

[Note: with the publication of the Fifth Edition of AP-42, the Chapter and Section number for Phosphoric Acid changed to 8.9.]

BACKGROUND REPORT

AP-42 SECTION 5.11

PHOSPHORIC ACID

Prepared for

**U.S. Environmental Protection Agency
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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, NC 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 (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 and 11 test reports to support revision of emission factors for the phosphoric acid industry.

Including the introduction (Chapter 1), this report contains four chapters. Chapter 2 gives a description of the phosphoric acid 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 phosphoric acid manufacturing.

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 details criteria and noncriteria pollutant emission factor development. It includes the review of specific data sets and the results of a data gap analysis. Appendix A presents AP-42 Section 5.11.

2.0 INDUSTRY DESCRIPTION

2.1 GENERAL^{1,2,3}

Phosphoric acid (H_3PO_4) can be manufactured using either a thermal or a wet process; however, the majority of phosphoric acid, approximately 96 percent, is produced using the wet process method. Wet process phosphoric acid is used for fertilizer production. Thermal process phosphoric acid is commonly used in the manufacture of high grade chemicals, which require a much higher purity. 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 which are used to temporarily store excess precipitation for subsequent evaporation and to allow recirculation of the process water to the plant for re-use.

There are about 25 phosphoric acid plants currently operating in seven states with production capacity ranging from 160 to 1,500 thousand megagrams (180 to 1,700 thousand tons) per year.¹ The majority of the facilities are located in the Southeast. Florida has 15 phosphoric acid plants, the most of any state. Louisiana has the second highest total with three plants, followed by Idaho and Mississippi with two plants each. Wyoming, Texas, and North Carolina each have one facility. Table 2.1-1 gives the distribution of phosphoric acid plants by state with 1991 production capacity. Approximately 11.6 million megagrams (12.8 million tons) of phosphoric acid were produced in the U.S. in 1991.¹

**TABLE 2.1-1
DISTRIBUTION OF WET PHOSPHORIC ACID PLANTS
BY STATE WITH 1991 CAPACITY^a**

State	Facility name/location	Total capacity (10 ³ tons/yr)
Florida	Agrico Chemical, Pierce	450
	Bartow Chem, Bartow	b
	Cargill Fertilizer, Inc., Tampa	750
	CF Industries, Inc., Bartow	540
	CF Industries, Inc. Plant City	940
	Conserv, Inc., Nichols	260
	Consolidated Minerals, Piney Point	b
	Farmland Industries, Inc., Pierce	600
	W.R. Grace, Bartow	b
	IMC Fertilizer, Inc., New Wales	1,700
	Oxychem Ag Products, Inc., White Springs	1,120
	Royster, Mulberry	320
	Royster, Piney Point	230
	Seminole Fertilizer Corp., Bartow	720
U.S. Agri-Chemicals, Fort Meade	500	
Idaho	Nu-West Industries, Conda	280
	J.R. Simplot Co., Pocatello	380
Louisiana	Agrico Chemical, Donaldsonville	510
	Agrico Chemical, Uncle Sam	880
	Arcadian Corporation, Geismar	180
Mississippi	Mississippi Phosphate Corp., Pascagoula	b
	Nu-South Industries, Pascagoula	b
North Carolina	Texasgulf Chemicals Co., Lee Creek	1,270
Texas	Mobil Mining & Minerals, Pasadena	255
Wyoming	Chevron Chemical Co., Rock Springs	225

^a Reference 1.

^bThe production capacity data for 1991 are not available.

2.2 PROCESS DESCRIPTION^{5,6}

Wet Process Acid Production

In a wet process facility (shown schematically in Figures 2.2-1a and 2.2-1b), phosphoric acid is produced by reacting sulfuric acid (H₂SO₄) 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 (CaSO₄), 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 two molecules of water (CaSO₄ • 2H₂O or calcium sulfate dihydrate). Japanese facilities use a hemihydrate process which produces calcium sulfate with a half molecule of water (CaSO₄ • ½ H₂O). This one-step hemihydrate process has the advantage of producing wet process phosphoric acid with a higher P₂O₅ 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 follows:

