (CMA 1999). Production data for 1991 through 2002 were obtained from the American Chemistry Council's *Guide to the Business of Chemistry* (2003).

Table 4-45: Production of Selected Petrochemicals (Thousand Metric Tons)

Chemical	1990		1996	1997	1998	1999	2000	2001	2002
Carbon Black	1,306		1,560	1,588	1,610	1,642	1,674	1,583	1,683
Ethylene	16,542		22,217	23,088	23,474	25,118	24,971	22,521	23,623
Ethylene Dichloride	6,282		9,303	10,324	11,080	10,308	9,866	9,294	9,288
Styrene	3,637		5,402	5,171	5,183	5,410	5,420	4,277	4,974
Methanol	3,785		5,280	5,743	5,860	5,303	4,876	3,402	3,289

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 emission estimates, however, such data were not available. There may also be other significant sources of CH_4 arising from petrochemical production activities that have not been included in these estimates.

The preliminary results of the quantitative uncertainty analysis (see Table 4-46) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 1.4 to 1.6 Tg CO_2 Eq. (or that the actual CH_4 emissions are likely to fall within the range of approximately 7 percent below and 8 percent above the emission estimate of 1.5 Tg CO_2 Eq.).

Table 4-46: Quantitative Uncertainty Estimates for CH_4 Emissions from Petrochemical Production (Tg CO_2 Eq. and Percent)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Petrochemical Production	CH_4	1.5	1.4	1.6	-7%	+8%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

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[12] The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be ethylene dichloride ($C_2H_4Cl_2$) rather than dichloroethylene ($C_2H_2Cl_2$).

Recalculations Discussion

The estimates of petrochemical emissions for 2000 and 2001 have been revised due to methanol production modifications in the Guide to the Business of Chemistry 2002. Historical data for methanol production in 2000 decreased from 5,221 thousand metric tons to 4,876; methanol production for 2001 also decreased from 5,053 to 3,402 thousand metric tons. These changes resulted in a decrease of less than one percent and four percent of total petrochemical emissions for 2000 and 2001, respectively.

4.12. Silicon Carbide Production (IPCC Source Category 2B4)

Methane is emitted from the production of silicon carbide, a material used as an industrial abrasive. To make silicon carbide (SiC), quartz (SiO_2) is reacted with carbon in the form of petroleum coke. Methane is produced during this reaction from volatile compounds in the petroleum coke. Although CO_2 is also emitted from this production process, the requisite data were unavailable for these calculations. However, emissions associated with the utilization of petroleum coke in this process are accounted for under the Non-Energy Uses of Fossil Fuel section of the Energy chapter. Emissions of CH_4 from silicon carbide production in 2002 were 0.3 Gg CH_4 (0.01 Tg CO_2 Eq.) (see Table 4-47).

Table 4-47: CH_4 Emissions from Silicon Carbide Production

Year	Tg CO_2 Eq.	Gg
1990	+	1
1996	+	1
1997	+	1
1998	+	1
1999	+	1
2000	+	1
2001	+	+
2002	+	+

+ Does not exceed 0.05 Tg CO_2 Eq. or 0.5 Gg

Methodology

Emissions of CH_4 were calculated by multiplying annual silicon carbide production by an emission factor (11.6 kg CH_4/metric ton silicon carbide). This emission factor was derived empirically from measurements taken at Norwegian silicon carbide plants (IPCC/UNEP/OECD/IEA 1997).

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 2002 (see Table 4-48) 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, 2002, 2003).

Table 4-48: 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
2001	40,000
2002	30,000

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.

4.13. Nitric Acid Production (IPCC Source Category 2B2)

Nitric acid (HNO_3) 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, N_2O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for NO and NO_2 (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 effective at destroying N_2O. 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. Approximately 20 percent of 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 N_2O emissions.

Nitrous oxide emissions from this source were estimated at 16.7 Tg CO_2 Eq. (54.0 Gg) in 2002 (see Table 4-49). Emissions from nitric acid production have decreased 6.2 percent since 1990, with the trend in the time series closely tracking the changes in production.

Table 4-49: N_2O Emissions from Nitric Acid Production

Year	Tg CO$_2$ Eq.	Gg
1990	17.8	57.6
1996	20.7	66.8
1997	21.2	68.4
1998	20.9	67.4
1999	20.1	64.9
2000	19.6	63.2
2001	15.9	51.3
2002	16.7	54.0

Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of N_2O emitted per unit of nitric acid produced. The emissions factor was determined as a weighted average of 2 kg N_2O / metric ton HNO_3 for plants using non-selective catalytic reduction (NSCR) systems and 9.5 kg N_2O / metric ton HNO_3 for plants not equipped with NSCR (Choe et al. 1993). In the process of destroying NO_x, NSCR systems destroy 80 to 90 percent of the N_2O, which is accounted for in the emission factor of 2 kg N_2O / metric ton HNO_3. An estimated 20 percent of HNO_3 plants in the United States are equipped with NSCR (Choe et al. 1993). Hence, the emission factor is equal to $(9.5 \times 0.80) + (2 \times 0.20) = 8$ kg N_2O per metric ton HNO_3.

Nitric acid production data for 1990 (see Table 4-50) was obtained from *Chemical and Engineering News*, "Facts and Figures" (C&EN 2001). Nitric acid production data for 1991 through 1999 (see Table 4-50) were obtained from *Chemical and Engineering News*, "Facts and Figures" (C&EN 2002). Nitric acid production data for 2000

through 2002 were obtained from *Chemical and Engineering News*, "Facts and Figures" (C&EN 2003). The emission factor range was taken from Choe et al. (1993).

Table 4-50: Nitric Acid Production

Year	Thousand Metric Tons
1990	7,196
1991	7,191
1992	7,379
1993	7,486
1994	7,904
1995	8,018
1996	8,349
1997	8,556
1998	8,421
1999	8,113
2000	7,898
2001	6,416
2002	6,752

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 quantity 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. The uncertainty for nitric acid production was assumed to be ±10 percent. The emissions factor accounts for emissions from plants with and without NSCR. Assuming a ±10 percent uncertainty for both the percentage of NSCR and non-NSCR plants and a ±10 percent uncertainty for the associated emissions from each type of plant, results in an overall ±13 percent uncertainty in the emissions factor. Using these uncertainty estimates and a Tier 1 analysis results in an uncertainty of 17 percent for emissions from nitric acid production (see Table 4-51).

Table 4-51: Quantitative Uncertainty Estimates for N_2O Emissions from Nitric Acid Production (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Nitric Acid Production	N_2O	16.7	17%	13.9	19.6

QA/QC and Verification

An IPCC Tier 1 level QA/QC verification was performed. This process resulted in the creation of a mechanism to track production and emissions values from past reporting years.

Recalculations Discussion

The nitric acid production values for 2000 to 2001 were updated. These changes resulted in a 3 percent increase in 2000 production and emissions and a 10 percent decrease in 2001 production and emissions.

Planned Improvements

Planned improvements are focused on assessing the plant-by-plant implementation of NO_x abatement technologies to more accurately match plant production capacities to appropriate emission factors, instead of using a national

profiling of abatement implementation. Also, any large scale updates to abatement configurations would be useful in revising the national profile.

4.14. Adipic Acid Production (IPCC Source Category 2B3)

Adipic acid production is an anthropogenic source of N_2O emissions. Worldwide, few adipic acid plants exist. The United States is the major producer with three companies in four locations accounting for approximately one-third 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. Food grade adipic acid is also used to provide some foods with a "tangy" flavor (Thiemems and Trogler 1991). Approximately 90 percent of all adipic acid produced in the United States is used in the production of nylon 6,6 (CMR 2001).

