

8.7 Hydrofluoric Acid

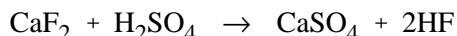
8.7.1 General⁵⁻⁶

Hydrogen fluoride (HF) is listed as a Title III Hazardous Air Pollutant. Hydrogen fluoride is produced in 2 forms, as anhydrous hydrogen fluoride and as aqueous hydrofluoric acid. The predominant form manufactured is hydrogen fluoride, a colorless liquid or gas that fumes on contact with air and is water soluble.

Traditionally, hydrofluoric acid 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. Hydrofluoric 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.

8.7.2 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:



A typical HF plant is shown schematically in Figure 8.7-1. 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 and 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.

8.7.3 Emissions And Controls^{1-2,4}

Emission factors for various HF process operations are shown in Tables 8.7-1 and 8.7-2. Units are expressed in terms of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton). 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

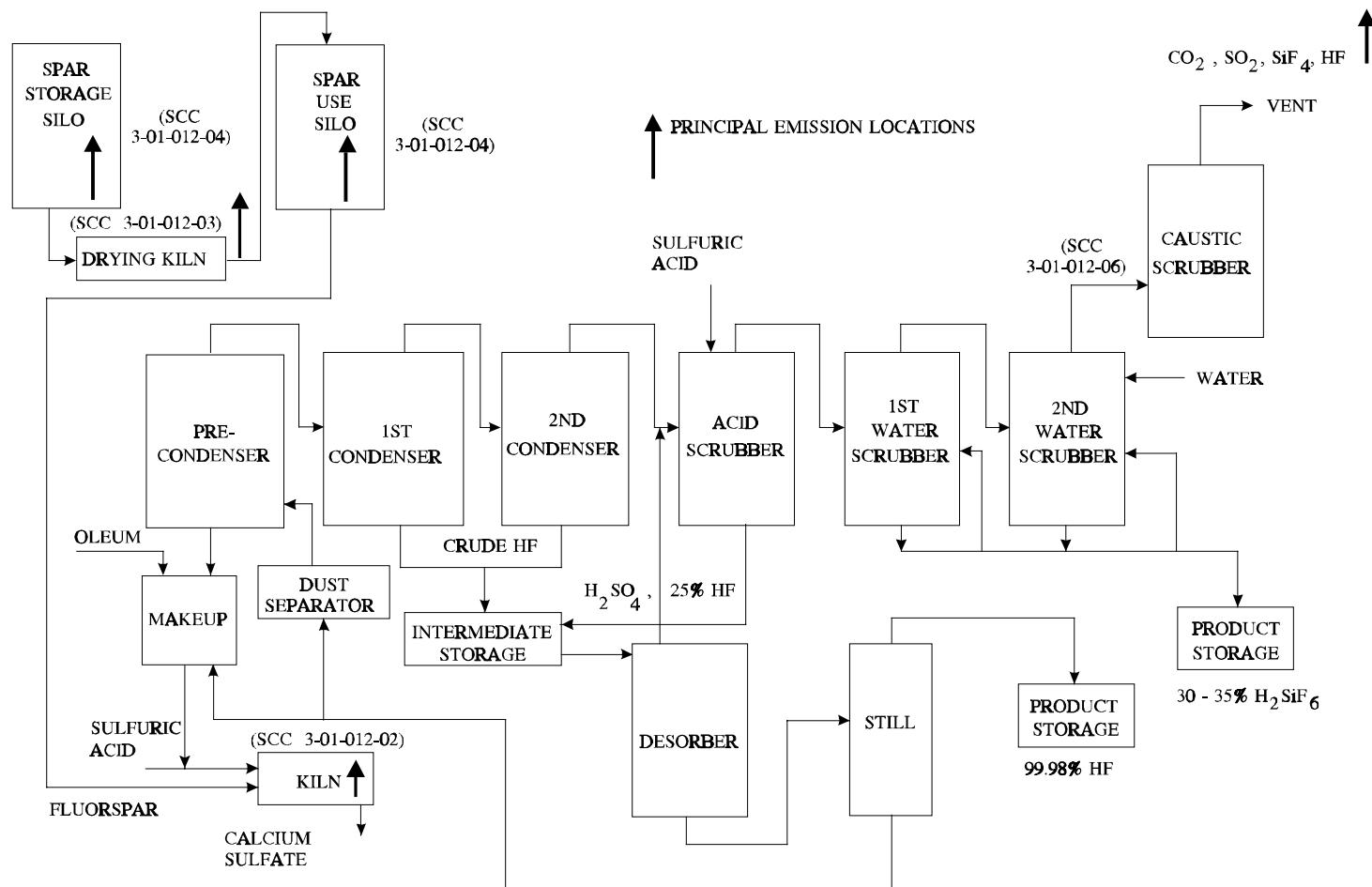


Figure 8.7-1. Hydrofluoric acid process flow diagram.
(Source Classification Codes in parentheses.)

