[Note: with the publication of the Fifth Edition of AP-42, the Chapter and Section number for Hydrofluoric Acid was changed to 8.7.]

BACKGROUND REPORT

AP-42 SECTION 5.8

HYDROFLUORIC ACID

Prepared for

U.S. Environmental Protection Agency
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1-96

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AP-42 Background Report

TECHNICAL SUPPORT DIVISION

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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1.0 INTRODUCTION

The document "Compilation of Air Pollutant Emission Factors" (AP-42) has been published by the U.S. Environmental Protection Agency (the EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by the EPA to respond to new emission factor needs of the EPA, State, and local air pollution control programs and industry.

An emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source. The uses for the emission factors reported in AP-42 include:

1. Estimates of area-wide emissions;
2. Emission estimates for a specific facility; and
3. Evaluation of emissions relative to ambient air quality.

The purpose of this report is to provide background information from process information obtained from industry comment. No new test reports were received to support revision of the process description and/or emission factors for hydrofluoric acid production.

Including the introduction (Chapter 1), this report contains four chapters. Chapter 2 gives a description of the hydrofluoric acid production industry. It includes a characterization of the industry, an overview of the different process types, a description of emissions, and a description of the technology used to control emissions resulting from hydrofluoric acid production.

Chapter 3 is a review of emissions data collection and analysis procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Chapter 4 includes the review of specific data sets and details criteria and noncriteria pollutant emission factor development. It also includes the results of a data gap analysis. Particle size determination and particle size data analysis methodology are described when applicable. Appendix A presents AP-42 Section 5.8

2.0 INDUSTRY DESCRIPTION

2.1 GENERAL[5,6]

Hydrogen fluoride is listed as a Title III Hazardous Air Pollutant (HAP). Hydrogen fluoride is produced in two forms, as anhydrous hydrogen fluoride and as aqueous hydrofluoric acid. The predominate form manufactured is anhydrous hydrogen fluoride, a colorless liquid or gas which fumes on contact with air and is water soluble.

Traditionally, hydrofluoric acid (HF) has been used to etch and polish glass. Currently, the largest use for HF is in aluminum production. Other HF uses include uranium processing, petroleum alkylation, and stainless steel pickling. Hydrofluroic acid is also used to produce fluorocarbons used in aerosol sprays and in refrigerants. Although fluorocarbons are heavily regulated due to environmental concerns, other applications for fluorocarbons include manufacturing of resins, solvents, stain removers, surfactants, and pharmaceuticals.

2.2 PROCESS DESCRIPTION[1-3,6]

Hydrofluoric acid is manufactured by the reaction of acid-grade fluorspar (CaF_2) with sulfuric acid (H_2SO_4) as shown below:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF \quad (1)$$

A typical HF plant is shown schematically in Figure 2.2-1.