Adipic acid is produced through a two-stage process during which N_2O 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 (Thiemens and Trogler 1991). Process emissions from the production of adipic acid 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 N_2O abatement technologies in place and as of 1998, the three major adipic acid production facilities had control systems in place.[13] Only one small plant, representing approximately two percent of production, does not control for N_2O (Reimer 1999).

Nitrous oxide emissions from this source were estimated to be 5.9 Tg CO_2 Eq. (19.0 Gg) in 2002 (see Table 4-52).

Table 4-52: N_2O Emissions from Adipic Acid Production

Year	Tg CO_2 Eq.	Gg
1990	15.2	49.0
1996	17.0	55.0
1997	10.3	33.3
1998	6.0	19.3
1999	5.5	17.7
2000	6.0	19.5
2001	4.9	15.9
2002	5.9	19.0

National adipic acid production has increased by approximately 25 percent over the period of 1990 through 2002, to approximately 0.9 million metric tons. At the same time, emissions have been significantly reduced due to the widespread installation of pollution control measures.

Methodology

For two production plants, 1990 to 2002 emission estimates were obtained directly from the plant engineer and account for reductions due to control systems in place at these plants during the time series. For the other two plants, N_2O emissions were calculated by multiplying adipic acid production by the ratio of N_2O emitted per unit of adipic acid produced and adjusting for the actual percentage of N_2O released as a result of plant-specific emission controls. On the basis of experiments (Thiemens and Trogler 1991), the overall reaction stoichiometry for N_2O

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[13]During 1997, the N_2O emission controls installed by the third plant operated for approximately a quarter of the year.

production in the preparation of adipic acid was estimated at approximately 0.3 mt of N_2O per metric ton of product. Emissions are estimated using the following equation:

N_2O emissions = [production of adipic acid (mt of adipic acid)] $\times$ [0.3 mt N_2O / mt adipic acid] $\times$ [1 – (N_2O

destruction factor $\times$ abatement system utility factor)]

The "N_2O destruction factor" represents the percentage of N_2O emissions that are destroyed by the installed abatement technology. The "abatement system utility factor" represents the percentage of time that the abatement equipment operates during the annual production period. Overall, in the United States, two of the plants employ catalytic destruction, one plant employs thermal destruction, and the smallest plant uses no N_2O abatement equipment. The N_2O 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).

National adipic acid production data (see Table 4-53) for 1990 through 2002 were obtained from the American Chemistry Council (ACC 2002). Plant capacity data for 1990 through 1994 were obtained from *Chemical and Engineering News*, "Facts and Figures" and "Production of Top 50 Chemicals" (C&EN 1992, 1993, 1994, 1995). Plant capacity data for 1995 and 1996 were kept the same as 1994 data. The 1997 plant capacity data were taken from *Chemical Market Reporter* "Chemical Profile: Adipic Acid" (CMR 1998). The 1998 plant capacity data for all four plants and 1999 plant capacity data for three of the plants were obtained from *Chemical Week,* Product focus: adipic acid/adiponitrile (CW 1999). Plant capacity data for 2000 for three of the plants were updated using *Chemical Market Reporter*, "Chemical Profile: Adipic Acid" (CMR 2001). For 2001 and 2002, the plant capacity for these three plants were kept the same as the year 2000 capacity. Plant capacity data for 1999 to 2002 for the one remaining plant was kept the same as 1998. The emission factor was based on Thiemens and Trogler (1991). The national production and plant capacities were utilized for two of the four plants. Information for the other two plants was obtained directly from the plant engineer (Childs 2002, 2003).

Table 4-53: Adipic Acid Production

Year	Thousand Metric Tons
1990	735
1991	708
1992	724
1993	769
1994	821
1995	830
1996	839
1997	871
1998	862
1999	907
2000	925
2001	835
2002	921

Uncertainty

To calculate emissions for the two plants where emissions were not provided by the plant engineer, production data on a plant-specific basis was needed. However, these production data are considered confidential and were not available from the plants. As a result, plant-specific production figures for the two plants were calculated by allocating national adipic acid production using existing plant capacities. This allocation creates a degree of uncertainty in the adipic acid production data as all plants are assumed to operate at equivalent utilization levels as represented by their capacities. Also, plant capacity reference data is inconsistently available from year to year, which can affect the uncertainty of the allocated production through the time series.

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 N_2O 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.

A 5 percent uncertainty was assumed for the two plants with directly reported emissions. For the remaining two plants, a 20 percent uncertainty was assumed for production. Abatement factor uncertainty for these two plants was based on a 5 percent IPCC estimate for the N_2O destruction factor and an assumed 5 percent uncertainty in the abatement system utility factor (IPCC 2000). These estimates result in an overall abatement uncertainty of 7 percent. Combining this abatement uncertainty with the 10 percent IPCC emissions factor uncertainty results in an overall 12 percent emissions/abatement uncertainty. Combining the 5 percent plant-specific emissions uncertainty and the 20 percent activity and 12 percent emissions/abatement uncertainty for the remaining two plants yields an overall uncertainty for the inventory estimate of 10 percent (see Table 4-54).

Table 4-54: Quantitative Uncertainty Estimates for N_2O Emissions from Adipic Acid Production (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Adipic Acid Production	N_2O	5.9	10%	5.3	6.5

QA/QC and Verification

An IPCC Tier 1 level QA/QC verification was performed. This process resulted in the creation of a mechanism to track production and emissions values from past reporting years. National production values were compared to previous estimates based on alternative data sources, which resulted in order of magnitude verification on the total national levels.

Planned Improvements

Improvement efforts are focused on obtaining direct measurement data from the remaining two plants when and if they become available. If they become available, cross verification with top-down approaches will provide a useful Tier 2 level QA check. Also, additional information on the actual performance of the latest catalytic and thermal abatement equipment at plants with continuous emission monitoring may support the re-evaluation of current default abatement values.

4.15. Substitution of Ozone Depleting Substances (IPCC Source Category 2F)

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used 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.[14] 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 4-55 and Table 4-56.

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[14] [42 U.S.C § 7671, CAA § 601]

Table 4-55: Emissions of HFCs and PFCs from ODS Substitution (Tg CO_2 Eq.)

Gas	1990		1996	1997	1998	1999	2000	2001	2002
HFC-23	+		+	+	+	0.1	0.1	0.1	0.1
HFC-32	+		0.1	0.2	0.3	0.3	0.3	0.3	0.3
HFC-125	+		5.2	7.0	8.8	10.0	11.2	12.3	13.4
HFC-134a	+		24.5	31.4	36.7	42.2	48.0	52.7	56.9
HFC-143a	+		2.0	3.5	5.2	6.6	8.2	10.1	12.2
HFC-236fa	+		+	0.1	0.4	0.9	1.4	1.8	2.1
CF_4	+		+	+	+	+	+	+	+
Others*	0.3		3.1	4.2	5.2	5.7	6.0	6.2	6.6
Total	**0.3**		**35.0**	**46.4**	**56.5**	**65.8**	**75.1**	**83.4**	**91.7**

+ Does not exceed 0.05 Tg CO_2 Eq.
* Others include HFC-152a, HFC-227ea, HFC-245fa, 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 C_6F_{14}.
Note: Totals may not sum due to independent rounding.

Table 4-56: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990		1996	1997	1998	1999	2000	2001	2002
HFC-23	+		2	3	4	5	6	7	8
HFC-32	+		139	289	430	439	441	459	492
HFC-125	+		1,868	2,516	3,134	3,571	4,004	4,385	4,777
HFC-134a	+		18,870	24,136	28,202	32,491	36,888	40,512	43,798
HFC-143a	+		531	926	1,369	1,738	2,162	2,647	3,203
HFC-236fa	+		+	9	64	142	214	281	341
CF_4	+		+	+	1	1	1	1	2
Others*	M		M	M	M	M	M	M	M

M (Mixture of Gases)
+ Does not exceed 0.5 Mg
* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

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.[15] 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 91.7 Tg CO_2 Eq. in 2002. 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.