Table 8.7-1 (Metric Units). EMISSION FACTORS FOR HYDROFLUORIC ACID MANUFACTURE^a

EMISSION FACTOR RATING: E

Operation And Controls	Control Efficiency (%)	Emissions	
		Gases	Particulate (Spar)
		kg/Mg Acid Produced	kg/Mg Fluorspar Produced
Spar drying ^b (SCC 3-01-012-03)			
Uncontrolled	0	ND	37.5
Fabric filter	99	ND	0.4
Spar handling silos ^c (SCC 3-01-012-04)			
Uncontrolled	0	NA	30.0
Fabric filter	99	NA	0.3
Transfer operations (SCC 3-01-012-05)			
Uncontrolled	0	NA	
Covers, additives	80	NA	3.0
			0.6
Tailgas ^d (SCC 3-01-012-06)			
Uncontrolled	0	12.5 (HF) 15.0 (SiF ₄) 22.5 (SO ₂)	ND ND ND
Caustic scrubber	99	0.1 (HF) 0.2 (SiF ₄) 0.3 (SO ₂)	ND ND ND

^a SCC = Source Classification Code. ND = no data. NA = not applicable.

^b Reference 1. Averaged from information provided by 4 plants. Hourly fluorspar input calculated from reported 1975 year capacity, assuming stoichiometric amount of calcium fluoride and 97.5% content in fluorspar. Hourly emission rates calculated from reported baghouse controlled rates. Values averaged are as follows:

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

^c Reference 1. Four plants averaged for silo emissions, 2 plants for transfer operations emissions.

^d Three plants averaged from Reference 1. Hydrogen fluoride and SiF₄ factors from Reference 4.

Table 8.7-2 (English Units). EMISSION FACTORS FOR HYDROFLUORIC ACID MANUFACTURE^a

EMISSION FACTOR RATING: E

Operation And Control	Control Efficiency (%)	Emissions	
		Gases	Particulate (Spar)
		lb/ton Acid Produced	lb/ton Fluorspar Produced
Spar drying ^b (SCC 3-01-012-03)			
Uncontrolled	0	ND	75.0
Fabric filter	99	ND	0.8
Spar handling silos ^c (SCC 3-01-012-04)			
Uncontrolled	0	NA	60.0
Fabric Filter	99	NA	0.6
Transfer operations (SCC 3-01-012-05)			
Uncontrolled	0	NA	6.0
Covers, additives	80	NA	1.2
Tailgas ^d (SCC 3-01-012-06)			
Uncontrolled	0	25.0 (HF) 30.0 (SiF ₄) 45.0 (SO ₂)	ND ND ND
Caustic scrubber	99	0.2 (HF) 0.3 (SiF ₄) 0.5 (SO ₂)	ND ND ND

^a SCC = Source Classification Code. ND = no data. NA = not applicable.

^b Reference 1. Averaged from information provided by 4 plants. Hourly fluorspar input calculated from reported 1975 year capacity, assuming stoichiometric amount of calcium fluoride and 97.5% content in fluorspar. Hourly emission rates calculated from reported baghouse controlled rates. Values averaged are as follows:

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

^c Reference 1. Four plants averaged for silo emissions, 2 plants for transfer operations emissions.

^d Three plants averaged from Reference 1. Hydrogen fluoride and SiF₄ factors from Reference 4.

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, SiF₄, SO₂, and CO₂ 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.

References For Section 8.7

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*, Interscience Publishers, New York, 1965.
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5. "Fluorine", *Encyclopedia Of Chemical Processing And Design*, Marcel Dekker, Inc., New York, 1985.
6. "Fluorine Compounds, Inorganic", *Kirk-Othmer Encyclopedia Of Chemical Technology*, John Wiley & Sons, New York, 1980.