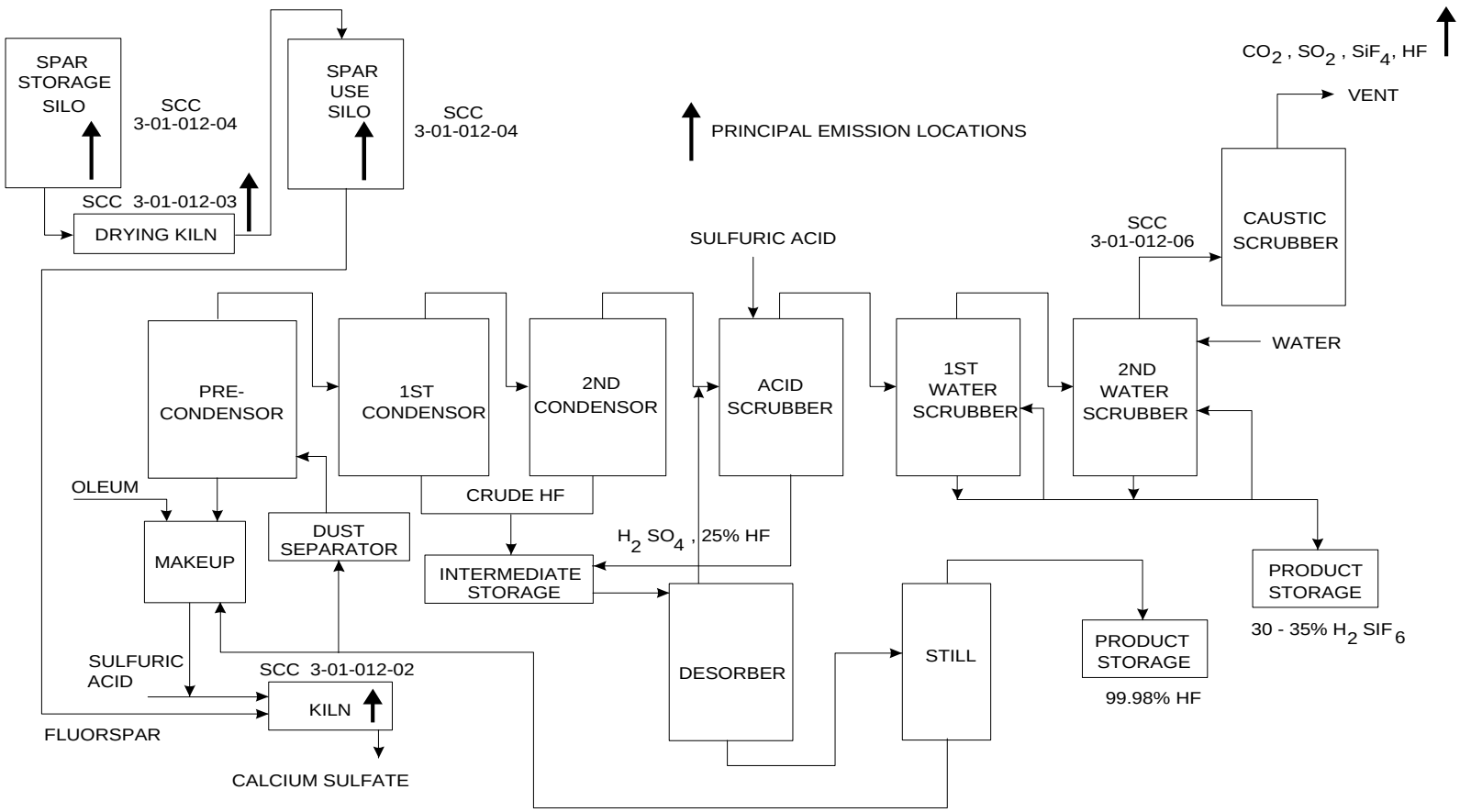

Figure 2.2-1 Hydrofluoric acid process flow diagram

The endothermic reaction requires 30 to 60 minutes in horizontal rotary kilns externally heated to 200 to 250°C (390 to 480°F). Dry fluorspar ("spar") and a slight excess of sulfuric acid are fed continuously to the front end of a stationary prereactor or directly to the kiln by a screw conveyor. The prereactor mixes the components prior to charging to the rotary kiln. Calcium sulfate ($CaSO_4$) is removed through an air lock at the opposite end of the kiln. The gaseous reaction products—hydrogen fluoride and excess H_2SO_4 from the primary reaction, silicon tetrafluoride (SiF_4), sulfur dioxide (SO_2), carbon dioxide (CO_2), and water produced in secondary reactions—are removed from the front end of the kiln along with entrained particulate. The particulates are removed from the gas stream by a dust separator and returned to the kiln. Sulfuric acid and water are removed by a precondenser. Hydrogen fluoride vapors are then condensed in refrigerant condensers forming "crude HF," which is removed to intermediate storage tanks. The remaining gas stream passes through a sulfuric acid absorption tower or acid scrubber, removing most of the remaining hydrogen fluoride and some residual sulfuric acid, which are also placed in intermediate storage. The gases exiting the scrubber then pass through water scrubbers, where the SiF_4 and remaining HF are recovered as fluosilicic acid (H_2SiF_6). The water scrubber tailgases are passed through a caustic scrubber before being released to the atmosphere. The hydrogen fluoride and sulfuric acid are delivered from intermediate storage tanks to distillation columns, where the hydrofluoric acid is extracted at 99.98 percent purity. Weaker concentrations (typically 70 to 80 percent) are prepared by dilution with water.

2.3 EMISSIONS AND CONTROLS[1,2,4]

Emission factors for various HF process operations are shown in Table 2.3-1. Emissions are suppressed to a great extent by the condensing, scrubbing, and absorption equipment used in the recovery and purification of the hydrofluoric and fluosilicic acid products. Particulate in the gas stream is controlled by a dust separator near the outlet of the kiln and is recycled to the kiln for further processing. The precondenser removes water vapor and sulfuric acid mist, and the condensers, acid scrubber and water scrubbers remove all but small amounts of HF, SiF_4, SO_2, and CO_2 from the tailgas. A caustic scrubber is employed to further reduce the levels of these pollutants in the tailgas.

Particulates are emitted during handling and drying of the fluorspar. They are controlled with bag filters at the spar silos and drying kilns. Fugitive dust emissions from spar handling and storage are controlled with flexible coverings and chemical additives.

Hydrogen fluoride emissions are minimized by maintaining a slight negative pressure in the kiln during normal operations. Under upset conditions, a standby caustic scrubber or a bypass to the tail caustic scrubber are used to control HF emissions from the kiln.

