5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

The most important natural starting material for the production of fluorine chemicals, including fluorine, hydrogen fluoride, and sodium fluoride, is the mineral fluorite (calcium fluoride [CaF_2]), commonly called fluorspar. Other important fluorine minerals are fluorapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6). There has been no fluorspar mine production in the United States since 1996; supplies were imported or purchased from the National Defense Stockpile. In addition, some byproduct calcium fluoride was recovered from industrial waste streams. An estimated 8,000–10,000 metric tons of fluorspar are recovered each year from uranium enrichment, stainless steel pickling, and petroleum alkylation. To supplement fluorspar supplies, fluorosilicic acid is recovered from phosphoric acid plants processing phosphate rock. In 2001, the main fluorspar-producing countries, in order of importance, were China, Mexico, South Africa, Russia, Spain, and France (USGS 2002b). The apparent consumption of fluorspar (excluding fluorspar equivalents of fluorosilicic acid, hydrofluoric acid, and cryolite) in the United States was 601,000 metric tons in 2000 and was estimated to be 636,000 metric tons in 2001 (USGS 2002a). Approximately 60–65% of the fluorspar consumed goes into the production of hydrogen fluoride. Large amounts are also used as a flux in steel production.

In 2001, 65,200 tons of byproduct fluorosilicic acid (equivalent to 104,000 tons of fluorspar) were produced by 10 plants owned by 6 companies. Fluorosilicic acid was used primarily in water fluoridation, either directly or after processing into sodium silicofluoride. Fluorosilicic acid is also used to make aluminum fluoride for the aluminum industry. About 41,200, 4,700, and 13,200 tons of byproduct fluorosilicic acid were sold for water fluoridation, AlF_3 production for the aluminum industry, and for other uses, such as sodium silicofluoride production, respectively. Domestic production data for fluorosilicic acid for 2001 were developed by the U.S. Geological Survey from voluntary surveys of U.S. operations. Of the 11 fluorosilicic acid operations surveyed, 10 respondents reported production and 1 respondent reported zero production (USGS 2002b).

Anhydrous hydrogen fluoride is manufactured by the action of sulfuric on calcium fluoride. Powdered acid-grade fluorspar (≥97% CaF_2) is distilled with concentrated sulfuric acid; the gaseous hydrogen fluoride that leaves the reactor is condensed and purified by distillation (Smith 1994). The U.S. capacity for hydrogen fluoride production was 208,000 metric tons in 2001 (SRI 2002). The demand for hydrofluoric acid, which was 350,000 metric tons in 2001, is expected to increase to 364,000 metric tons in 2005 (CMR 2002).

Sodium fluoride is manufactured by the reaction of hydrofluoric acid with sodium carbonate or sodium hydroxide. The salt is centrifuged and dried (Mueller 1994). Information concerning the amount of sodium fluoride produced is not available. Fluorosilicic acid is a byproduct of the action of sulfuric acid on phosphate rock containing fluorides and silica or silicates. Hydrogen fluoride acts on silica to produce silicon tetrafluoride, which reacts with water to form fluorosilicic acid (Lewis 1997).

Fluorine is produced commercially by electrolyzing anhydrous hydrogen fluoride containing dissolved potassium fluoride to achieve adequate conductivity (Jaccaud and Faron 1988; Shia 1994). Potassium fluoride and hydrogen fluoride form potassium bifluoride (KHF_2 or $KF{\cdot}HF$). Fluoride is oxidized at the anode, producing fluorine, and the hydrogen ion is reduced at the cathode, producing hydrogen gas. Information concerning the amount of fluorine produced is not available. The commercial fluorine production capacity of the United States and Canada is over 5,000 tons/year (Shia 1994).

Current U.S. manufacturers of fluorine, hydrogen fluoride, sodium fluoride, fluorosilicic acid, and sodium silicofluoride are given in Table 5-1. Tables 5-2 and 5-3 list the number of facilities in each state that manufacture, process, or use hydrogen fluoride and fluorine, respectively, their intended uses, and the range of maximum amounts of these substances that are stored on-site. In 2000, there were, respectively, 1,031 and 15 reporting facilities that produced, processed, or used hydrogen fluoride or fluorine in the United States. The data listed in Tables 5-2 and 5-3 are derived from the Toxics Release Inventory (TRI01 2003). Only certain types of facilities were required to report. Therefore, this is not an exhaustive list. Sodium fluoride or other fluoride salts are not listed on TRI.