[15] R-404A contains HFC-125, HFC-143a, and HFC-134a.

Methodology

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 3.8.

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.

The Vintaging Model estimates emissions from over 40 end-uses, but the uncertainty estimation was performed on only the top 14 end-uses, which account for 95 percent of emissions from this source category. In order to calculate uncertainty, functional forms were developed to simplify some of the complex "vintaging" aspects of some end-use sectors, especially with respect to refrigeration and air-conditioning, and to a lesser degree, fire extinguishing. These sectors calculate emissions based on the entire lifetime of equipment, not just equipment put into commission in the current year, which necessitated these simplifying equations. The functional forms used variables that included growth rates, emission factors, transition from ODSs, change in charge size as a result of the transition, disposal quantities, disposal emission rates, and either stock for the current year or original ODS consumption. Uncertainty was estimated around each variable within the functional forms based on expert judgment, and a Monte Carlo analysis was performed.

The preliminary results of the quantitative uncertainty analysis (see Table 4-57) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 90.7 to 116.5 Tg CO_2 Eq. (or that the actual HFC and PFC emissions are likely to fall within the range of approximately 1 percent below and 27 percent above the emission estimate of 91.7 Tg CO_2 Eq.).

Table 4-57: Quantitative Uncertainty Estimates for HFC and PFC Emissions from ODS Substitution (Tg CO_2 Eq. and Percent)

Source	Gases	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Substitution of Ozone Depleting Substances	HFC and PFC	91.7	90.7	116.5	-1%	+27%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Recalculations Discussion

An extensive review of the chemical substitution trends, market sizes, growth rates, and charge sizes, together with input from industry representatives, resulted in updated assumptions for the Vintaging Model. Additionally, a new

version of the Vintaging Model was developed for this Inventory year. This model incorporated improvements to the emission estimating methodologies, differences in charge sizes between original chemicals and substitutes, and improvements to the way retrofits and recovery and recycling are accounted for. These changes resulted in an average annual increase of 6.7 Tg CO_2 Eq. (9.1 percent) in HFC and PFC emissions for the period 1990 through 2001.

4.16. HCFC-22 Production (IPCC Source Category 2E1)

Trifluoromethane (HFC-23 or CHF_3) 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.[16] Feedstock production, however, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform ($CHCl_3$) and hydrogen fluoride (HF) in the presence of a catalyst, $SbCl_5$. 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 ($CHCl_2F$), HCFC-22 ($CHClF_2$), HFC-23 (CHF_3), 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.

Emissions of HFC-23 in 2002 were estimated to be 19.8 Tg CO_2 Eq. (1.7 Gg). This quantity is the same as the quantity of emissions in 2001, and represents a 43 percent decrease from emissions in 1990 (see Table 4-58). Although HCFC-22 production has increased by 4 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 46 percent over the same period, lowering emissions. Three HCFC-22 production plants operated in the United States in 2002, two of which used thermal oxidation to significantly lower (and in at least one case, virtually eliminate) their HFC-23 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.

Table 4-58: HFC-23 Emissions from HCFC-22 Production

Year	Tg CO$_2$ Eq.	Gg
1990	35.0	3.0
1996	31.1	2.7
1997	30.0	2.6
1998	40.2	3.4
1999	30.4	2.6
2000	29.8	2.5
2001	19.8	1.7

[16] 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]

| 2002 | 19.8 | 1.7 |

Methodology

The methodology employed for estimating emissions is based upon measurements at individual HCFC-22 production plants. Plants using thermal oxidation to abate their HFC-23 emissions monitor the performance of their oxidizers to verify that the HFC-23 is almost completely destroyed. The other plants periodically measure HFC-23 concentrations in the output stream using gas chromatography. This information is combined with information on quantities of critical feed components (e.g., HF) and/or products (HCFC-22) to estimate HFC-23 emissions using a material balance approach. HFC-23 concentrations are determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Production data and emission estimates were prepared in cooperation with the U.S. manufacturers of HCFC-22 (ARAP 2003). Annual estimates of U.S. HCFC-22 production are presented in Table 4-59.

Table 4-59: 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
2001	152.4
2002	144.2

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. Reported emissions are roughly within 10 percent of the true value (see Table 4-60). 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.

Table 4-60: Quantitative Uncertainty Estimates for HFC-23 Emissions from HCFC-22 Production (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
HCFC-22 Production	HFC-23	19.8	10%	17.8	21.8

4.17. Electrical Transmission and Distribution (IPCC Source Category 2F7)

Sulfur hexafluoride's largest use, both domestically and internationally, is as an electrical insulator and interrupter in equipment that transmits and distributes electricity (RAND 2002). 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 SF_6 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 SF_6 to the atmosphere during servicing and disposal; however, increased awareness and the relatively high cost of the gas have reduced this practice.

Emissions of SF_6 from electrical transmission and distribution systems were estimated to be 14.8 Tg CO_2 Eq. (0.6 Gg) in 2002. This quantity represents a 49 percent decrease below the estimate for 1990 (see Table 4-61 and Table 4-62). This decrease, which is reflected in the atmospheric record, is believed to be a response to increases in the price of SF_6 and to growing awareness of the environmental impact of SF_6 emissions.

Table 4-61: SF_6 Emissions from Electric Power Systems and Original Equipment Manufactures (Tg CO_2 Eq.)

Year	Electric Power Systems	Original Equipment Manufactures	Total
1990	28.9	0.3	**29.2**
1996	23.8	0.4	**24.3**
1997	21.3	0.3	**21.7**
1998	16.7	0.4	**17.1**
1999	15.8	0.6	**16.4**
2000	15.2	0.7	**15.9**
2001	14.9	0.7	**15.6**
2002	14.1	0.7	**14.8**

Table 4-62: SF_6 Emissions from Electric Power Systems and Original Equipment Manufactures (Gg)

Year	Total
1990	1.2
1996	1.0
1997	0.9
1998	0.7
1999	0.7
2000	0.7
2001	0.7
2002	0.6

Methodology

The 2002 estimate of SF_6 emissions from electrical equipment (14.8 Tg CO_2 Eq.) is comprised of (1) estimated emissions of approximately 14.1 Tg CO_2 Eq. from U.S. electric power systems, and (2) estimated emissions of approximately 0.7 Tg CO_2 Eq. from U.S. electrical equipment manufacturers (original equipment manufacturers, or OEMs). The 2002 estimate of emissions from electric power systems is based on the reported 2002 emissions (5.2 Tg CO_2 Eq.) of participating utilities in EPA's SF_6 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 analysis further showed that the relationship between emissions and transmission miles differed for facilities with less or more than 10,000 miles. Therefore two regression equations were developed for small plants (with less than 10,000 miles of transmission lines) and large facilities (with 10,000 miles or more of transmission lines).

For 1999, the following regression equations were developed based on SF_6 emissions reported by 49 partner utilities (representing approximately 45 percent of U.S. net generation):

Small utilities (less than 10,000 transmission miles, 1999, in kilograms):

$$\text{Emissions} = 0.874 \times \text{Transmission Miles}$$

Large utilities (more than 10,000 transmission miles, 1999, in kilograms):

$$\text{Emissions} = 0.558 \times \text{Transmission Miles}$$

These regression equations were used to determine 1999 SF_6 emissions from both the non-reporting partner utilities and the non-partner utilities. Extrapolating the equations above, SF_6 emissions were estimated for the non-reporting partner utilities and the non-partner utilities. The results of the extrapolation were added to the emissions reported by partner utilities to estimate that U.S. electric power systems emitted a total of 660,000 kg of SF_6 (15.8 Tg CO_2 Eq.) in 1999.