TABLE 2.3-1 (METRIC UNITS)
EMISSION FACTORS FOR HYDROFLUORIC ACID MANUFACTURE
All Emission Factors are for kg/Mg of Production
Factors (A-E) Follow Each Factor

Type of Operation and Control	Control efficiency (%)	Emissions			
		Gases		Particulates (Spar)	
		kg/Mg acid		Fluorspar (kg/Mg)	
Spar drying[a]					
Uncontrolled	0			37.5	E
Fabric filter	99			0.4	E
(SCC 3-01-012-03)					
Spar handling silos[b]					
Uncontrolled	0			30.0	E
Fabric Filter	99			0.3	E
(SCC 3-01-012-04)					
Transfer operations					
Uncontrolled	0			3.0	E
Covers, additives	80			0.6	E
(SCC 3-01-012-05)					
Tail Gas[c]					
Uncontrolled	0	12.5 (HF)	E		
		15.0 (SiF_4)	E		
		22.5 (SO_2)	E		
Caustic Scrubber	99	0.1 (HF)	E		
(SCC 3-01-012-06)		0.2 (SiF_4)	E		
		0.3 (SO_2)	E		

[a] Reference 1. Averaged from information provided by four plants. Hourly fluorspar input calculated from reported 1975 year capacity, assuming stoichiometric amount of calcium fluoride and 97.5 percent content in fluorspar. Hourly emission rates calculated from reported baghouse controlled rates. Values averaged are as follows:

Plant	1975 Capacity	Emissions fluorspar kg/Mg
1	13,600 Mg HF	53
2	18,100 Mg HF	65
3	45,400 Mg HF	21
4	10,000 Mg HF	15

[b] Four plants averaged for silo emissions, two plants for transfer operations emissions.
[c] Three plants averaged. Hydrogen fluoride and SiF_4 emission factors verified by information in Reference 4.

TABLE 2.3-1 (ENGLISH UNITS)
EMISSION FACTORS FOR HYDROFLUORIC ACID MANUFACTURE
All Emission Factors are for lb/ton of Production
Ratings (A-E) Follow Each Factor

Type of Operation and Control	Control efficiency (%)	Emissions			
		Gases		Particulates (Spar)	
		lb/ton acid		lb/ton Fluorspar	
Spar drying[a]					
Uncontrolled	0			75.0	E
Fabric filter (SCC 3-01-012-03)	99			0.8	E
Spar handling silos[b]					
Uncontrolled	0			60.0	E
Fabric Filter (SCC 3-01-012-04)	99			0.6	E
Transfer operations					
Uncontrolled	0			6.0	E
Covers, additives (SCC 3-01-012-05)	80			1.2	E
Tail Gas[c]					
Uncontrolled	0	25.0 (HF)	E		
		30.0 (SiF_4)	E		
		45.0 (SO_2)	E		
Caustic Scrubber (SCC 3-01-012-06)	99	0.2 (HF)	E		
		0.3 (SiF_4)	E		
		0.5 (SO_2)	E		

[a] Reference 1. Averaged from information provided by four plants. Hourly fluorspar input calculated from reported 1975 year capacity, assuming stoichiometric amount of calcium fluoride and 97.5 percent content in fluorspar. Hourly emission rates calculated from reported baghouse controlled rates. Values averaged are as follows:

Plant	1975 Capacity	Emissions fluorspar lb/ton
1	15,000 ton HF	106
2	20,000 ton HF	130
3	50,000 ton HF	42
4	11,000 ton HF	30

[b] Four plants averaged for silo emissions, two plants for transfer operations emissions.

[c] Three plants averaged. Hydrogen fluoride and SiF_4 emission factors verified by information in Reference 4.

2.4 REVIEW OF SPECIFIC DATA SETS

Pacific Environmental Services (PES) contacted the following sources to obtain the most up-to-date information on process descriptions and emissions for this industry:

1) Alcoa Industrial Chemicals, Point Comfort, Texas
2) Allied-Signal, Geismar, Louisiana
3) Aluminum Company of America, Pittsburg, Pennsylvania
4) Atochem North America, Inc., Calvert City, Kentucky
5) Chemical Manufacturers' Association, Washington, DC
6) E.I. duPont de Nemours, Laporte, Texas
7) E.I. duPont de Nemours, Wilmington, Delaware
8) Elf-Atochem North America, Inc., Calvert City, Kentucky
9) Kentucky Department of Natural Resources and Environment Protection, Frankfort, Kentucky
10) United States EPA Chemical Emergency and Preparedness Center, Washington, DC

Pacific Environmental Services received one new source test report from Atochem North American, Inc., located in Calvert City, Kentucky (Source #4). Unfortunately, this report lacks production rate data and cannot be used for the revision of this section. In addition, there is no documentation of the volumetric flow rate, calculations for EPA Method 1 through 4 are missing or incomplete, and the field data are also incomplete.

The Chemical Manufacturers' Association (Source #5) agreed to provide process descriptions and emission information compiled by the ChemStar Panel on Hydrofluoric Acid. However, this information has not been received to date. No other information was received from the sources contacted.

The process description in the previous AP-42 Section 5.8 (February 1980) was obtained from References 1, 2, and 3. References 5 and 6 are new references that provided a general industry overview and a more detailed process description. These references are discussed below.

Reference 1: Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture

Reference 1 contains process description information included in the previous version of this section (February 1980) that still applies to the industry.