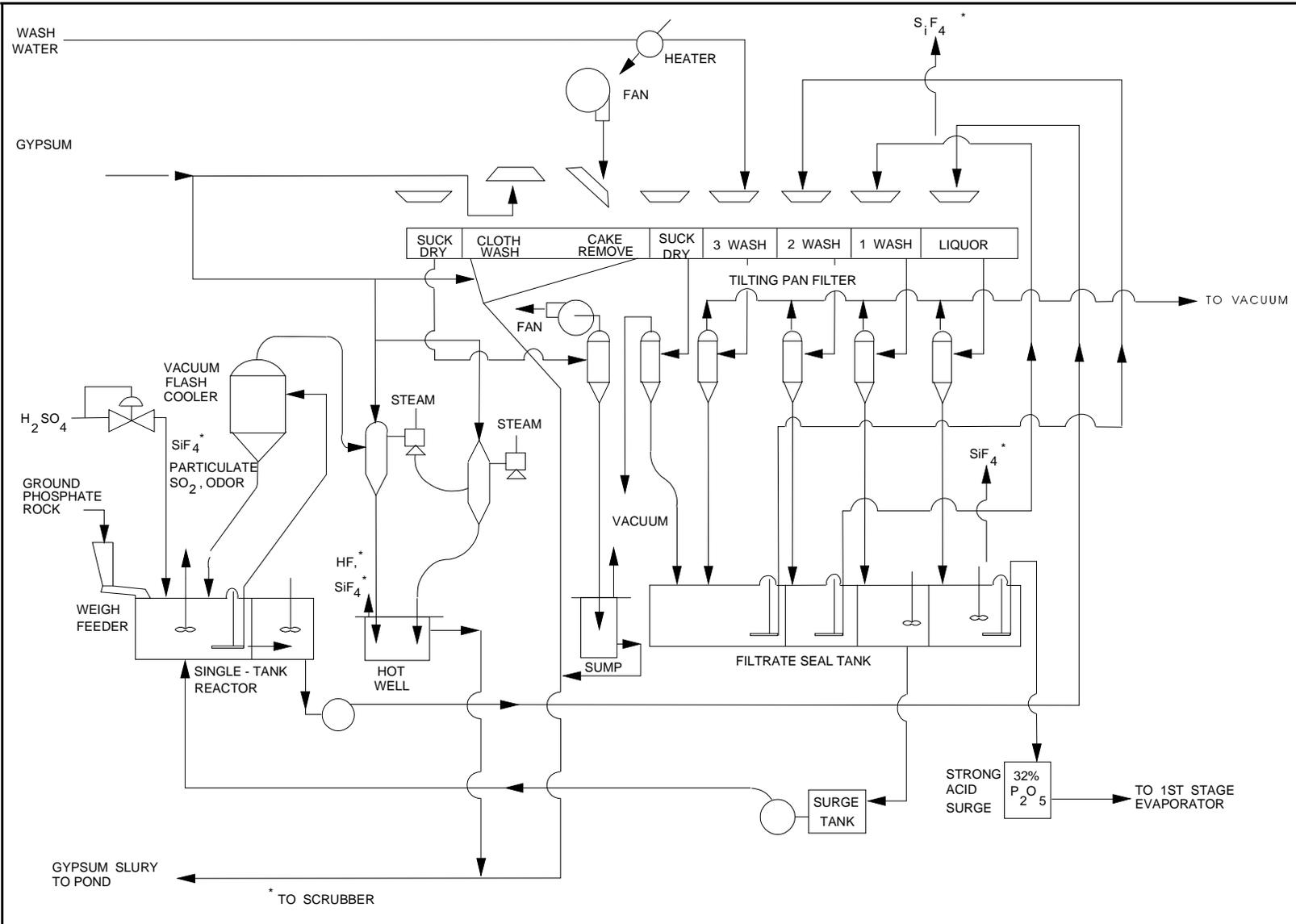


In order to make the strongest phosphoric acid possible and to decrease evaporation costs, 93 percent sulfuric acid is normally used. Because the proper ratio of acid to rock in the reactor is critical, precise automatic process control equipment is employed in the regulation of these two feed streams.

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 storage. Water is siphoned off and recycled through a surge cooling pond to the phosphoric acid process. Approximately 0.7 acres of cooling and settling pond area is required for every ton of daily P₂O₅ 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.