The estimate of 2000 emissions was developed similarly. Fifty partners reported emissions totaling 264,600 kg of SF_6, or 6.3 Tg CO_2 Eq. Because it appeared that partners had significantly reduced their emission rate from the previous year, a statistical analysis of the trend in emissions between 1999 and 2000 was performed. This analysis showed that the downward trend was statistically significant (at a 95 percent confidence level), and new regression equations were developed to extrapolate 2000 partner-reported emissions to non-reporting partners. This approach was selected because it was assumed that the emission trends of the non-reporting partners would be similar to those of the reporting partners, because all partners commit to reducing SF_6 emissions through technically and economically feasible means. However, non-partners were assumed to have implemented no changes that would have reduced emissions over the previous year. Hence, the 1999 regression equation was used to determine SF_6 emissions from non-partners. Total 2000 emissions were then determined by summing the partner-reported emissions, the non-reporting partner emissions (determined with the 2000 regression equation) and the non-partner emissions (determined using the 1999 regression equation). Using this approach, total 2000 emissions from electric power systems were estimated to be 635,300 kg of SF_6 (15.2 Tg CO_2 Eq.).

The approach used to determine the 2000 emissions was applied in subsequent years (i.e., new regression equations were developed using partner-reported emissions and miles and extrapolated to non-reporting partners; and the 1999 regression equations are applied to the non-partners). The 2002 regression equations used to estimate non-reporting partner emissions were:

Small utilities (less than 10,000 transmission miles, 2002, in kilograms):

$$\text{Emissions} = 0.598 \times \text{Transmission Miles}$$

Large utilities (more than 10,000 transmission miles, 2002, in kilograms):

$$\text{Emissions} = 0.40 \times \text{Transmission Miles}$$

Using this approach, total 2002 emissions from electric power systems were estimated to be 588,900 kg of SF_6 (14.1 Tg CO_2 Eq.).

The 2002 emissions estimate for OEMs (0.7 Tg CO_2 Eq.) was derived by assuming that manufacturing emissions equal 10 percent of the quantity of SF_6 charged into new equipment. The quantity of SF_6 charged into new equipment was estimated based on statistics compiled by the National Electrical Manufacturers Association (NEMA). The 10 percent emission rate is the average of the "ideal" and "realistic" manufacturing emission rates (4 percent and 17 percent, respectively) identified in a paper prepared under the auspices of the International Council on Large Electric Systems (CIGRE) in February 2002 (O'Connell, et al., 2002). Emissions for 1999 through 2001 were estimated similarly.

Because most participating utilities reported emissions only for 1999 through 2002, it was necessary to model SF_6 emissions from electric power systems for the years 1990 through 1998. To do so, it was assumed that during this period, U.S. emissions from this source followed the same trajectory as global emissions from this source. To estimate global emissions, the RAND survey of global SF_6 sales to electric utilities was used, together with the

following equation, which is derived from the equation for emissions in the IPCC report, *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2000):

$$\text{Emissions} = SF_6 \text{ purchased to refill existing equipment} + \text{nameplate capacity of retiring equipment}$$

Note that the above equation holds whether the gas from retiring equipment is released or recaptured; if the gas is recaptured, it is used to refill existing equipment, lowering the amount of SF_6 purchased by utilities for this purpose.

It was assumed that the SF_6 used to refill existing equipment in a given year approximately equaled the SF_6 purchased by utilities in that year. Nameplate capacity of retiring equipment in a given year was assumed to equal 77.5 percent of the amount of gas purchased by electrical equipment manufacturers 30 years previous. The remaining 22.5 percent was assumed to have been emitted at the time of manufacture. These results were then summed to yield estimates of global SF_6 emissions from 1990 through 1998. Gas purchases by utilities and equipment manufacturers from 1961 through 2001 are available from the RAND (2002) survey. It was assumed that SF_6 purchases were strongly related to emissions. The 22.5 percent emission rate is an average of IPCC SF_6 emission rates for Europe and Japan for years before 1996 (IPCC 2000). The 30-year lifetime for electrical equipment is also drawn from IPCC (2000).

To estimate U.S. emissions for 1990 through 1998, estimated global emissions for each year from 1990 through 1998 were divided by the estimated global emissions 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 SF_6 from electric power systems in 1999 (estimated to be 15.8 Tg CO_2 Eq.) to estimate U.S. emissions of SF_6 from electrical equipment in that year. This yielded a time series that was related to statistics for both SF_6 emissions and SF_6 sales. Emissions from OEMs were estimated for 1990 through 1998 using OEM statistics for this period.

Uncertainty

Using IPCC Good Practice Guidance Tier 1 methodology, the overall uncertainty associated with the 1999 through 2002 SF_6 emission estimates from the electric transmission and distribution is estimated to be ±13 percent (see Table 4-63). This estimate incorporates uncertainties associated with SF_6 emissions from electric power systems of ±13 percent, and SF_6 emissions from OEMs of ±66 percent. For electric power systems, the regression equations used to extrapolate U.S. emissions from participant reports have a variance (at the 95 percent confidence level) of ±2 Tg CO_2 Eq. for 1999 through 2002. In addition, emission rates for utilities that were not participants, which accounted for approximately 65 percent of U.S. transmission miles, may differ from those that were participants. There is uncertainty in using global sales data to extrapolate 1990 through 1998 emissions from 1999 emissions; however, global sales of SF_6 appear to closely reflect global emissions. That is, global sales declined by 24 percent between 1995 and 1998, while atmospheric measurements indicate that world emissions of SF_6 declined by 27 percent during the same period. However, U.S. emission patterns may differ from global emission patterns. For OEMs, uncertainty estimates are based on the assumption that SF_6 statistics obtained from NEMA have an uncertainty of 10 percent. Additionally, the OEMs SF_6 emissions rate has an uncertainty bounded by the proposed "actual" and "ideal" emission rates defined in O'Connell, et al. (2002). That is, the uncertainty in the emission rate is approximately 65 percent.

Table 4-63: Quantitative Uncertainty Estimates for SF_6 Emissions from Electrical Transmission and Distribution (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Electrical Transmission and Distribution	SF_6	14.8	13%	12.8	16.7

Recalculations Discussion

The methodology and activity data used for estimating 1990 through 1998 emissions have been updated relative to the previous inventory. As in previous inventories, U.S. SF_6 emissions from utilities are assumed to have followed the trend of global SF_6 emissions from utilities during this period. However, the method for estimating global emissions now accounts for SF_6 that is recaptured and/or released from retiring equipment, rather than assuming that global emissions are equal to global sales of SF_6 to electric utilities. With this new methodology, global emissions are estimated to equal the sum of global sales to electric utilities and 77.5 percent of the global sales to manufacturers of electrical equipment 30 years previous. The remaining 22.5 percent is assumed to have been emitted at the time of equipment manufacture. In addition to this methodological change, the revised estimates reflect a more recent (2002) version of the RAND survey of SF_6 manufacturers. For 1990, emission estimates from electric power systems have decreased from 32.1 Tg CO_2 Eq. to 29.2 Tg CO_2 Eq., while for 1998, estimates decreased from 20.9 Tg CO_2 Eq. to 17.1 Tg CO_2 Eq.

Additionally, electric power system emission estimates for 2000 and 2001 were recalculated using additional data that partners submitted subsequent to the publication of the previous inventory. Using these additional submissions, the regression equations were updated and new extrapolations to non-reporting partners were made. Following this recalculation, 2000 and 2001 SF_6 emissions from electric power systems increased slightly from 15.4 Tg CO_2 Eq. to 15.6 Tg CO_2 Eq., and 15.3 Tg CO_2 Eq. to 14.8 Tg CO_2 Eq., respectively.