Reference 2: "Hydrofluoric Acid," Kirk-Othmer Encyclopedia of Chemical Technology

Reference 2, used in an earlier revision of this AP-42 section (February 1980), contains process description information that still applies to this industry.

Reference 3: "Hydrofluoric Acid Manufacture," Chemical Engineering Progress

This reference was used in the previous section (February 1980) to describe emission sources and to provide a process flow diagram for the manufacture of hydrofluoric acid.

Reference 4: Engineering and Cost Effectiveness Study of Fluoride Emissions Control

Reference 4 was used in the development of emission factors and is addressed in Section 4.1.

Reference 5: "Fluorine," Encyclopedia of Chemical Processing and Design

Reference 5 provided current information on hydrogen fluoride uses, including aluminum production, uranium processing, petroleum alkylation, stainless steel pickling, and fluorocarbon manufacturing.

Reference 6: "Fluorine Compounds, Inorganic," Kirk-Othmer Encyclopedia of Chemical Technology

Reference 6 provided additional details of the process description. In the process description section, the sulfuric acid, dry fluorspar reaction process is further detailed by describing the mixture feed into a stationary prereactor or kiln by a screw conveyor. This reference was also used for writing the general description section.

2.5 REFERENCES FOR CHAPTER 2

1. Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture, EPA-450/3-78-109, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1978.

2. "Hydrofluoric Acid," Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 9, Interscience Publishers, New York, 1965.

3. W.R. Rogers and K. Muller, "Hydrofluoric Acid Manufacture," Chemical Engineering Progress, 59(5):85-8, May 1963.

4. J.M. Robinson, et al., Engineering and Cost Effectiveness Study of Fluoride Emissions Control, Vol. 1, PB 207 506, National Technical Information Service, Springfield, VA, 1972.

5. "Fluorine," Encyclopedia of Chemical Processing and Design, Vol. 23, Marcel Dekker, Inc., New York, 1985.

6. "Fluorine Compounds, Inorganic," Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 10, John Wiley & Sons, New York, 1980.

3.0 GENERAL EMISSION DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING SOURCE TESTS

The first step in the investigative process involved a search of available literature relating to criteria and noncriteria pollutant emissions associated with hydrofluoric acid manufacture. This search included the following references:

1) AP-42 background files maintained by the Emission Factor and Methodologies Section.
2) The EPA databases, including the *VOC/Particulate Matter* (PM) *Speciation Database Management System* (SPECIATE) and the *Crosswalk/Air Toxic Emission Factor Data Base Management System* (XATEF).

To reduce the amount of literature collected to a final group of references pertinent to this report, the following general criteria were used:

1. Emissions data must be from a primary reference, i.e. the document must constitute the original source of test data.
2. The referenced study must contain test results based on more than one test run.
3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions.

A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria.

3.2 EMISSION DATA QUALITY RATING SYSTEM

As part of Pacific Environmental Services' analysis of the emission data, the quantity and quality of the information contained in the final set of reference documents were evaluated and assigned a quality rating. The rating system used was that specified by the OAQPS for the preparation of AP-42 sections. The data were rated as follows:

A Rating

Multiple tests performed on the same source using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the

methodology specified in the EPA reference test methods, although these methods were certainly used as a guide for the methodology actually used.

B Rating

Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

C Rating

Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D Rating

Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented In the report. The source was operating within typical parameters during the test.
2. Sampling procedures. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent such alternative procedures could influence the test results.
3. Sampling and process data. Adequate sampling and process data are documented in the report. Many variations can occur unnoticed and without warning during testing. Such variations can induce wide deviations in sampling results. If a large spread between test results cannot be explained by information contained in the test report, the data are suspect and were given a lower rating.
4. Analysis and calculations. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by the EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM

The quality of the emission factors developed from analysis of the test data was rated utilizing the following general criteria:

A (Excellent)

Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B (Above average)

Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

C (Average)

Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

D (Below average)

The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E (Poor)

The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always noted.

The use of these criteria is somewhat subjective and depends to an extent on the individual reviewer. Details of the rating of each candidate emission factor are provided in Chapter 4 of this report.

3.4 REFERENCES FOR CHAPTER 3

1. Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections. U.S. Environmental Protection Agency, Emissions Inventory Branch, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 27711, April, 1992. [Note: this document is currently being revised at the time of this printing.]

2. AP-42, Supplement A, Appendix C.2, "Generalized Particle Size Distributions." U.S. Environmental Protection Agency, October, 1986.

4.0 POLLUTANT EMISSION FACTOR DEVELOPMENT

4.1 REVIEW OF SPECIFIC DATA SETS

This chapter describes the test data and methodology used to develop pollutant emission factors for hydrofluoric acid manufacturing. PES received one new emission test report from Atochem North America, Inc., in Calvert City, Kentucky. Unfortunately, this report lacks production rate data and could not be used for revision of the emission factors. Therefore, no changes were made to the existing emission factors. This review of data sets discusses the references that were used to support the existing factors (February 1980).