5.2 IMPORT/EXPORT

In 2000, the United States imported 484,000 metric tons of acid grade (>97%) fluorspar and 39,000 metric tons of metallurgical-grade (<97%) fluorspar (USGS 2002a). This importation was supplemented by the fluorspar equivalent of 208,000 metric tons from hydrofluoric acid plus cryolite. The estimated imports of fluorspar for 2001 were 530,000 metric tons of acid-grade, 33,000 of metallurgical-grade, and 181,000 tons from hydrofluoric acid plus cryolite. Between 1997 and 2000, 63% of fluorspar imports came from China, 26% from South Africa, and 11% from Mexico. Exports of

Table 5-1. U.S. Manufacturers of Hydrogen Fluoride, Fluorine, Sodium Fluoride, Fluosilicic Acid, and Sodium Silicofluoride[a]

Company	Location
Hydrogen Fluoride[b,c]	
Dupont	La Porte, Texas
Honeywell[d]	Geismar, Louisiana
Fluorine	
Honeywell[d]	Metropolis, Illinois
Sodium fluoride	
Mallinckrodt Baker, Inc.	Phillipsburg, New Jersey
Ozark Fluorine Specialties, Inc.	Tulsa, Oklahoma
Solvay Fluorides, Inc.	Alorton, Illinois
Sodium silicofluoride	
IMC Phosphates Company, IMC-Agrico Phosphates	Faustina, Louisiana
Kaiser Aluminum and Chemical Corporation	Mulberry, Florida
Solvay Fluorides, Inc.	Alorton, Illinois
Fluosilicic acid	
Cargill Fertilizer, Inc.	Riverview, Florida
Farmland Hydro, L.P.	Bartow, Florida
IMC Phosphates Company, IMC-Agrico Phosphates	Faustina, Louisiana; Nichols, Florida; South Pierce, Florida; Uncle Sam, Louisiana
PCS Phosphate Co. Inc.	Aurora, North Carolina
Royster-Clark Inc.	Americus, Georgia; Chesapeake, Virginia; Florence, Alabama; Hartsville, South Carolina
Solvay Fluorides, Inc.	Alorton, Illinois
U.S. Agri-Chemicals Corporation	Fort Meade, Florida

[a]Derived from SRI 2002
[b]Plant capacity was available only for hydrogen fluoride, and was reported as 80,000 and 120,000 metric tons for DuPont and Honeywell, respectively.
[c]Merchant producers. Alcoa produces hydrogen fluoride as a nonisolatable product.
[d]Formally General Electric

Table 5-2. Facilities that Produce, Process, or Use Hydrogen Fluoride

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AK	2	0	99,999	1, 5, 13
AL	28	0	9,999,999	1, 5, 6, 11, 12, 13
AR	13	0	9,999,999	1, 5, 6, 7, 8, 11, 12, 13
AZ	23	0	999,999	1, 4, 5, 6, 7, 9, 10, 11, 12, 13
CA	34	0	49,999,999	1, 3, 4, 5, 6, 7, 9, 10, 11, 12, 14
CO	16	0	999,999	1, 5, 7, 9, 11, 12
CT	5	100	99,999	1, 5, 10, 11, 12
DE	3	0	999,999	1, 5, 6
FL	24	0	999,999	1, 2, 3, 5, 6, 7, 9, 10, 11, 12, 13, 14
GA	26	0	999,999	1, 5, 7, 11, 12, 13
IA	15	0	99,999	1, 5, 7, 12
ID	5	100	99,999	1, 5, 10, 11, 12, 13, 14
IL	41	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13
IN	36	0	999,999	1, 5, 7, 10, 11, 12, 13, 14
KS	14	0	9,999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 13
KY	29	0	9,999,999	1, 2, 3, 5, 6, 9, 10, 11, 12
LA	19	0	9,999,999	1, 3, 4, 5, 6, 10, 12
MA	11	0	99,999	1, 5, 10, 11, 12
MD	12	0	9,999	1, 5, 11, 13
ME	3	0	9,999	1, 11, 13
MI	25	0	99,999	1, 2, 3, 5, 6, 7, 10, 11, 12, 13
MN	14	0	99,999	1, 5, 6, 10, 11, 12, 13
MO	27	0	99,999	1, 5, 7, 11, 12
MS	9	0	999,999	1, 5, 8, 11, 13
MT	6	0	999,999	1, 5, 10
NC	37	0	999,999	1, 5, 11, 12, 13
ND	8	0	999,999	1, 5, 10, 12, 13
NE	8	0	999,999	1, 3, 5, 9, 13
NH	4	0	99,999	1, 5, 12
NJ	15	0	9,999,999	1, 5, 6, 10, 12
NM	7	0	999,999	1, 5, 10, 11, 13
NV	2	0	999,999	1, 5
NY	29	0	99,999	1, 5, 6, 10, 11, 12
OH	62	0	999,999	1, 5, 6, 7, 8, 9, 10, 11, 12, 13
OK	17	0	999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13
OR	20	0	999,999	1, 3, 4, 5, 7, 9, 10, 11, 12
PA	67	0	9,999,999	1, 2, 3, 5, 6, 7, 9, 10, 11, 12, 13
PR	1	100,000	999,999	6
RI	3	100	99,999	6, 10, 11
SC	30	0	999,999	1, 3, 5, 6, 10, 11, 12, 14