Planned Improvements

Currently, there are over 70 companies in EPA's SF_6 Emissions Reduction Partnership for Electric Power Systems; however, not all of these report every year. As companies report emissions data to fill in their historical data gaps, regression equations will need to be revised to reflect the new information. This will result in a change to prior reported emission estimates, but will lead to a reduction in the uncertainty of the value.

4.18. Aluminum Production (IPCC Source Category 2C3)

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 2002, the United States was the third largest producer of primary aluminum, with 11 percent of the world total (USGS 2003). 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 CO_2 and two perfluorocarbons (PFCs): perfluoromethane (CF_4) and perfluoroethane (C_2F_6).

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al_2O_3) 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 (Na_3AlF_6). 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 CO_2.

Process emissions of CO_2 from aluminum production were estimated at 4.2 Tg CO_2 Eq. (4,223 Gg) in 2002 (see Table 4-64). The carbon anodes consumed during aluminum production consist of petroleum coke and, to a minor extent, coal tar pitch. The petroleum coke portion of the total CO_2 process emissions from aluminum production is considered to be a non-energy use of petroleum coke, and is accounted for here and not with Fossil Fuel Combustion emissions in the Energy chapter. Similarly, the coal tar pitch portion of these CO_2 process emissions is accounted for here rather than in the Iron and Steel section, where it would otherwise be counted.

Table 4-64: CO_2 Emissions from Aluminum Production

Year	Tg CO_2 Eq.	Gg
1990	6.3	6,315

1996	5.6	5,580
1997	5.6	5,621
1998	5.8	5,792
1999	5.9	5,895
2000	5.7	5,723
2001	4.1	4,114
2002	4.2	4,223

In addition to CO_2 emissions, the aluminum production industry is also a source of PFC emissions. 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 CF_4 and C_2F_6. In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. As the anode effects become longer and more frequent, a corresponding rise in emission levels occurs.

Primary aluminum production-related emissions of PFCs are estimated to have declined 71 percent since 1990. Since 1990, emissions of CF_4 and C_2F_6 have each declined 71 percent to 4.5 Tg CO_2 Eq. of CF_4 (0.7 Gg) and 0.7 Tg CO_2 Eq. of C_2F_6 (0.1 Gg) in 2002, as shown in Table 4-65 and Table 4-66. 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 4-65: PFC Emissions from Aluminum Production (Tg CO_2 Eq.)

Year	CF_4	C_2F_6	Total
1990	15.8	2.3	18.1
1996	11.1	1.4	12.5
1997	9.8	1.2	11.0
1998	8.1	1.0	9.0
1999	8.0	0.9	8.9
2000	8.0	0.9	8.9
2001	3.5	0.5	4.0
2002	4.5	0.7	5.2

Note: Totals may not sum due to independent rounding.

Table 4-66: PFC Emissions from Aluminum Production (Gg)

Year	CF_4	C_2F_6
1990	2.4	0.2
1996	1.7	0.1
1997	1.5	0.1
1998	1.2	0.1
1999	1.2	0.1
2000	1.2	0.1
2001	0.5	0.1
2002	0.7	0.1

U.S. primary aluminum production for 2002—totaling 2,700 thousand metric tons—increased by 3 percent from 2001. Due to high electric power costs in various regions of the country, aluminum production has been curtailed at several U.S. smelters resulting in current production levels being nearly 26 percent lower than 2000 levels. The transportation industry remained the largest domestic consumer of aluminum, accounting for about 34 percent (USGS 2003).

Methodology

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

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$
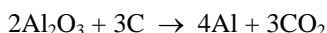
The CO_2 emission factor employed was estimated from the production of primary aluminum metal and the carbon consumed by the process. Emissions vary depending on the specific technology used by each plant (e.g., Prebake or Soderberg). The *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) provide CO_2 emission factors for each technology type. During alumina reduction in a prebake anode cell process, approximately 1.5 metric tons of CO_2 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 CO_2 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, production was assumed to be 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:

$$PFC\ (CF_4\ or\ C_2F_6)\ kg/metric\ ton\ Al = S \times Anode\ Effect\ Minutes/Cell\text{-}Day$$

where,

      S = Slope coefficient
      Anode Effect Minutes/Cell-Day = Anode Effect Frequency $\times$ Anode Effect Duration

For 9 out of the 23 U.S. smelters, smelter-specific slope coefficients based on field measurements have been used to develop PFC estimates. In 2002, only 3 out of the 16 operating smelters use smelter-specific slope coefficients. For the remaining smelters, technology-specific slope coefficients from *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2000) were applied. The slope coefficients were combined with smelter-specific anode effect data, collected by aluminum companies and reported to the VAIP, to estimate emission factors over time. Where smelter-specific anode effect data were not available between 1990 and 2001 (2 out of 23 smelters), industry averages were used. Emission factors were multiplied by annual production to estimate annual emissions at the smelter level. In 2002, smelter-specific production data was available for 14 of the 16 operating smelters; production at one of the remaining smelters was estimated based on national aluminum production and capacity data (USGS), and the other one was held constant at 2001 levels. Between 1990 and 2001, production data has been provided by 21 of the 23 U.S. smelters; however, the specific number has varied by year based on smelter-specific data availability or production curtailment. 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).

National primary aluminum production data for 1990 through 1999 and 2001 (see Table 4-67) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000, 2001, 2002). The USGS requested data from the 11 domestic producers, all of whom responded. Primary aluminum production data for 2000 were obtained by using information from VAIP program submittals and from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 2001). Comparing a subset of smelter specific production data from VAIP submittals and the USGS *Mineral Industry Surveys: Aluminum Annual Report* (USGS 2001), it was observed that in 2000, 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 for 2000. This shortfall is again observed for 2002, and again the VAIP data were used.

The CO_2 emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). PFC emission estimates were provided by aluminum smelters participating in the VAIP program. Where smelter-

specific operational data were not available (i.e., aluminum production, slope coefficients, and anode effect data), estimates were drawn from other sources. For aluminum production data, estimates were developed based on smelter-specific production capacities, as reported by USGS. Default 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).

Table 4-67: 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	3,668
2001	2,637
2002	2,707

Uncertainty

Carbon dioxide emissions vary depending on the specific technology used by each plant. A more accurate method would be to calculate CO_2 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.

The preliminary results of the quantitative uncertainty analysis (see Table 4-68) indicate that, on average, in 19 out of 20 times (i.e., there is a 95 percent probability), the total greenhouse gas emissions estimate from this source is within the range of approximately 3.3 to 5.1 Tg CO_2 Eq. (or that the actual CO_2 emissions are likely to fall within the range of approximately 23 percent below and 21 percent above the emission estimate of 4.2 Tg CO_2 Eq.).

Table 4-68: Quantitative Uncertainty Estimates for CO_2 Emissions from Aluminum Production (Tg CO_2 Eq.)

Source	Gas	2002 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Aluminum Production	CO_2	4.2	3.3	5.1	-23%	+21%

[a] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95% confidence interval.