Reference 1: Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture

Reference 1 provided most of the emission information used to calculate emission factors in the previous section (February 1980). Most of the data came from a summary table of emissions from several hydrofluoric acid manufacturing plants. A verification of the methodology used for calculating the emission factors as presented in the previous section (February 1980) is discussed in Sections 4.2 and 4.3. In accordance with the criteria discussed in Chapter 3, this reference was rated "D" because data presented in this reference were based on plant visits and contacts with the industry, and not on source tests.

Reference 4: Engineering and Cost Effectiveness Study of Fluoride Emissions Control, Vol 1

The EPA Background File for the hydrofluoric acid production section contains documentation of the emission factor calculation used in the previous section (February 1980). The calculation from Reference 1 for the hydrogen fluoride emission factor was not used because the resulting emission factor represented only 0.5 percent of production. Therefore, the author of the previous section used a hydrogen fluoride emission factor of 12.5 kg/Mg, taken from Reference 4.

4.2 CRITERIA POLLUTANT EMISSIONS DATA

No data on emissions of volatile organic compounds, lead, nitrogen oxides, or carbon monoxide were found nor expected for the hydrofluoric acid production process. The remaining criteria pollutants, sulfur dioxide and particulate matter, are discussed below.

Sulfur dioxide.

The sulfur dioxide emission factor for hydrofluoric acid manufacturing has not been updated in the current revision due to a lack of new primary source tests. The emission factor for sulfur dioxide, rated "D" in the previous draft (February 1980), was lowered to "E." This rating was lowered because the previous draft referenced a point scale rating system that does not comply with the current, accepted rating system discussed in Section 3.2. The data in Reference 1, which were used to calculate emission factors in the previous draft (February 1980), were based on plant visits and contacts with the industry. Therefore, this reference was rated "D" because the data presented did not come from a source test. Reference 1 presented production capacity, control efficiency, and controlled emission rates for three plants as shown in Table 4.2-1. This information was used to calculate the sulfur dioxide emission factor as shown below.

In an example calculation for Plant 1, it is assumed that there were 8000 production hours in a year. The derivation is as follows:

To calculate hydrofluoric acid production

= Plant capacity / production hours
= 40,872 (Mg/yr) / 8,000 (hr/yr)
= 5.109 (Mg/hr)

To calculate uncontrolled emission rates

= Controlled emissions / (1 - control efficiency)
= 0.27 (kg/hr) / (1 - .99)
= 27 (kg/hr)

To calculate uncontrolled emission factors

= Uncontrolled emissions / hydrofluoric acid production
= 27 (kg/hr) / 5.109 (Mg/hr)
= 5.28 (kg SO_2/Mg HF)

To calculate controlled emission factors

= Uncontrolled emission factor x (1 - control efficiency)
= 5.28 x .01

$= 0.053$ (kg SO_2/Mg HF)

Similar calculations are done for the other two plants. The average controlled emission factor of 0.23 kg SO_2 per Mg HF produced and the average uncontrolled emission factor of 23.0 kg SO_2 per Mg HF produced are then computed.

TABLE 4.2-1 (METRIC UNITS)
SULFUR DIOXIDE EMISSION DATA FOR
HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (Mg/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (kg/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (kg/Mg)	Controlled Emission Factor (kg/Mg)
1	40,872	8,000	0.270	99	5.28	0.053
2	18,165	8,000	0.816	99	36.0	0.36
3	90,827	8,000	3.13	99	27.6	0.28
Average					23.0	0.23

TABLE 4.2-1 (ENGLISH UNITS)
SULFUR DIOXIDE EMISSION DATA FOR
HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (ton/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (lb/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (lb/ton)	Controlled Emission Factor (lb/ton)
1	45,000	8,000	0.60	99	10.67	0.1
2	20,000	8,000	1.8	99	72.00	0.7
3	100,000	8,000	6.9	99	55.20	0.6
Average					45.90	0.5

Total Suspended Particulate.

Emissions of particulate matter can be divided into three categories: filterable, organic condensible, and inorganic condensible. Filterable particulate matter is that which collects on the filter and in the sampling probe assembly of a particulate sampling train. When emissions testing is performed in accordance with Method 5, the filter and probe are maintained at approximately 120°C (248°F); materials that condense at a temperature lower than this will pass through the filter. Many emissions tests also quantify emissions of condensible particulate matter, typically that which condenses at or above 20°C (68°F). This condensible particulate matter is collected by passing the effluent gas through ice water-cooled impingers such that the gas exiting the last impinger is at a temperature less than 20°C. The preferred method for quantification of emissions of condensible particulate matter is EPA Reference Method 202. This method entails extraction of the organic portion of the condensible, or back-half, catch with methylene chloride, evaporation of the extract at room temperature, desiccation, and weighing. The inorganic portion of the back-half catch is evaporated at 105°C (221°F), desiccated, and weighed.

