8.9 Phosphoric Acid

8.9.1 General[1-2]

Phosphoric acid (H_3PO_4) is produced by 2 commercial methods: wet process and thermal process. Wet process phosphoric acid is used in fertilizer production. Thermal process phosphoric acid is of a much higher purity and is used in the manufacture of high grade chemicals, pharmaceuticals, detergents, food products, beverages, and other nonfertilizer products. In 1987, over 9 million megagrams (Mg) (9.9 million tons) of wet process phosphoric acid was produced in the form of phosphorus pentoxide (P_2O_5). Only about 363,000 Mg (400,000 tons) of P_2O_5 was produced from the thermal process. Demand for phosphoric acid has increased approximately 2.3 to 2.5 percent per year.

The production of wet process phosphoric acid generates a considerable quantity of acidic cooling water with high concentrations of phosphorus and fluoride. This excess water is collected in cooling ponds that are used to temporarily store excess precipitation for subsequent evaporation and to allow recirculation of the process water to the plant for re-use. Leachate seeping is therefore a potential source of groundwater contamination. Excess rainfall also results in water overflows from settling ponds. However, cooling water can be treated to an acceptable level of phosphorus and fluoride if discharge is necessary.

8.9.2 Process Description[3-5]

8.9.2.1 Wet Process Acid Production -

In a wet process facility (see Figure 8.9-1A and Figure 8.9-1B), phosphoric acid is produced by reacting sulfuric acid (H_2SO_4) with naturally occurring phosphate rock. The phosphate rock is dried, crushed, and then continuously fed into the reactor along with sulfuric acid. The reaction combines calcium from the phosphate rock with sulfate, forming calcium sulfate ($CaSO_4$), commonly referred to as gypsum. Gypsum is separated from the reaction solution by filtration. Facilities in the U. S. generally use a dihydrate process that produces gypsum in the form of calcium sulfate with 2 molecules of water (H_2O) ($CaSO_4 \bullet 2\ H_2O$ or calcium sulfate dihydrate). Japanese facilities use a hemihydrate process that produces calcium sulfate with a half molecule of water ($CaSO_4 \bullet \frac{1}{2}\ H_2O$). This one-step hemihydrate process has the advantage of producing wet process phosphoric acid with a higher P_2O_5 concentration and less impurities than the dihydrate process. Due to these advantages, some U. S. companies have recently converted to the hemihydrate process. However, since most wet process phosphoric acid is still produced by the dihydrate process, the hemihydrate process will not be discussed in detail here. A simplified reaction for the dihydrate process is as follow:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3[CaSO_4 \bullet 2H_2O]\downarrow \quad (1)$$

In order to make the strongest phosphoric acid possible and to decrease evaporation costs, 93 percent sulfuric acid is normally used. Because the proper ratio of acid to rock in the reactor is critical, precise automatic process control equipment is employed in the regulation of these 2 feed streams.

During the reaction, gypsum crystals are precipitated and separated from the acid by filtration. The separated crystals must be washed thoroughly to yield at least a 99 percent recovery of the filtered phosphoric acid. After washing, the slurried gypsum is pumped into a gypsum pond for