Using IPCC Good Practice Guidance Tier 1 methodology, the overall uncertainty associated with the 2002 CF_4 and C_2F_6 emission estimates is ±12 and ±19 percent, respectively (see Table 4-69). For the 2001 estimates, the uncertainty was estimated to be ±16 percent ±18 percent, respectively; and for 1990, the corresponding uncertainties are ±8 percent and ±10 percent, respectively. For each smelter, uncertainty associated with the quantity of aluminum produced, the frequency and duration of anode effects, and the slope factor was estimated. Error propagation analysis was then applied to estimate the overall uncertainty of the emissions estimate for each smelter and for the U.S. aluminum industry as a whole. The uncertainty of aluminum production estimates ranged between 1 percent and 25 percent, depending on whether a smelter's production was reported or estimated. The uncertainty of the frequency and duration of anode effects ranged between 2 percent and 78 percent, depending on whether these parameters were reported or were estimated using industry-wide averages. Given the limited uncertainty data

on site-specific slope coefficients (i.e., those developed using IPCC Tier 3b methodology), it was assumed that the overall uncertainty associated with the slope coefficients would be similar to that given by the IPCC guidance for technology-specific slope coefficients. Consequently, the uncertainty assigned to the slope coefficients ranged between 7 percent and 35 percent, depending upon the gas and the smelter technology type. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

Table 4-69: Quantitative Uncertainty Estimates for PFC Emissions from Aluminum Production (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Aluminum Production	CF_4	4.5	12%	4.0	5.1
Aluminum Production	C_2F_6	0.7	19%	0.6	0.8

Occasionally, SF_6 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, SF_6 is mixed with nitrogen or CO_2 and injected above the surface of molten aluminum; as a fluxing and degassing agent, SF_6 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 metric tons of SF_6 per year (Maiss and Brenninkmeijer 1998); however, this estimate is highly uncertain.

Historically, SF_6 from aluminum activities has been omitted from estimates of global SF_6 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 SF_6 in the mixtures is small and a portion of the SF_6 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 SF_6 from aluminum fluxing and degassing have not been estimated. Uncertainties exist as to the quantity of SF_6 used by the aluminum industry and its rate of destruction in its uses as a degassing agent or cover gas.

Recalculations Discussion

The smelter-specific emission factors used for estimating PFC emissions, as well as aluminum production levels, were revised to reflect recently reported data concerning smelter operating parameters. These data were provided in cooperation with participants in the VAIP program. These revisions resulted in a reduction of total PFC emissions of approximately 1 percent for the years 1990 through 1994, as well as an increase in total PFC emissions by 12 percent for 2000, and a decrease in total PFC emissions by 4 percent 2001.

Planned Improvements

A measurement study is currently taking place at three U.S. aluminum smelters to develop facility-specific slope coefficients. Consequently, use of these coefficients, instead of IPCC defaults, will enable the calculation of more accurate PFC emission estimates from these facilities.

4.19. Semiconductor Manufacture (IPCC Source Category 2F6)

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 (c-C_4F_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 2002, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 4.4 Tg CO_2 Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 4-70 and Table 4-71 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 52 percent since 1990. However, the growth rate in emissions began to slow in 1997, and emissions declined by 40 percent between 1999 and 2002. This decline is due both to a drop in production (with a continuing decline in silicon consumption) and to the initial implementation of PFC emission reduction methods, such as process optimization.

Table 4-70: PFC, HFC, and SF_6 Emissions from Semiconductor Manufacture (Tg CO_2 Eq.)

Year	1990		1996	1997	1998	1999	2000	2001	2002
CF_4	0.7		1.4	1.6	1.8	1.8	1.8	1.3	1.1
C_2F_6	1.5		2.8	3.2	3.6	3.7	3.0	2.1	2.2
C_3F_8	0.0		0.0	0.0	0.0	0.0	0.1	0.1	0.1
C_4F_8	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
HFC-23	0.2		0.3	0.4	0.4	0.4	0.3	0.2	0.2
SF_6	0.5		1.0	1.1	1.3	1.3	1.1	0.8	0.7
NF_3*	0.0		0.1	0.1	0.1	0.1	0.1	0.1	0.3
Total	**2.9**		**5.5**	**6.3**	**7.1**	**7.2**	**6.3**	**4.5**	**4.4**

Note: Totals may not sum due to independent rounding.
* NF_3 emissions are presented for informational purposes, using a GWP of 8,000, and are not included in totals.

Table 4-71: PFC, HFC, and SF_6 Emissions from Semiconductor Manufacture (Mg)

Year	1990		1996	1997	1998	1999	2000	2001	2002
CF_4	115		214	245	277	281	281	202	175
C_2F_6	160		302	347	391	397	324	231	244
C_3F_8	0		0	0	0	0	17	14	9
C_4F_8	0		0	0	0	0	0	0	5
HFC-23	15		29	33	37	37	23	16	15
SF_6	22		42	48	54	55	46	31	28
NF_3	3		7	8	9	9	11	12	32

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 Reduction/Climate 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 GWPs.

For 1995 through 1999, total U.S. emissions were extrapolated from the total annual emissions reported by the partnership participants. The emissions reported by the participants were divided by the ratio of the total layer-weighted capacity of the plants operated by the participants and the total layer-weighted capacity of all of the semiconductor plants in the United States; this ratio represents the share of layer-weighted capacity attributable to partnership 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.

The U.S. estimate for the years 2000 through 2002—the period during which partners began the consequential application of PFC-reduction measures—used a different estimation method. The emissions reporting by partnership participants for each year were accepted as the quantity emitted from the corresponding share of the industry. Remaining emissions (those from non-partners), however, were estimated using EPA's PFC Emissions Vintage Model (PEVM). PEVM provides, among other things, estimates of U.S. PFC emissions by year, and assumes no adoption of PFC-reduction measures. The portion of the U.S. total attributed to non-partners is obtained by multiplying PEVM's total U.S. figure by the non-partner share of total layer-weighted silicon capacity for each year (as described above).

Two different approaches were also used to estimate the distribution of emissions of specific PFCs. Before 1999, when there was no consequential adoption of PFC-reducing measures, a fixed distribution was used. This distribution is based upon the average PFC purchases by semiconductor manufacturers during this period and the application of IPCC default emission factors for each gas. For the 2000 through 2002 period, partners' reports of emissions included gas-specific emissions. During this period, the emissions of each gas represents the sum of the portion reported by partners and the portion from non-partners, which is obtained by assuming the distribution for earlier years is applicable.

Participants estimate their emissions using a range of methods. For 2002, most participants cited 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 used to develop emission estimates were prepared in cooperation with the Partnership. 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 2003). Estimates of silicon consumed by line-width from 1990 through 1994 were derived from information from VLSI Research (2003), and the number of layers per line-width was obtained from International SEMATECH's *International Technology Roadmap: 2000 Update.*

Uncertainty

Using IPCC Good Practice Guidance Tier 1 methodology, the overall uncertainty associated with the 2002 emissions estimates is estimated to be ±10 percent (see Table 4-72)

For partnership participants, an uncertainty of 15 percent was assigned to PFC emissions data that they supplied to the partnership. This value accounts for uncertainty in partners' estimates of gas-volume usage. Based on this assumption, the relative error associated with partnership emissions in 2002 is ±7 percent (or ±0.2 Tg CO_2 Eq. of 3.4 Tg CO_2 Eq.). Non-partner emission estimates incorporate uncertainties associated with PEVM emission factors (±30 percent), U.S. silicon consumption estimates (±13 percent), and estimates of non-partner shares of U.S.

manufacturing capacity (±5 percent). Using these data, the relative error associated with non-partner emissions estimates in 2002 is estimated to be ±32 percent (or ±0.4 Tg CO_2 Eq. of 1.2 Tg CO_2 Eq.).

Table 4-72: Quantitative Uncertainty Estimates for HFC, PFC, and SF_6 Emissions from Semiconductor Manufacture (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Semiconductor Manufacture	HFC, PFC, and SF_6	4.4	10%	3.9	4.8

Recalculations Discussion

Emissions estimates reported above reflect several revisions to those figures previously reported. Changes have resulted from updates to EPA's PEVM—the model responsible for estimating non-partner emissions—that incorporate more current reference data (i.e., plant capacities and silicon consumption by line-width), as well as updates to the historical data supplied by several partnership participants. These updates have resulted in an average reduction in emission estimates on the order of 9 percent for the period 1995 through 2001. Additionally, the methodology used to estimate the distribution of historical emissions by gas type has changed. The current estimates use market and confidential gas sales survey information and IPCC emission factors to calculate emissions by gas type.