Figure 2.2-1a Flow diagram of a wet process phosphoric acid plant



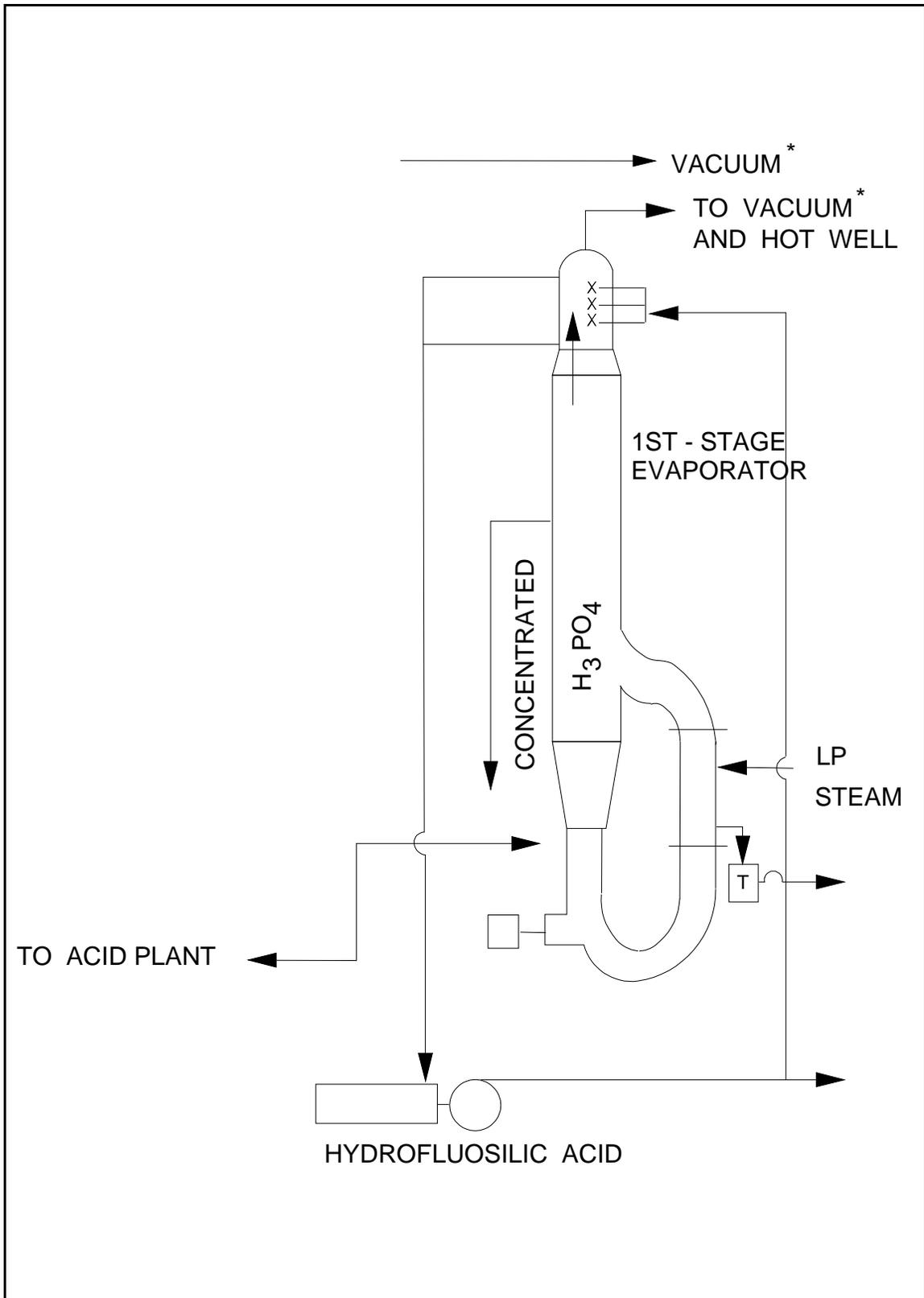


Figure 2.2-1b Flow diagram of a wet process phosphoric acid plant (continued)