The only quantitative data available from the hydrofluoric acid manufacturing process were obtained from Reference 1. As discussed in Section 4.1, Reference 1 is a summary report rated "D." No documentation of the method by which the particulate data were measured was contained in this reference. Therefore, the particulate emission factors have been rated "E" as discussed below.

Particulate (spar) emission factors for hydrofluoric acid manufacturing have not been updated in the current revision due to a lack of new primary source tests. The emission factor for particulates emitted during spar drying, rated "C" in the previous section (February 1980), was lowered to "E." The emission factor for particulates emitted during spar handling, originally rated "D," were also lowered to "E." The ratings were lowered because the previous section (February 1980) referenced a point scale rating system that does not comply with the current accepted rating system discussed in Section 3.2. Data in Reference 1, which were used to calculate emission factors in the previous section (February 1980), were gathered from plant visits and contacts with the industry. Therefore, this reference was rated "D" because the data presented did not come from an emission test. Reference 1 presented production capacity, control efficiency, and controlled emission rates as shown in Table 4.2-2. This information was used to calculate the particulate emission factor for spar drying. These calculations were executed for

four plants and the final emission factor resulted from their average as detailed in the sample calculations below.

In an example calculation for Plant 1, it is assumed that there were 8000 production hours in a year. The derivation is as follows:

To calculate hydrofluoric acid production

= Plant capacity / production hours
= 13,624 (Mg/yr) / 8,000 (hr/yr)
= 1.703 (Mg/hr)

To calculate fluorspar input

= Hydrofluoric acid production x stoichiometric ratio / average acid-grade spar
= 1.703 (Mg/hr) x 0.885 (kg CaF_2/kg HF)/0.442 (kg CaF_2/kg fluors)
= 3.41 (Mg/hr)

To calculate uncontrolled emission rates

= Controlled emissions / (1 - control efficiency)
= 1.81 (kg/hr) / (1 - .99)
= 181 (kg/hr)

To calculate controlled emission factors

= Uncontrolled emissions / fluorspar input
= 181 (kg/hr) / 3.41 (kg/hr)
= 53.1 (kg spar/Mg HF)

To calculate uncontrolled emission factors

= Uncontrolled emission factor x (1 - control efficiency)
= 53.1 x .01
= 0.53 (kg spar/Mg HF)

Similar calculations were done for the other three plants. The average controlled emission factor of 0.38 kg/Mg and the uncontrolled emission factor of 38.40 kg/Mg were then computed.

TABLE 4.2-2 (METRIC UNITS)
PARTICULATE EMISSION DATA DURING SPAR DRYING
FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (Mg/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (kg/hr)	Control Efficiency (%)	Uncontrolled Emission Factors (kg/Mg)	Controlled Emission Factors (kg/Mg)
1	13,624	8,000	1.81	99	53.10	0.53
2	18,165	8,000	2.95	99	64.98	0.65
3	45,413	8,000	2.40	99	21.13	0.21
4	9,991	8,000	0.360	99	14.40	0.14
Average					38.40	0.38

TABLE 4.2-2 (ENGLISH UNITS)
PARTICULATE EMISSION DATA DURING SPAR DRYING
FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (ton/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (lbs/hr)	Control Efficiency (%)	Uncontrolled Emission Factors (lb/ton)	Controlled Emission Factor (lb/ton)
1	15,000	8,000	4.0	99	106.7	1.1
2	20,000	8,000	6.5	99	130.0	1.3
3	50,000	8,000	5.3	99	42.40	0.42
4	11,000	8,000	0.80	99	29.10	0.29
Average					77.05	0.78

The particulate emission factor for spar handling silos was calculated from the given production capacity, control efficiency, and controlled emission rate shown in Table 4.2-3. These calculations were executed for four plants and the final emission factor resulted from their average as detailed in the sample calculations below.

In an example calculation for Plant 1, it is assumed that there were 8000 production hours in a year. The derivation is as follows:

To calculate hydrofluoric acid production

= Plant capacity / production hours
= 40,872 (Mg/yr) / 8,000 (hr/yr)
= 5.109 (Mg/hr)

To calculate fluorspar input

= Hydrofluoric acid production x stoichiometric ratio / average acid-grade spar
= 5.109 (Mg/hr) x 0.885 (kg CaF_2/kg HF)/0.442 (kg CaF_2/kg fluors)
= 10.23 (Mg/hr)

To calculate uncontrolled emission rates

= Controlled emissions / (1 - control efficiency)
= 9.53 (kg/hr) / (1 - .99)
= 953 (kg/hr)

To calculate uncontrolled emission factors

= Uncontrolled emissions / fluorspar input
= 953 (kg/hr) / 10.23 (kg/hr)
= 93.16 (kg spar/Mg HF)

To calculate controlled emission factors

= Uncontrolled emission factor x (1 - control efficiency)
= 93.16 x .01
= 0.9316 (kg spar/Mg HF)

Similar calculations are done for the other three plants. The average controlled emission factor of 0.32 kg/Mg and the uncontrolled emission factor of 31.8 kg/Mg are then computed.