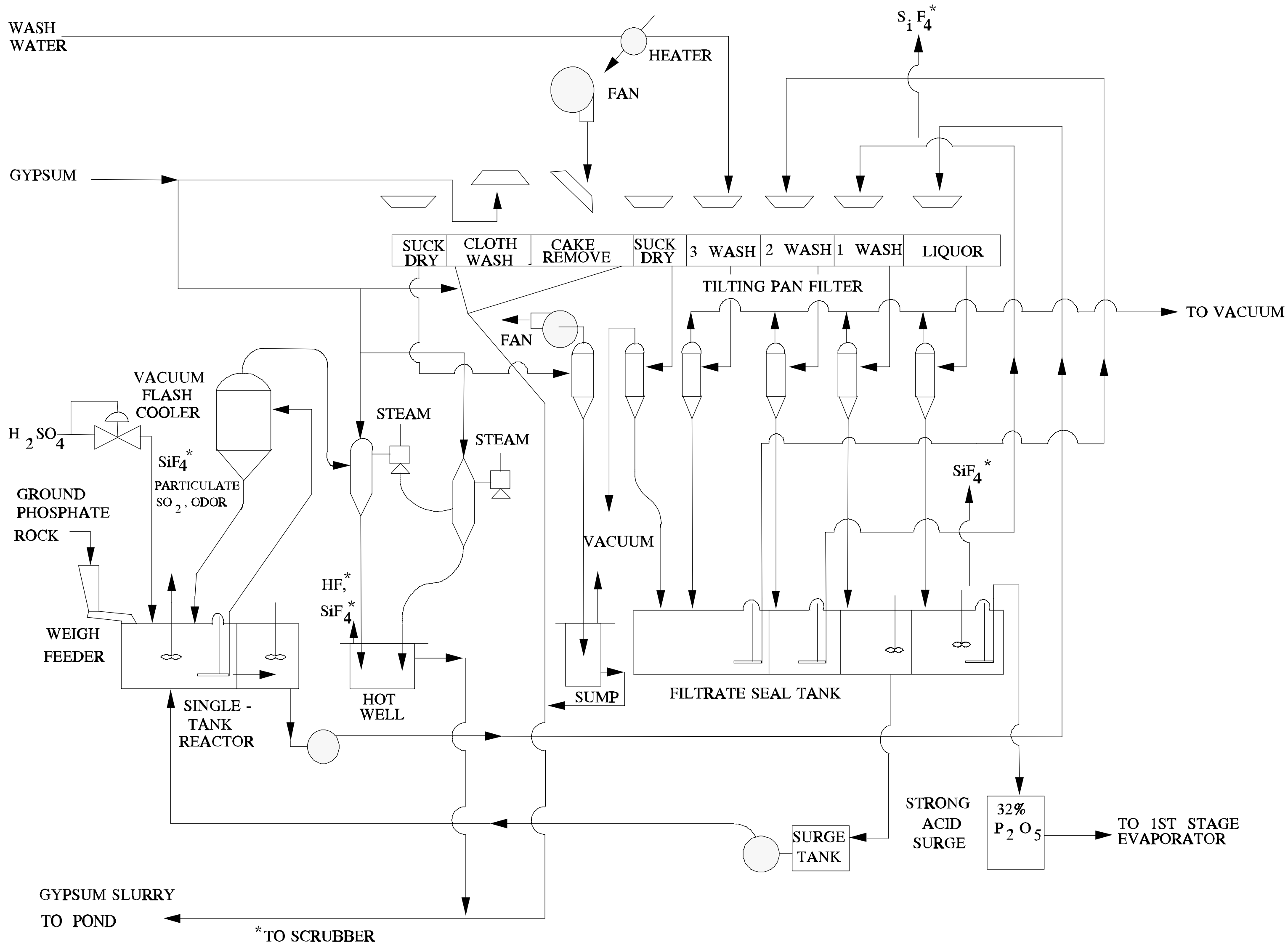

Figure 8.9-1A. Flow diagram of a wet process phosphoric acid plant.

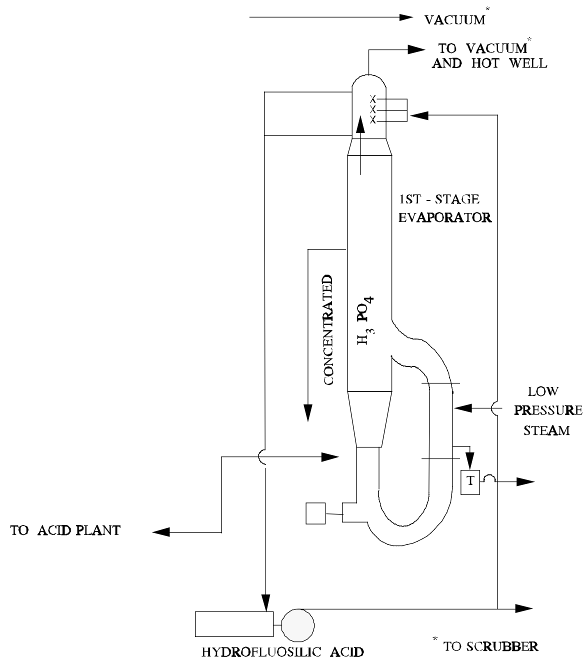

Figure 8.9-1B. Flow diagram of a wet process phosphoric acid plant (cont.).