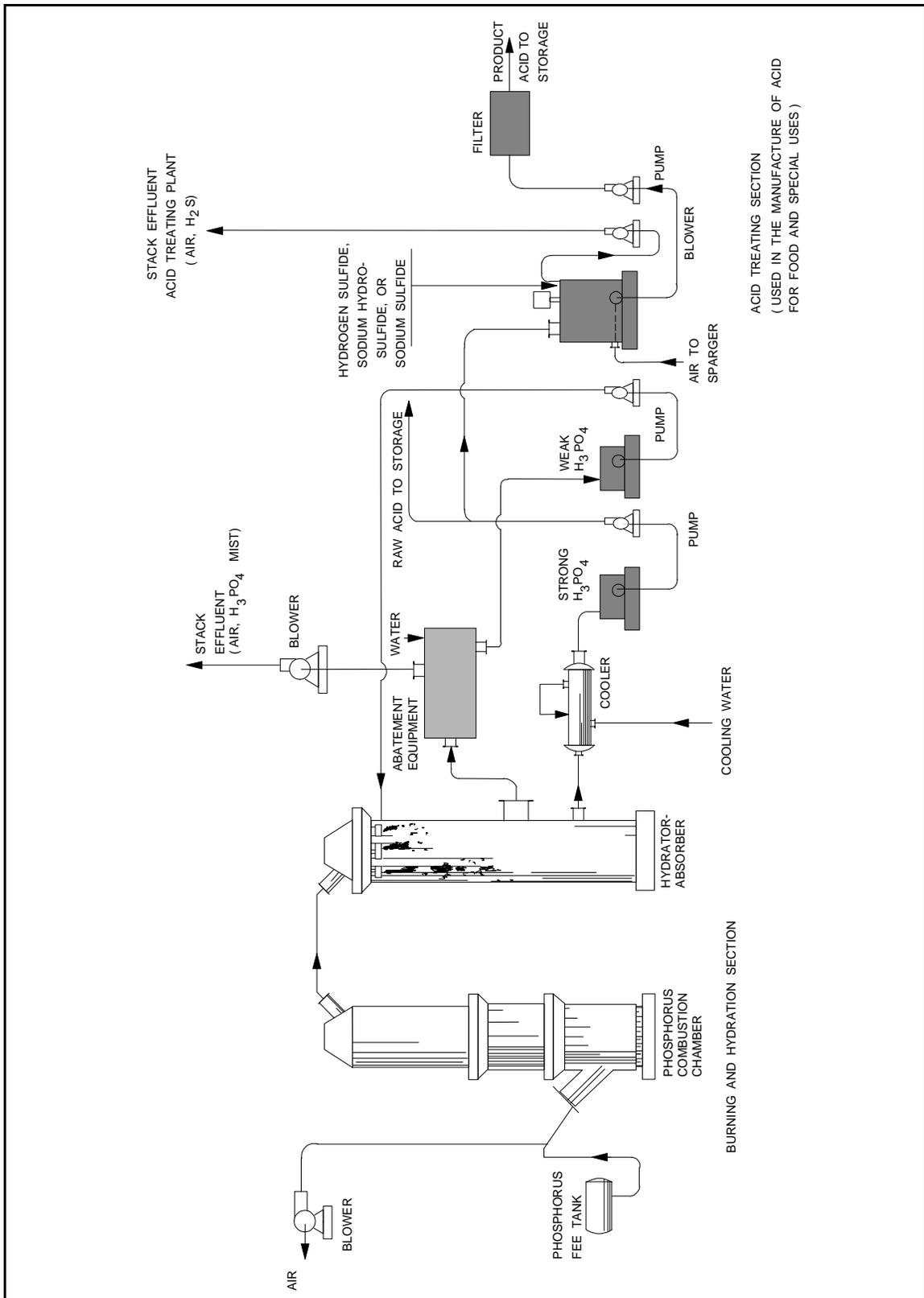


Figure 2.2-2 Flow diagram of a thermal process phosphoric acid plant

Wet process phosphoric acid normally contains 26 to 30 percent P₂O₅. 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 P₂O₅ by using two or three vacuum evaporators.

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 2.2-2, involves three 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 as shown in Reaction 2 below. The phosphorus pentoxide is then hydrated with dilute phosphoric acid (H₃PO₄) or water to produce strong phosphoric acid liquid as shown in Reaction 3 below. 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 demisters.



Concentration of phosphoric acid (H₃PO₄) produced from the thermal process normally ranges from 75 to 85 percent. This 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.