TABLE 4.2-3 (METRIC UNITS)
PARTICULATE EMISSION DATA OF SPAR HANDLING SILOS FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (Mg/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (kg/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (kg/Mg)	Controlled Emission Factors (kg/Mg)
1	40,872	8,000	9.53	99	93.2	0.93
2	18,165	8,000	0.0454	99	0.998	0.010
3	90,827	8,000	6.80	99	30.0	0.30
4	45,413	8,000	0.363	99	3.20	0.32
Avg.					31.8	0.32

TABLE 4.2-3 (ENGLISH UNITS)
PARTICULATE EMISSION DATA OF SPAR HANDLING SILOS FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (ton/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (lbs/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (lb/ton)	Controlled Emission Factor (lb/ton)
1	45,000	8,000	21	99	187	1.9
2	20,000	8,000	0.1	99	2.00	0.020
3	100,000	8,000	15	99	60.0	0.60
4	50,000	8,000	0.8	99	6.00	0.060
Avg.					64.0	0.64

The emission factor calculated from the average of the three plants during transfer operations was 2.05 kg/Mg (4.1 lb/ton). This value was discarded because it was considered too low. Instead, according to the hand-written calculations contained in the EPA Background File, an undocumented estimate of 1 kg/Mg (2 lb/ton) each was made for loading, unloading, and fugitive emissions. Thus, the emission factor for transfer operations was reported at 3.0 kg/Mg (6 lb/ton).

4.3 NONCRITERIA POLLUTANT EMISSIONS DATA

Hazardous Air Pollutants.

The emission factor for hydrogen fluoride, a Title III Hazardous Air Pollutant, has not been updated in the current revision due to a lack of new source tests. The emission factor for hydrogen fluoride, rated "D" in the previous section (February 1980), was lowered to "E." This rating was lowered because the previous section referenced a point scale rating system that does not comply to the current, accepted rating system discussed in Section 3.2. Data in Reference 1, which were used to calculate emission factors in the previous section (February 1980), were gathered from plant visits and contacts with the industry. Therefore, this reference was rated "D" because the data presented did not come from an emission test. Reference 1 presented production capacity, control efficiency, and controlled emission rates for two plants, as shown in Table 4.3-1. This information was used to calculate the emission factor for hydrogen fluoride, as shown below:

In an example calculation for plant 1, it is assumed that there were 8000 production hours in a year. The derivation is as follows:

To calculate hydrofluoric acid production

= Plant capacity / production hours
= 40,872 (Mg/yr) / 8,000 (hr/yr)
= 5.109 (Mg/hr)

To calculate uncontrolled emission rates

= Controlled emissions / (1 - control efficiency)
= 0.36 (kg/hr) / (1 - .99)
= 36 (kg/hr)

To calculate uncontrolled emission factors

= Uncontrolled emissions / hydrofluoric acid production
= 36 (kg/hr) / 5.109 (Mg/hr)
= 7.05 (kg HAP/Mg HF)

To calculate controlled emission factors

= Uncontrolled emission factor x (1 - control efficiency)
= 7.05 x .01
= 0.0705 (kg HAP/Mg HF)

Similar calculations are done for the other plant and an average of controlled and uncontrolled emission factors are computed. According to the EPA Background File, the hydrofluoric emission factor was considered low in the previous section (February 1980), only 0.5 percent of production. Another, more acceptable emission factor of 12.5 kg/Mg was found in Reference 4 and was used to replace the result calculated from Reference 1.

Global Warming Gases.

Pollutants such as methane, carbon dioxide, and N_2O have been found to contribute to overall global warming. No data on emissions of methane and N_2O were found for the hydrofluoric acid production process. As discussed in Sections 2.2 and 2.3, small amounts of CO_2 are emitted from the hydrofluoric acid production process. However, no quantitative data were available. Therefore, a CO_2 emission factor could not be developed for this revision.

TABLE 4.3-1 (METRIC UNITS)
HYDROGEN FLUORIDE EMISSION DATA FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (Mg/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (kg/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (kg/Mg)	Controlled Emission Factors (kg/Mg)
1	40,872	8,000	0.36	99	7.05	0.070
3	90,827	8,000	0.36	99	3.17	0.032
Average					5.11	0.051

TABLE 4.3-1 (ENGLISH UNITS)
HYDROGEN FLUORIDE EMISSION DATA FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (ton/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (lb/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (lb/ton)	Controlled Emission Factors (lb/ton)
1	45,000	8,000	0.8	99	14.2	0.14
3	100,000	8,000	0.8	99	6.40	0.064
Average					10.3	0.10

Silicon Tetrafluoride.