storage. Water is syphoned off and recycled through a surge cooling pond to the phosphoric acid process. Approximately 0.3 hectares of cooling and settling pond area is required for every megagram of daily P_2O_5 capacity (0.7 acres of cooling and settling pond area for every ton of daily P_2O_5 capacity).

Considerable heat is generated in the reactor. In older plants, this heat was removed by blowing air over the hot slurry surface. Modern plants vacuum flash cool a portion of the slurry, and then recycle it back into the reactor.

Wet process phosphoric acid normally contains 26 to 30 percent P_2O_5. In most cases, the acid must be further concentrated to meet phosphate feed material specifications for fertilizer production. Depending on the types of fertilizer to be produced, phosphoric acid is usually concentrated to 40 to 55 percent P_2O_5 by using 2 or 3 vacuum evaporators.

8.9.2.2 Thermal Process Acid Production -

Raw materials for the production of phosphoric acid by the thermal process are elemental (yellow) phosphorus, air, and water. Thermal process phosphoric acid manufacture, as shown schematically in Figure 8.9-2, involves 3 major steps: (1) combustion, (2) hydration, and (3) demisting.

In combustion, the liquid elemental phosphorus is burned (oxidized) in ambient air in a combustion chamber at temperatures of 1650 to 2760°C (3000 to 5000°F) to form phosphorus pentoxide (Reaction 2). The phosphorus pentoxide is then hydrated with dilute H_3PO_4 or water to produce strong phosphoric acid liquid (Reaction 3). Demisting, the final step, removes the phosphoric acid mist from the combustion gas stream before release to the atmosphere. This is usually done with high-pressure drop demistors.