Table 5-2. Facilities that Produce, Process, or Use Hydrogen Fluoride

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
SD	1	0	99	1, 13
TN	19	0	999,999	1, 2, 5, 6, 10, 11, 13
TX	82	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14
UT	14	0	999,999	1, 5, 6, 10, 11, 12, 13
VA	23	0	99,999	1, 5, 10, 11, 12
VT	2	1,000	99,999	11
WA	18	0	999,999	1, 5, 10, 11, 12
WI	24	0	99,999	1, 5, 7, 10, 11, 12, 13
WV	20	0	999,999	1, 5, 10, 11, 12
WY	9	0	99,999	1, 2, 3, 5, 10, 13

Source: TRI01 2003

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Table 5-3. Facilities that Produce, Process, or Use Fluorine

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	1	0	99	1, 13
IL	1	10,000	99,999	1, 3, 6, 7
KS	1	0	99	1, 5, 12
LA	1	1,000	9,999	1, 3, 6, 12
OK	1	1,000	9,999	8
PA	2	1,000	999,999	1, 3, 4, 6, 9, 10
PR	1	1,000	9,999	10
TX	1	1,000	9,999	12

Source: TRI01 2003

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

fluorspar for 2000 were 40,000 metric tons and are estimated to be 21,000 in 2001 (USGS 2002a). Exports consist of imported material that was reexported or material obtained from the National Defense Stockpile. In 2001, no disposal of metalurgical-grade fluorspar from the stockpile was reported. In 2001, most of the exports were to Canada and Taiwan (USGS 2002a, 2002b).

U.S. imports for consumption are available for three other fluorides: hydrofluoric acid, cryolite, and aluminum fluoride. For 2001, these were 112,000, 6,750, and 17,400 metric tons, respectively. For hydrofluoric acid, 74% of imports came from Mexico and 23% from Canada (USGS 2002b).

5.3 USE

Hydrogen fluoride is the most important compound of fluorine. Anhydrous hydrogen fluoride is used in the production of most fluorine-containing chemicals. It is used in the production of refrigerants, herbicides, pharmaceuticals, high-octane gasoline, aluminum, plastics, electrical components, and fluorescent light bulbs. Aqueous hydrofluoric acid is used in stainless steel pickling, glass etching, metal coatings, exotic metal extraction, and quartz purification (Hance et al. 1997). The most important use of hydrogen fluoride is in the production of fluorocarbon chemicals, including hydrofluorocarbons, hydrofluorochlorocarbons, and fluoropolymers; 60% of production is used for this purpose. Demand for hydrogen fluoride for fluorocarbons, broadly used as refrigerants, is increasing as a nonchlorinated alternative to ozone-depleting chlorofluorocarbons. (Production of fluorocarbons uses more hydrogen fluoride than production of chlorofluorocarbons.) The next most important uses of hydrogen fluoride are: chemical derivatives, 18%; aluminum manufacturing, 6%; stainless steel pickling, 5%; petroleum alkylation catalysts, 4%; and uranium chemicals production, 3%. Miscellaneous other uses include glass etching, herbicides, and rare metals (CMR 2002). Generally, the aluminum industry consumes 10–40 kg of fluoride per metric ton of aluminum produced. The AlF_3 used in aluminum reduction cells may be produced directly from acid-grade fluorspar or byproduct fluorosilicic acid, rather than from hydrogen fluoride. Anhydrous hydrogen fluoride is used as a catalyst in the petroleum alkylation, a process that increases the octane rating of petroleum. In uranium chemicals production, hydrogen fluoride is used to convert uranium oxide (yellow cake, U_3O_8) to UF_4 before further fluorination to UF_6.