Planned Improvements

The method by which non-partner related emissions are estimated (PEVM) is not expected to change (with the exception of possible future updates to emission factors and added technology nodes). Future improvements to the national emissions estimates will primarily be associated with determining the portion of national emissions to attribute to partner report totals (currently about 80 percent) and, as the nature of the reports change through time and reduction efforts increase, determining what emission reduction efforts—if any—are assumed to be occurring at non-partner facilities (currently none).

4.20. Magnesium Production and Processing (IPCC Source Category 2C4)

The magnesium metal production and casting industry uses SF_6 as a cover gas to prevent the violent oxidation of molten magnesium in the presence of air. A dilute gaseous mixture of SF_6 with dry air and/or CO_2 is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A minute portion of the SF_6 reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. It is currently assumed that the amount of SF_6 reacting in magnesium production and processing is negligible and thus all SF_6 used is emitted into the atmosphere. Sulfur hexafluoride has been used in this application around the world for the last twenty years. It has largely replaced salt fluxes and SO_2, which are more toxic and corrosive than SF_6.

The magnesium industry emitted 2.4 Tg CO_2 Eq. (0.1 Gg) of SF_6 in 2002 (see Table 4-73). This represents a significant decline from previous years. The decline is attributable to decreased production and casting levels, as well as reductions in SF_6 usage via process optimizations by industry participants in EPA's SF_6 Emission Reduction Partnership for the Magnesium Industry. One of the two remaining U.S. primary producers closed in October 2001. 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.

Table 4-73: SF_6 Emissions from Magnesium Production and Processing

Year	Tg CO_2 Eq.	Gg

1990	5.4	0.2
1996	6.5	0.3
1997	6.3	0.3
1998	5.8	0.2
1999	6.0	0.3
2000	3.2	0.1
2001	2.5	0.1
2002	2.4	0.1

Methodology

Emission estimates for the magnesium industry incorporate information provided by industry participants in EPA's SF_6 Emission Reduction Partnership for the Magnesium Industry. The partnership started in 1999, and currently participating companies represent 100 percent of U.S. primary production and over 80 percent of the casting sector (i.e., die, gravity, wrought and anode casting). Emissions for 1999 through 2002 from primary production, some secondary production, and a large fraction of die casting were reported by participants. The 1999 through 2002 emissions from the remaining secondary production and casting were estimated by multiplying industry emission factors (kg SF_6 per metric ton of Mg produced or processed) by the amount of metal produced or consumed in the five major processes (other than primary production) that require SF_6 melt protection: 1) secondary production; 2) die casting; 3) gravity casting; 4) wrought products; and 5) anodes. The emission factors are provided below in Table 4-74. Because there was only one primary producer in the United States in 2002, the emission factor for primary production is withheld to protect production information. However, the emission factor has not risen above the 1995 value of 1.1 kg SF_6 per metric ton.

Die casting emissions for 1999 through 2002, which is believed to account for about 40 percent of all SF_6 emissions from U.S. casting and recycling processes, were estimated using emission factors derived from information supplied by industry partners. The weighted average 2002 emission factor for die casting was estimated to be 0.71 kg SF_6 per metric ton of magnesium processed. In 2002, it was assumed that partnership participants accounted for a significant proportion of all U.S. die casting. In prior years, when this was not the case, it was assumed that non-participant die casters, were similar to participants who cast small parts. Due to process requirements, it is understood that these casters consume larger quantities of SF_6 per metric ton of processed magnesium compared to those that cast large parts. Consequently, emissions estimates from this group of die casters were developed using an average emission factor of 5.2 kg SF_6 per metric ton of magnesium. The emission factors for the other industry sectors were based on discussions with industry representatives.

Table 4-74: SF_6 Emission Factors (kg SF_6 per metric ton of magnesium)

Year	Secondary	Die Casting[a]	Gravity	Wrought	Anodes
1999	1	2.14	2	1	1
2000	1	0.71	2	1	1
2001	1	0.73	2	1	1
2002	1	0.71	2	1	1

[a] Emission factor only applied to partnership participants; for non-partners, an emission factor of 5.2 kg SF_6 per metric ton of magnesium was used.

Data used to develop these emission estimates were provided in cooperation with the partnership participants and the U.S. Geological Survey (USGS). U.S. magnesium metal production (primary and secondary) and consumption (casting) data from 1990 through 2002 are available from the USGS (USGS 2003). Emission factors from 1990 through 1998 were based on a number of sources. Emission factors for primary production were available from U.S. primary producers for 1994 and 1995, and an emission factor for die casting was available for the mid-1990s from an international survey (Gjestland & Magers 1996).

To estimate emissions for 1990 through 1998, industry emission factors were multiplied by the corresponding metal production and consumption statistics from USGS. The primary production emission factors were 1.1 kg per metric ton in both 1994 and 1995, and the die casting factor was 4.1 kg per metric ton. It was assumed that these emission factors have remained constant throughout the early 1990s. However, it was assumed that after 1996, the emission

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factors for primary production and die casting declined linearly to the level estimated based on partner reports. This assumption is consistent with the trend in sales to the magnesium sector that is reported in the RAND survey of major SF_6 manufacturers, which shows a decline of 70 percent from 1996 to 1999 (RAND 2002). The emission factors for the other processes (i.e., secondary production, and gravity, wrought, and anode casting), about which less is known, were assumed to remain constant.

Uncertainty

Using IPCC Good Practice Guidance Tier 1 methodology, the overall uncertainty associated with the 2002 and 2001 SF_6 emissions estimates is estimated to be ±16 percent (see Table 4-75)

For partnership participants, an uncertainty of 5 percent was assigned to SF_6 emissions data that they supplied to the partnership. These data have low uncertainty since they are prepared through facility-specific tracking of SF_6 cylinder purchases, usage and returns. If partners did not report emissions data during the current reporting year, SF_6 emissions data were estimated using available emission factor and production information reported in prior years, 1999, 2000 or 2001. For example, to estimate 2002 emission factors, the average change in emission factor from 2001 to 2002 for reporting partners was applied to the 2001 emission factor of the non-reporting partner. It was assumed that the uncertainty associated with this extrapolated emission factor is 25 percent. For production data, if estimates were unavailable for the current reporting year, data from the last reported year was applied. The uncertainty associated with this approach ranged from 30 to 50 percent depending on whether the production data was obtained from the previous or an earlier year's partner report.

For those industry processes, such as gravity, anode, wrought casting that are not represented in EPA's partnership, SF_6 emissions were estimated using production and consumption statistics reported by USGS and an estimated process-specific emission factor (see Table 4-75). The uncertainty associated with USGS-reported statistics and emission factors were assumed to be 25 percent and 75 percent, respectively. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

There are additional uncertainties in these estimates, such as the basic assumption that SF_6 neither reacts nor decomposes during use. It is possible that the melt surface reactions and high temperatures associated with molten magnesium cause some gas degradation. Recent measurement studies have identified SF_6 cover gas degradation at hot-chambered die casting machines on the order of 10 percent (Bartos et al. 2003). As is the case for other sources of SF_6 emissions, total SF_6 consumption data for magnesium production and processing in the United States were not available. Sulfur hexafluoride may also be used as a cover gas for the casting of molten aluminum with high magnesium content; however, it is unknown to what extent this technique is used in the United States.

Table 4-75: Quantitative Uncertainty Estimates for SF_6 Emissions from Magnesium Production and Processing (Tg CO_2 Eq. and Percent)

IPCC Source Category	Gas	Year 2002 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2002 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Magnesium Production and Processing	SF_6	2.4	16%	2.0	2.8

Recalculations Discussion

The emission estimate for 2001 was adjusted downward slightly from that previously reported. This revision reflects an update to historical data supplied by partnership participants. This change has resulted in a decrease of 0.014 Tg CO_2 Eq. (0.5 percent) in SF_6 emissions in 2001.