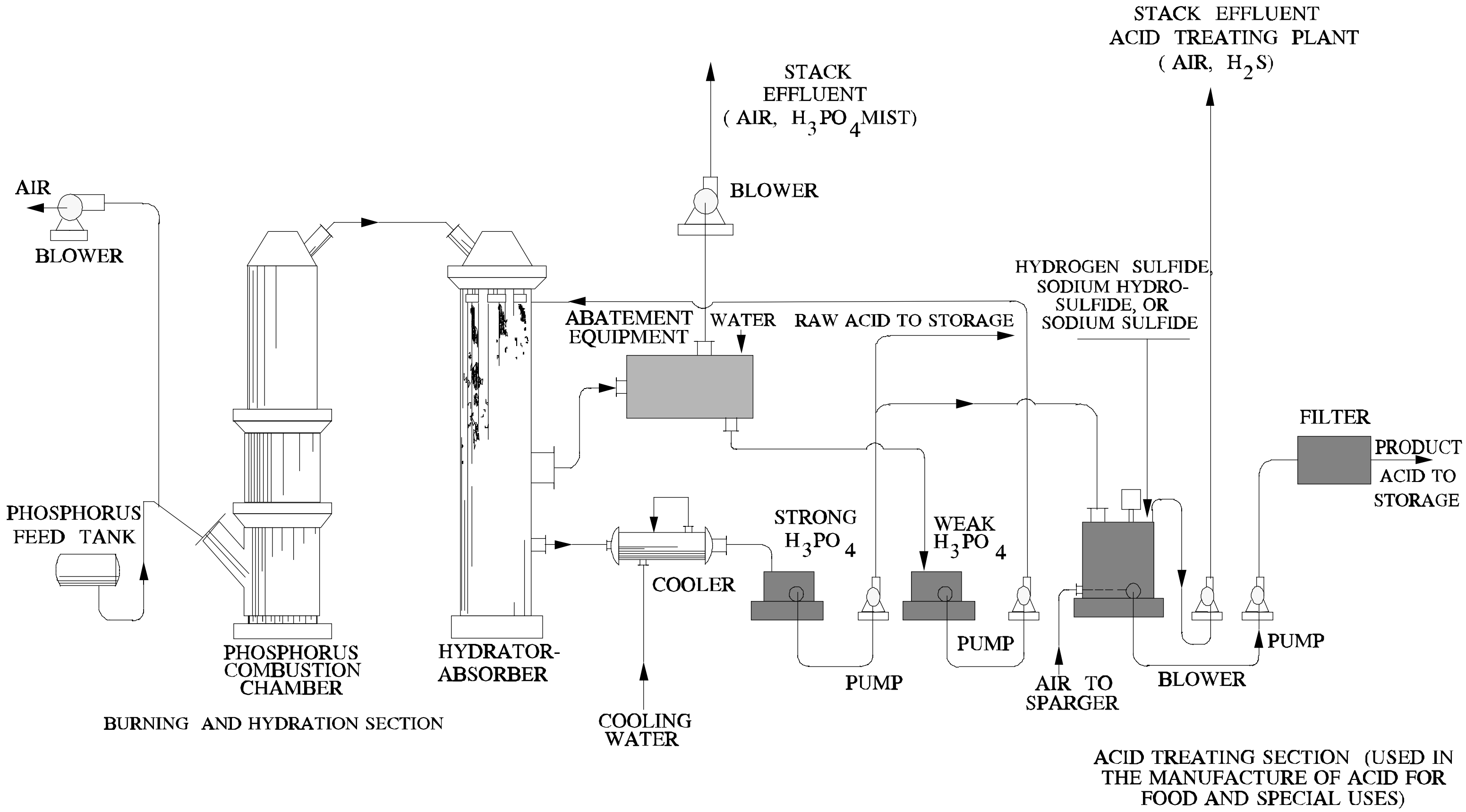

Figure 8.9-2. Flow diagram of a thermal process phosphoric acid plant.

$$P_4 + 5O_2 \rightarrow 2P_2O_5 \quad (2)$$

$$2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4 \quad (3)$$

Concentration of H_3PO_4 produced from thermal process normally ranges from 75 to 85 percent. This high concentration is required for high grade chemical production and other nonfertilizer product manufacturing. Efficient plants recover about 99.9 percent of the elemental phosphorus burned as phosphoric acid.

8.9.3 Emissions And Controls[3-6]

Emission factors for controlled and uncontrolled wet phosphoric acid production are shown in Tables 8.9-1 and 8.9-2, respectively. Emission factors for controlled thermal phosphoric acid production are shown in Table 8.9-3.

8.9.3.1 Wet Process -

Major emissions from wet process acid production includes gaseous fluorides, mostly silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF). Phosphate rock contains 3.5 to 4.0 percent fluorine. In general, part of the fluorine from the rock is precipitated out with the gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporized in the reactor or evaporator. The relative quantities of fluorides in the filter acid and gypsum depend on the type of rock and the operating conditions. Final disposition of the volatilized fluorine depends on the design and operation of the plant.

Scrubbers may be used to control fluorine emissions. Scrubbing systems used in phosphoric acid plants include venturi, wet cyclonic, and semi-cross-flow scrubbers. The leachate portion of the fluorine may be deposited in settling ponds. If the pond water becomes saturated with fluorides, fluorine gas may be emitted to the atmosphere.

The reactor in which phosphate rock is reacted with sulfuric acid is the main source of emissions. Fluoride emissions accompany the air used to cool the reactor slurry. Vacuum flash cooling has replaced the air cooling method to a large extent, since emissions are minimized in the closed system.

Acid concentration by evaporation is another source of fluoride emissions. Approximately 20 to 40 percent of the fluorine originally present in the rock vaporizes in this operation.