2.3 EMISSIONS AND CONTROLS⁵⁻⁷

Wet Process Emissions and Controls

Gaseous fluorides such as silicon tetrafluoride (SiF₄) and hydrogen fluoride (HF) are major emissions from wet process acid production. Phosphate rock contains 3.5 to 4.0 percent fluorine. Part of the fluorine from the rock is precipitated 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 fluoride depends on the design and operation of the plant.

Scrubbers may be used to control fluoride emissions. Scrubbing systems used in phosphoric acid plants include venturi, wet cyclonic, and semi-cross flow scrubbers. The leachate portion of the fluoride 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. Particulate matter can be emitted directly from process equipment. About three to six percent of the particulate can be fluorides, as measured for one digester and filter. Particulate emissions occurring from phosphate rock handling are discussed in Section 8.18 of AP-42, "Phosphate Rock Processing."

Thermal Process Emissions and Controls

The major source of emissions from the thermal process is phosphoric acid mist (H_3PO_4) contained in the gas stream from the hydrator. The particle size of the acid mist ranges from 1.4 to 2.6 micrometers (μm). It is not uncommon for most of the total phosphorus pentoxide (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 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 (ESP).

2.4 REVIEW OF REFERENCES FOR CHAPTER 2

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) Cargill Fertilizer, Inc., Riverview, FL

- 2) Florida Department of Environmental Regulation, Tallahassee, FL
- 3) Idaho Department of Health and Welfare, Boise, ID
- 4) J.R. Simplot Co., Pocatello, ID
- 5) New Jersey Department of Environmental Protection, Trenton, NJ
- 6) North Carolina Department of Environment, Health, and Natural Resources, Raleigh, NC
- 7) Nu-West Industries, Soda Springs, ID
- 8) Texasgulf, Inc., Aurora, NC
- 9) Tennessee Valley Authority, Muscle Shoals, AL

Responses were received from Sources 2, 3, 5, 6, and 9. The Florida Department of Environmental Regulation (Source #2) provided three source tests from IMC Fertilizer, Inc., in Mulberry, Florida, and two source tests from Seminole Fertilizer Corporation in Bartow, Florida. The Idaho Department of Health and Welfare (Source #3) provided one source test from Nu-West Industries, Soda Springs, Idaho. The New Jersey Department of Environmental Protection (Source #5) provided one source test from the FMC Corporation in Carteret, New Jersey. The North Carolina Department of Environmental Health and Natural Resources (Source #6) provided four source tests from Texasgulf, Inc., in Aurora, North Carolina. These source tests are discussed in detail in Chapter 4.0 of this background report.

The Tennessee Valley Authority (Source #9) provided a 1991 report entitled "North American Fertilizer Capacity Data," from which PES obtained current phosphoric acid production statistics.

Reference 1 "North American Fertilizer Capacity Data"

Provided current phosphoric acid production statistics for wet process plants.

Reference 2 "Phosphoric Acid"

A new reference which provided general information regarding current phosphoric acid manufacturing practices.

Reference 3 "Sulfuric/Phosphoric Acid Plant Operation"

A new reference which provided general information regarding current phosphoric acid manufacturing practices.

Reference 4 "Phosphates and Phosphoric Acid, Raw Materials, Technology, and Economics of the Wet Process"

A new reference which provided general information regarding current phosphoric acid manufacturing practices including information on the hemihydrate process to which some U.S. facilities have recently converted.

References 5 through 8

Cited in the previous version of section 5.11 (February 1980).

Reference 9 "Phosphoric Acid Manufacturing"

An unpublished chapter from Air Pollution Engineering Manual (AP-40), was obtained from Gordan F. Palm and Associates in Lakeland, Florida. This reference was used to support the omission of a fluoride emission factor from gypsum settling and cooling ponds. This is discussed in detail in Chapter 4.

Reference 10 Evaluation of Emissions and Control Techniques for Reducing Fluoride Emission from Gypsum Ponds in the Phosphoric Acid Industry

Cited in the draft AP-40 and was obtained from the EPA Environmental Research Center Library in RTP, NC. This reference was used to support the omission of a fluoride emission factor from gypsum settling and cooling ponds. This is discussed in detail in Chapter 4.0 of this background report.