Planned Improvements

A study is currently taking place to measure the degree of destruction of cover gas compounds, such as SF_6 and HFC-134a, at magnesium die casting facilities. Results from this work, which have so far indicated SF_6 degradation on the order of 10 percent in a hot-chambered die casting process (Bartos et al. 2003), could be applied to the inventory methodology to account for cover gas decomposition.

Additionally, as more companies join the partnership, in particular those from sectors not currently represented, such as gravity and anode casting, emission factors will be refined to incorporate these additional data.

[BEGIN BOX]

Box 4-1: Potential Emission Estimates of HFCs, PFCs, and SF_6

Emissions of HFCs, PFCs and SF_6 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 CF_4 and C_2F_6 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.

Table 4-76 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances, HFCs, PFCs, and SF_6 from semiconductor manufacture, and SF_6 from magnesium production and processing, and electrical transmission and distribution.[17] 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. Estimates of HFCs, PFCs, and SF_6 consumed by semiconductor manufacture were developed by dividing chemical-by-chemical emissions by the appropriate chemical-specific emission factors from the IPCC Good Practice Guidance (Tier 2c). Estimates of CF_4 consumption were adjusted to account for the conversion of other chemicals into CF_4 during the semiconductor manufacturing process, again using the default factors from the IPCC Good Practice Guidance. U.S. utility purchases of SF_6 for electrical equipment from 1999 through 2002 were estimated based on reports by participants in EPA's SF_6 Emission Reduction Program for Electric Power Systems. U.S. utility purchases of SF_6 for electrical equipment from 1990 through 1998 were backcasted based on world sales of SF_6 to utilities. Purchases of SF_6 by utilities were added to

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[17] See Annex 5 for a discussion of sources of SF_6 emissions excluded from the actual emissions estimates in this report.

SF_6 purchases by electrical equipment manufacturers to obtain total SF_6 purchases by the electrical equipment sector.

Table 4-76: 2002 Potential and Actual Emissions of HFCs, PFCs, and SF_6 from Selected Sources (Tg CO_2 Eq.)

Source	Potential	Actual
Substitution of Ozone Depleting Substances	169.7	91.7
Aluminum Production	-	5.2
HCFC-22 Production	-	19.8
Semiconductor Manufacture	6.6	4.4
Magnesium Production and Processing	2.4	2.4
Electrical Transmission and Distribution	16.3	14.8

- Not applicable.

[END BOX]

4.21. 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 2002 are reported in Table 4-77.

Table 4-77: NO_x, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990		1996	1997	1998	1999	2000	2001	2002
NO_x	**591**		**596**	**629**	**637**	**605**	**631**	**662**	**649**
Chemical & Allied Product Manufacturing	152		113	115	117	102	104	106	98
Metals Processing	88		75	81	81	79	82	87	84
Storage and Transport	3		14	15	15	9	9	10	9
Other Industrial Processes	343		393	417	424	415	435	458	457
Miscellaneous*	5		1	1	1	1	1	1	1
CO	**4,124**		**3,016**	**3,153**	**3,163**	**2,145**	**2,214**	**2,327**	**2,304**
Chemical & Allied Product Manufacturing	1,074		954	971	981	326	335	346	345
Metals Processing	2,395		1,451	1,551	1,544	1,118	1,155	1,230	1,224
Storage and Transport	69		64	64	65	145	151	158	158
Other Industrial Processes	487		509	528	535	517	536	556	542
Miscellaneous*	101		39	38	38	39	37	37	36
NMVOCs	**2,426**		**1,997**	**2,038**	**2,047**	**1,890**	**1,845**	**1,829**	**1,818**
Chemical & Allied Product Manufacturing	575		352	352	357	265	269	277	261
Metals Processing	111		66	71	71	60	62	65	63
Storage and Transport	1,356		1,174	1,205	1,204	1,104	1,039	1,043	1,039
Other Industrial Processes	364		395	397	402	449	465	434	445
Miscellaneous*	20		10	13	13	12	11	10	11

* Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Field Burning of Agricultural Residues source.
Note: Totals may not sum due to independent rounding.

Methodology

These emission estimates were obtained from preliminary data (EPA 2003), which, in its final iteration, will be published on the National Emission Inventory (NEI) Air Pollutant Emission Trends web site. 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.
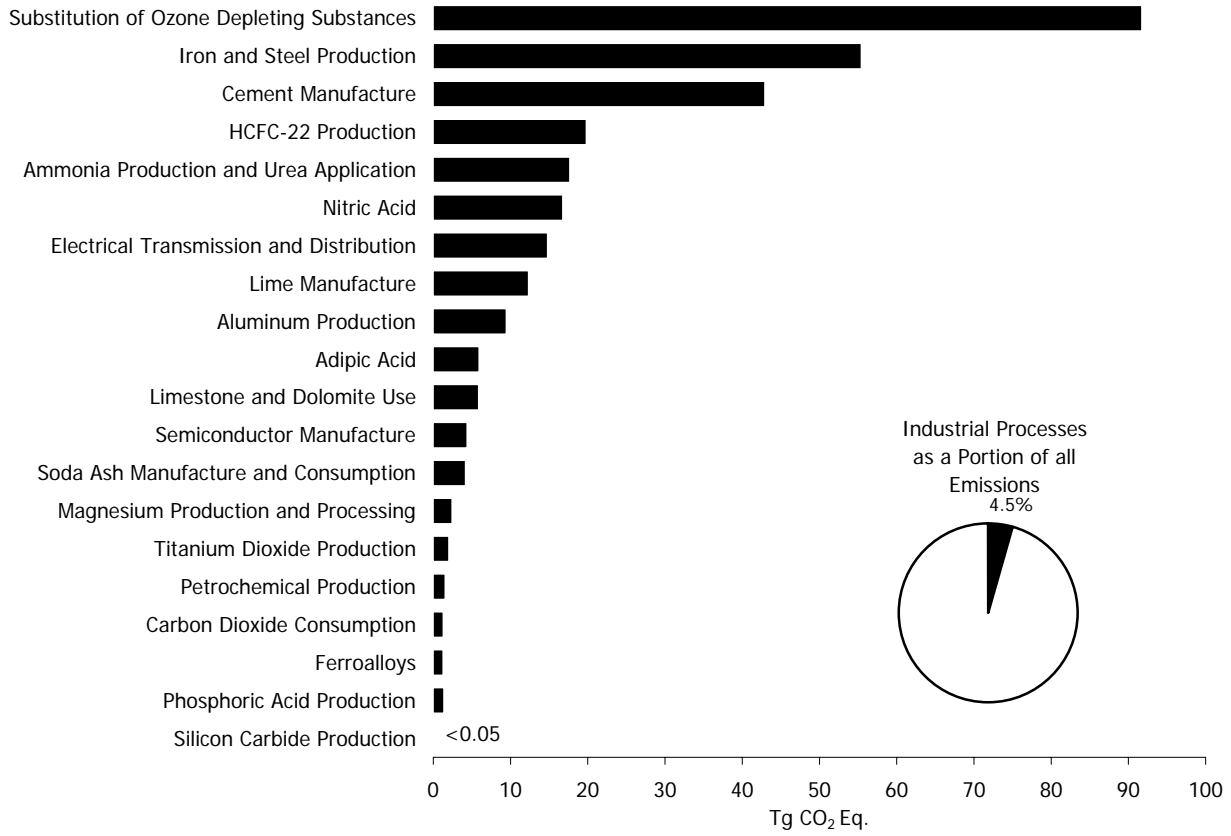
Figure 4-1: 2002 Industrial Processes Chapter Greenhouse Gas Sources

Descriptions of Figures: Industrial Processes

Figure 4-1 illustrates the data presented in Table 4-1.