Total particulate emissions from process equipment were measured for 1 digester and for 1 filter. As much as 5.5 kilograms of particulate per megagram (kg/Mg) (11 pounds per ton [lb/ton]) of P_2O_5 were produced by the digester, and approximately 0.1 kg/Mg (0.2 lb/ton) of P_2O_5 were released by the filter. Of this particulate, 3 to 6 percent were fluorides.

Particulate emissions occurring from phosphate rock handling are discussed in Section 11.21, Phosphate Rock Processing.

8.9.3.2 Thermal Process -

The major source of emissions from the thermal process is H_3PO_4 mist contained in the gas stream from the hydrator. The particle size of the acid mist ranges from l.4 to 2.6 micrometers. It is not uncommon for as much as half of the total P_2O_5 to be present as liquid phosphoric acid particles suspended in the gas stream. Efficient plants are economically motivated to control this potential loss

Table 8.9-1 (Metric And English Units). CONTROLLED EMISSION FACTORS FOR WET PHOSPHORIC ACID PRODUCTION[a]

EMISSION FACTOR RATING: B (except as noted)

Source	Fluorine	
	kg/Mg P_2O_5 Produced	lb/ton P_2O_5 Produced
Reactor[b] (SCC 3-01-016-01)	1.9×10^{-3}	3.8×10^{-3}
Evaporator[c] (SCC 3-01-016-99)	0.022×10^{-3}	0.044×10^{-3}
Belt filter[c] (SCC 3-01-016-99)	0.32×10^{-3}	0.64×10^{-3}
Belt filter vacuum pump[c] (SCC 3-01-016-99)	0.073×10^{-3}	0.15×10^{-3}
Gypsum settling & cooling ponds[d,e] (SCC 3-01-016-02)	Site-specific	Site-specific

[a] SCC = Source Classification Code.
[b] References 8-13. EMISSION FACTOR RATING: A
[c] Reference 13.
[d] Reference 18. Site-specific. Acres of cooling pond required: ranges from 0.04 hectare per daily Mg (0.10 acre per daily ton) P_2O_5 produced in the summer in the southeastern U. S. to 0 in the colder locations in the winter months when the cooling ponds are frozen.
[e] Reference 19 states "Based on our findings concerning the emissions of fluoride from gypsum ponds, it was concluded than no investigator had as yet established experimentally the fluoride emission from gypsum ponds".

Table 8.9-2 (Metric And English Units). UNCONTROLLED EMISSION FACTORS FOR WET PHOSPHORIC ACID PRODUCTION[a]

EMISSION FACTOR RATING: C (except as noted)

Source	Nominal Percent Control Efficiency	Fluoride	
		kg/Mg P_2O_5 Produced	lb/ton P_2O_5 Produced
Reactor[b] (SCC 3-01-016-01)	99	0.19	0.38
Evaporator[c] (SCC 3-01-016-99)	99	0.00217	0.0044
Belt filter[c] (SCC 3-01-016-99)	99	0.032	0.064
Belt filter vacuum pump[c] (SCC 3-01-016-99)	99	0.0073	0.015
Gypsum settling & cooling ponds[d,e] (SCC 3-01-016-02)	ND	Site-specific	Site-specific

[a] SCC = Source Classification Code. ND = No Data.
[b] References 8-13. EMISSION FACTOR RATING: B.
c Reference 13.
[d] Reference 18. Site specific. Acres of cooling pond required: ranges from 0.04 hectare per daily Mg (0.10 acre per daily ton) P_2O_5 produced in the summer in the southeastern U. S. to 0 in the colder locations in the winter months when the cooling ponds are frozen.
[e] Reference 19 states "Based on our findings concerning the emissions of fluoride from gypsum ponds, it was concluded than no investigator had as yet established experimentally the fluoride emission from gypsum ponds".