2.5 REFERENCES FOR CHAPTER 2.0

1. North American Fertilizer Capacity Data, Tennessee Valley Authority, Muscle Shoals, AL, December 1991.
2. Phosphoric Acid, Chemical and Engineering News, Volume 65, Number 9, p. 22, March 2, 1987.
3. Sulfuric/Phosphoric Acid Plant Operation, American Institute of Chemical Engineers, New York, 1982.
4. P. Becker, Phosphates and Phosphoric Acid, Raw Materials, Technology, and Economics of the Wet Process, 2nd Edition, Marcel Dekker, Inc., New York, 1989.
5. Atmospheric Emissions from Wet Process Phosphoric Acid Manufacture, AP-57, National Air Pollution Control Administration, Raleigh, NC, April 1970.
6. Atmospheric Emissions from Thermal Process Phosphoric Acid Manufacture, AP-48, National Air Pollution Control Administration, Durham, NC, October 1968.
7. Control Techniques for Fluoride Emissions, Unpublished, U.S. Public Health Service, Research Triangle Park, NC, September 1970.
8. Control Techniques for Particulate Emissions from Stationary Sources - Volume 1, EPA-450/3-81-005a, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1982.
9. Gordon F. Palm, Phosphoric Acid Manufacturing, unpublished draft Air Pollution Engineering Manual (AP-40), Air & Waste Management Association, Pittsburgh, PA, January 1992.
10. 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, Research Triangle Park, NC, 1978.

3.0 GENERAL EMISSION DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING

The first step of this investigation involved a search of available literature relating to criteria and noncriteria pollutant emissions associated with phosphoric acid. This search included the following references:

AP-42 background files maintained by the Emission Factor and Methodologies Section.

PES obtained the background file for the previous version of the AP-42 Section 5.11 (February 1980.)

EPA Library and local university libraries. PES conducted a literature search from which three new references were obtained (Reference 2, 3, and 4 in Chapter 2 of this report.)

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. For example, a technical paper was not included if the original study was contained in the previous document.
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 (e.g., one-page reports were generally rejected).

If no primary data were found and the previous update utilized secondary data, the secondary data were still used and the Emission Factor Rating lowered, if needed. A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria. The final set of reference materials is given in Chapter 4.0.

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. The following data were always excluded from consideration.

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods (e.g., comparison of the EPA Method 5 front-half with the EPA Method 5 front- and back-half);
3. Test series of controlled emissions for which the control device is not specified;
4. Test series in which the source process is not clearly identified and described; and
5. Test series in which it is not clear whether the emissions were measured before or after the control device.

Data sets that were not excluded were 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

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

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

C

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

D

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 industry. 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 4.0 of this report.

3.4 REFERENCES FOR CHAPTER 3.0

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. Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources, Supplement A, Appendix C.2, "Generalized Particle Size Distributions." U.S. Environmental Protection Agency, October 1986.

4.0 POLLUTANT EMISSION FACTOR DEVELOPMENT

The previous version of AP-42 Section 5.11 (February 1980), contained controlled and uncontrolled wet process fluorine emission factors and controlled thermal process particulate emission factors. The wet process uncontrolled fluoride emission factors were based on the following references:

- Atmospheric Emissions from Wet Process Phosphoric Acid Manufacture, AP-57, National Air Pollution Control Administration, Raleigh, NC, April 1970.
- Control Techniques for Fluoride Emissions, Unpublished, U.S. Public Health Service, Research Triangle Park, NC, September 1970.

Both of these documents are over 20 years old and are secondary references, not original source tests. Only the first reference, the AP-57 document, was available during this revision.

Furthermore, no handwritten calculations were contained in the EPA background file. However, a footnote in the emission factor table in the previous version of AP-42, section 5.11 states that the emission factors were "based on a material balance of fluorine from phosphate rock of 3.9% fluorine and 33% P₂O₅." These values were most likely obtained from page 10 of the AP-57 document which states that "commercial phosphate rock usually contains 31 to 35.5 percent P₂O₅. Fluorine content is usually in the 3.5 to 4 percent range." Furthermore, page 1 of the AP-57 document states that "half of [the fluorine] may be volatilized in the processing." Hence, the total amount of fluorine emitted per ton of P₂O₅ was most likely calculated as follows:

$$\frac{1}{2} \times \frac{0.039 \text{ lbs } F}{0.33 \text{ lbs } P_2O_5} \times \frac{2000 \text{ lbs } P_2O_5}{1 \text{ ton } P_2O_5} = 118 \text{ lbs } F \text{ per ton } P_2O_5$$

In the previous version of Section 5.11, the fluorine emission factors from the reactor (56.4 lbs F per ton P₂O₅), condenser (61.2 lbs F per ton P₂O₅), and from the settling and cooling ponds (1.12 lbs F per ton P₂O₅), total approximately 118 lbs F per ton P₂O₅. The rationale for the distribution of emissions among the three sources is unclear.