The silicon tetrafluoride emission factor for hydrofluoric acid manufacturing has not been updated in the current revision due to a lack of new source tests. The emission factor for silicon tetrafluoride, rated "D" in the previous section (February 1980), was lowered to "E." This rating was lowered because the previous section referenced a point scale rating system that does not comply with the current, accepted rating system discussed in Section 3.2. Data in Reference 1, which were used to calculate emission factors in the previous section (February 1980), were gathered from plant visits and contacts with the industry. Therefore, this reference was rated "D" because the data presented did not come from original source tests. Reference 1 presented production capacity, control efficiency, and controlled emission rates as shown in Table 4.3-2. The emission factor was calculated from the given production capacity, control efficiency, and controlled emission rate for one plant as shown in Table 4.3-2. This information was used to calculate the emission factor for silicon tetrafluoride, as shown below.

In the example calculation for Plant 2, it is assumed that there were 8000 production hours in a year. The derivation is as follows:

To calculate hydrofluoric acid production

= Plant capacity / production hours
= 18,165 (Mg/yr) / 8,000 (hr/yr)
= 2.27 (Mg/hr)

To calculate uncontrolled emission rates

= Controlled emissions / (1 - control efficiency)
= 0.36 (kg/hr) / (1 - .99)
= 36 (kg/hr)

To calculate uncontrolled emission factors

= Uncontrolled emissions / hydrofluoric acid production
= 36 (kg/hr) / 2.27 (Mg/hr)
= 15.9 (SiF_4 kg /Mg HF)

To calculate controlled emission factors

= Uncontrolled emission factor x (1 - control efficiency)
= 15.9 x .01
= 0.159 (SiF_4 kg /Mg HF)

TABLE 4.3-2 (METRIC UNITS)
SILICON TETRAFLUORIDE EMISSION DATA FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (Mg/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (kg/hr)	Control Efficiency (%)	Uncontrolled Emission Factor (kg/Mg)	Controlled Emission Factor (kg/Mg)
2	18,165	8,000	0.36	99	15.9	0.159

TABLE 4.3-2 (ENGLISH UNITS)
SILICON TETRAFLUORIDE EMISSION DATA FOR HYDROFLUORIC ACID MANUFACTURE[1]

Plant	1975 Capacity (ton/yr)	Assumed Production Hours (hr/yr)	Controlled Emission Rates (lb/hr)	Control Efficiency (%)	Uncontrolled Emission Factors (lb/ton)	Controlled Emission Factor (lb/ton)
2	20,000	8,000	0.8	99	32	0.32

Ozone Depletion Gases.

Chlorofluorocarbons have been found to contribute to ozone depletion. No data on emissions of these pollutants were found for the hydrofluoric acid production process.

4.4 DATA GAP ANALYSIS

As discussed in Section 2.4, PES contacted ten sources of information to obtain updated process descriptions and emission data. From those contacted, a response was received from only one source. The emission factors were downgraded to "E" in this revision because they were each calculated from one source, Reference 1, which contains data based on plant visits and contacts with the industry. This reference was rated "D" because the data presented was not based on an original source test, as discussed in Chapter 3.

Pacific Environmental Services received one emission test report from Atochem North America, Inc., in Calvert City, Kentucky. Unfortunately, this report lacks production rate data and could not be used for the revision of the emission factors.

The Chemical Manufacturers' Association agreed to provide emission information currently being gathered by the ChemStar Panel on Hydrofluoric Acid. They assured PES that the ChemStar Panel had compiled a selection of more recent emission tests and process descriptions, which would aid in the revision of AP-42. Unfortunately, this information has not been received to date.

TABLE 4.4-1

LIST OF CONVERSION FACTORS

Multiply:	**by:**	**To obtain:**
mg/dscm	4.37×10^{-4}	gr/dscf
m^2	10.764	ft^2
acm/min	35.31	acfm
m/s	3.281	ft/s
kg/hr	2.205	lb/hr
kPa	1.45×10^{-1}	psia
kg/Mg	2.0	lb/ton
Mg	1.1023	ton

Temperature conversion equations:

Fahrenheit to Celsius:

$$^{\circ}C = \frac{(^{\circ}F - 32)}{1.8}$$

Celsius to Fahrenheit:

$$^{\circ}F = 1.8(^{\circ}C) + 32$$

4.5 REFERENCES FOR CHAPTER 4

1. Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture, EPA-450/3-78-109, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1978.

2. "Hydrofluoric Acid," Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 9, Interscience Publishers, New York, 1965.

3. W.R. Rogers and K. Muller, "Hydrofluoric Acid Manufacture," Chemical Engineering Progress, 59(5):85-8, May 1963.

4. J.M. Robinson, et al., Engineering and Cost Effectiveness Study of Fluoride Emissions Control, Vol. 1, PB 207 506, National Technical Information Service, Springfield, VA, 1972.

5. "Fluorine," Encyclopedia of Chemical Processing and Design, Vol. 23, Marcel Dekker, Inc., New York, 1985.

6. "Fluorine Compounds, Inorganic," Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 10, John Wiley & Sons, New York, 1980.

APPENDIX A.

AP-42 SECTION 5.8

[Not presented here. See instead current AP-42 Section 8.7]