Table 8.9-3 (Metric And English Units). CONTROLLED EMISSION FACTORS FOR THERMAL PHOSPHORIC ACID PRODUCTION[a]

EMISSION FACTOR RATING: E

Source	Nominal Percent Control Efficiency	Particulate[b]	
		kg/Mg P_2O_5 Produced	lb/ton P_2O_5 Produced
Packed tower (SCC 3-01-017-03)	95.5	1.07	2.14
Venturi scrubber (SCC 3-01-017-04)	97.5	1.27	2.53
Glass fiber mist eliminator (SCC 3-01-017-05)	96 - 99.9	0.35	0.69
Wire mesh mist eliminator (SCC 3-01-017-06)	95	2.73	5.46
High pressure drop mist (SCC 3-01-017-07)	99.9	0.06	0.11
Electrostatic precipitator (SCC 3-01-017-08)	98 - 99	0.83	1.66

[a] SCC = Source Classification Code.
[b] Reference 6.

with various control equipment. Control equipment commonly used in thermal process phosphoric acid plants includes venturi scrubbers, cyclonic separators with wire mesh mist eliminators, fiber mist eliminators, high energy wire mesh contractors, and electrostatic precipitators.

References For Section 8.9

1. "Phosphoric Acid", *Chemical And Engineering News*, March 2, 1987.

2. *Sulfuric/Phosphoric Acid Plant Operation*, American Institute Of Chemical Engineers, New York, 1982.

3. P. Becker, *Phosphates And Phosphoric Acid, Raw Materials, Technology, And Economics Of The Wet Process*, 2nd Edition, Marcel Dekker, Inc., New York, 1989.

4. *Atmospheric Emissions From Wet Process Phosphoric Acid Manufacture*, AP-57, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1970.

5. *Atmospheric Emissions From Thermal Process Phosphoric Acid Manufacture*, AP-48, U. S. Environmental Protection Agency, Research Triangle Park, NC, October 1968.

6. *Control Techniques For Fluoride Emissions*, Unpublished, U. S. Public Health Service, Research Triangle Park, NC, September 1970.

7. *Final Guideline Document: Control Of Fluoride Emissions From Existing Phosphate Fertilizer Plants*, EPA-450/2-77-005, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1977.

8. *Summary Of Emission Measurements—East Phos Acid*, International Minerals And Chemical Corporation, Polk County, FL, August 1990.

9. *Summary Of Emission Measurements—East Phos Acid*, International Minerals And Chemical Corporation, Polk County, FL, February 1991.

10. *Summary Of Emission Measurements—East Phos Acid*, International Minerals And Chemical Corporation, Polk County, FL, August 1991.

11. *Source Test Report*, Seminole Fertilizer Corporation, Bartow, FL, September 1990.

12. *Source Test Report*, Seminole Fertilizer Corporation, Bartow, FL, May 1991.

13. *Stationary Source Sampling Report, Texasgulf Chemicals Company, Aurora, NC*, Entropy Environmentalists, Inc., Research Triangle Park, NC, December 1987.

14. *Stationary Source Sampling Report, Texasgulf Chemicals Company, Aurora, NC*, Entropy Environmentalists, Inc., Research Triangle Park, NC, March 1987.

15. *Sulfur Dioxide Emissions Test, Phosphoric Acid Plant, Texasgulf Chemicals Company, Aurora, NC*, Entropy Environmentalists, Inc., Research Triangle Park, NC, August 1988.

16. *Stationary Source Sampling Report, Texasgulf Chemicals Company, Aurora, NC*, Entropy Environmentalists, Inc., Research Triangle Park, NC, August 1987.

17. *Source Test Report, FMC Corporation, Carteret, NJ*, Princeton Testing Laboratory, Princeton, NJ, March 1991.

18. A. J. Buonicore and W. T. Davis, eds., *Air Pollution Engineering Manual*, Van Nostrand Reinhold, New York, 1992.

19. *Evaluation Of Emissions And Control Techniques For Reducing Fluoride Emission From Gypsum Ponds In The Phosphoric Acid Industry*, EPA-600/2-78-124, U. S. Environmental Protection Agency, Cinncinnati, OH, 1978.