During this revision, 11 new source tests were received. Unfortunately, the only fluorine emissions data contained in these tests were reported as controlled. Ideally, uncontrolled emissions data are used for emission factor development. However, due to the fact that the emission factors in the previous revision are based only on a material balance, coupled with assumptions from 20 year old documents (e.g., "half of [the fluorine] may be volatilized in the processing"), PES has used the controlled data to develop new uncontrolled emission factors by

applying a nominal control efficiency to "back-calculate" from the controlled factors. The calculations are presented in Section 4.3 of this background report.

The controlled wet process fluoride emission factor in the previous version of Section 5.11 (0.02 - 0.07 lb per ton of P₂O₅) was obtained from the following reference:

- Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, U.S. EPA, Research Triangle Park, NC, March 1977.

Page 5-12 of this document contains the following paragraph:

"Almost all existing wet-process phosphoric acid plants are equipped to treat the reactor and filter gases. A large number of installations also vent sumps, hotwells, and storage tanks to controls. Typical emissions range from 0.02 to 0.07 pounds of fluoride per ton of P₂O₅ input, however, emission factors as high as 0.60 pounds fluoride per ton P₂O₅ have been reported for a few poorly controlled plants."

The controlled emission factor range appears to have been taken directly from this 1977 reference and is not based on source test data. As stated above, new source tests were received during this revision from which new controlled and uncontrolled emission factors have been developed. These calculations are presented in detail in Section 4.3.

The controlled thermal process particulate emission factors were developed from the 1970 unpublished U.S. Public Health Service report Control Techniques for Fluoride Emissions, listed above. As stated previously, this document was not contained in the background file; therefore, the controlled thermal process particulate emission factors could not be verified. Only one source test received during this revision documented emissions from a thermal process facility (Reference 10). This single test, which documents H₃PO₄ emissions, was insufficient for new emission factor development. However, the results of this test are discussed in detail in Section 4.3 of this background report. The controlled thermal process emission factors from the previous version (February 1980) were retained in this revision unchanged and unverified. However, the emission factor ratings have been downgraded from "B" to "E."

Each of the new source tests received during this revision is discussed in detail on the following pages.

4.1 REVIEW OF SPECIFIC DATA SETS

During this revision, 11 new source tests were received. The Florida Department of Environmental Regulation provided three source tests from IMC Fertilizer, Inc. in Mulberry,

Florida (References 1, 2, and 3), and two source tests from Seminole Fertilizer Corporation in Bartow, Florida (References 4 and 5). The Idaho Department of Health and Welfare provided one source test from Nu-West Industries, Soda Springs, Idaho. Unfortunately, this source test did not meet the criteria listed in Chapter 3.0. No process description, raw analytical data, QA/QC documentation, or calibration data were contained in the report. Therefore, it could not be used to develop new emission factors and the data are not presented here. The North Carolina Department of Environment, Health, and Natural Resources provided four source tests from Texasgulf, Inc., in Aurora, North Carolina (References 6, 7, 8, and 9). The New Jersey Department of Environmental Protection provided one source test from the FMC Corporation in Carteret, New Jersey (Reference 10).

References 1, 2, and 3: Summary of Emission Measurements - East Phos Acid. IMC Corp., Mulberry, Florida. August 1990, February 1991, August 1991.

References 1, 2, and 3 are source tests measuring controlled fluoride emissions from a wet scrubber in a phosphate fertilizer facility in Mulberry, Florida. At this facility, phosphoric acid is produced as an intermediate product. Production rates are reported as tons of P_2O_5 input per day. The fluoride emissions are reported as pounds of fluoride per day. Assuming that the facility was operating 24 hours per day, the average controlled fluoride emission factors from References 1, 2, and 3 are 0.00508, 0.0108, and 0.00382 pounds of fluoride per ton of P_2O_5 input, respectively. All three of these controlled emission factors are below the controlled emission factor range of 0.02 to 0.07 lb F per ton P_2O_5 reported in the previous version of Section 5.11. These tests were performed in accordance with EPA Reference Method 13B, contain all field data, and have consistent results, and are thus rated "A." These test results are presented in Table 4.3-3 and are discussed in Section 4.3 of this background report.