Fluorine gas is used captively for the production of various inorganic fluorides. The preparation of fluorides of an element in its highest oxidation state makes use of fluorine's oxidizing and fluorinating ability. The most important product is uranium hexafluoride (UF_6), which is used in the gaseous diffusion process for producing enriched uranium-235 for the nuclear industry. This use consumes 70–80% of fluorine production. The second most important product is sulfur hexafluoride (SF_6), which is used as a gaseous dielectric for electrical and electronic equipment and a tracer gas for determining ventilation rates and air movements in buildings. Other uses of fluorine include: the treatment of polyolefin containers to reduce their permeability to organic liquids; the treatment of a polymer surface for the application of an adhesive or coating; and the production of some fluorinated organic compounds (Guo et al. 2001; Shia 1994).

The chemicals most commonly used by American waterworks for water fluoridation are fluorosilicic acid, sodium silicofluoride, and sodium fluoride (Urbansky 2002). Generally, 1.5–2.2 mg of sodium fluoride is added per liter of water (0.7–1.0 mg/L as fluoride) (Mueller 1994). Data from the Centers for Disease Control's (CDC) 1992 Fluoridation Census indicate that 25% of utilities reported using sodium fluoride; however, this corresponds to 9.2% of the U.S. population drinking fluoride-supplemented tap water (Urbansky 2002). Sodium fluoride may also be applied topically to teeth as a 2% solution to prevent tooth decay. It is also used as a flux for deoxidizing rimmed steel, as a component of laundry sours (removal of iron stains), and in the re-smelting of aluminum, manufacture of vitreous enamels, pickling of stainless steel, wood preservative compounds, casein glues, manufacture of coated papers, and heat-treating salts (Mueller 1994). Fluorosilicic acid, as a 1–2% solution, is used widely for sterilizing equipment in brewing and bottling. Other concentrations of fluorosilicic acid solutions are used in electrolytic refining of lead, in electroplating, for hardening cement, for crumbling lime or brick work, for removal of lime from hides during the tanning process, for removals of molds, and as a preservative for timber. Sodium fluorosilicate is also used in enamels for china and porcelain, in the manufacturing of opal glass, as an insecticide, as a rodentcide, and for mothproofing of wool. It is also an intermediate in the production of synthetic cryolite (Budavari 2001).

5.4 DISPOSAL

According to the TRI, in 2001, an estimated 2.5 million pounds of hydrogen fluoride were transferred off-site, including to publicly owned-treatment works (POTWs), by 991 reporting facilities presumably for disposal (TRI01 2003). In 2001, 240,196 pounds of fluorine were transferred off-site by 9 reporting facilities. According to the TRI, in 2001, 77% of hydrogen fluoride that was recycled or treated was performed on-site (TRI01 2003). Of the hydrogen fluoride recycled in 2001, 23.8 million pounds were recycled on-site and 251,203 pounds were recycled off-site. Of the hydrogen fluoride that was treated, 234 million pounds were treated on-site and 2 million pounds were treated off-site (TRI01 2003). No information was found concerning how hydrogen fluoride is generally treated for disposal.

Fluorine gas can be disposed of by conversion to perfluorocarbons or fluoride salts. Because of the long atmospheric lifetimes of perfluorocarbons, conversion to fluoride salts is preferable. Industrially, the waste stream is scrubbed with a caustic solution, KOH or NaOH, and for dilute streams, allowed to react with limestone (Shia 1994). Adequate contact and residence time is essential in the scrubber to ensure complete neutralization of the intermediate oxygen difluoride to prevent it from leaving the scrub tower. According to the TRI, in 2001, 18,973 pounds of fluorine were treated on-site and 240,196 pounds were treated off-site (TRI01 2003).

No information was found regarding the disposal of sodium fluoride. It would appear from its use that most of it is disposed of in municipal landfills or POTWs.