References 4 and 5: Source Test Reports, Seminole Fertilizer Corporation, Bartow, Florida. September 1990 and May 1991.

References 4 and 5 report fluoride emissions from a packed crossflow scrubber at a phosphate fertilizer company in Bartow, Florida. At this facility, phosphoric acid is produced as an intermediate product. Fluoride emissions are reported as pounds per hour, and production rates are presented as tons of P_2O_5 input per hour. Assuming that the facility was operating 24 hours per day, the average controlled fluoride emission factors from References 4 and 5 are 0.00497 and 0.00795 pounds of fluoride per ton of P_2O_5 input, respectively. Both of these

controlled emission factors are below the controlled emission factor range of 0.02 to 0.07 lb F per ton P₂O₅ reported in the previous version of Section 5.11. These tests were performed in accordance with EPA Reference Method 13B, contain all field data, have consistent results, and are thus rated "A." These test results are presented in Table 4.3-3 and are discussed in Section 4.3 of this background report.

Reference 6: Stationary Source Sampling Report, Texasgulf Chemicals Company, Aurora, NC. Entropy Environmentalists, Inc., Research Triangle Park, NC. December 1987.

This facility produces phosphoric acid for fertilizers from raw ore. Four units were tested at the crossflow scrubber, cyclonic scrubber, and the belt filter vacuum pump stack scrubber. EPA sampling Method 13B was used to measure fluoride emissions. Production rates were reported as tons of P₂O₅ input per day and fluoride emissions were reported as pounds of fluoride per ton of P₂O₅. From the handwritten calculations presented in this reference, it is assumed that the facility was a 24 hour continuous operation, the hourly production rates (tons P₂O₅ input per hour) were calculated by dividing the daily production rate (tons P₂O₅ input per day) by 24 hours. The hourly fluoride emission rates (lb F per hour) were calculated by multiplying the fluoride per ton of P₂O₅ by the hourly production rate (tons P₂O₅ input per hour). This test was performed in accordance with EPA Reference Method 13B, contains all necessary documentation for validation, has consistent results, and is thus rated "A." The test results are presented in Table 4.3-3 and are discussed in Section 4.3 of this background report.

Reference 7: Sulfur Dioxide Emission Test, Phosphoric Acid Plant and Super Phosphoric Acid Plant, Texasgulf Chemicals, Aurora, NC. Performed by Entropy Environmentalist, Inc., Research Triangle Park, NC. August 1988.

This facility produces phosphoric acid for fertilizers from raw ore. The crossflow scrubbers were tested for SO₂ emissions at four different units. EPA Reference Method 6 was used to determine the SO₂ emissions. Units 1, 2, and 4 processed calcined ore; Unit No. 3 processed uncalcined ore. The production rate was reported as tons P₂O₅ input per day and SO₂ emission rates were reported as lb per day. From the handwritten calculations presented in this reference, it is assumed that the facility operates 24 hours a day, the SO₂ emission factors were calculated to be 0.139, 0.143, 0.327, and 0.103 lb/ton, for Units 1, 2, 3, and 4, respectively. The previous version of Section 5.11 (February 1980) did not include emission factors for SO₂. Due to the fact that this was the only source test received which targeted SO₂ emissions, emission

factors were not developed for this revision. However, the data are presented in Section 4.2 for information purposes. This test was performed in accordance with EPA Reference Method 6, contains all necessary documentation for validation, has consistent results, and is thus rated "A." The results of this test are presented in Table 4.2-1 and discussed in Section 4.2 of this background report.

Reference 8: Stationary Source Sampling Report, Texasgulf Chemicals Company, Aurora, NC. Entropy Environmentalists, Inc., Research Triangle Park, NC. August 1987.

This source test was performed using EPA Reference Method 16 to determine the total reduced sulfur emissions reported as hydrogen sulfide (H_2S). Two units were tested: Unit No. 1, which processes calcined ore, and Unit No. 4, which processes uncalcined ore. Both units were tested at the same points: the belt filter fume scrubber, belt filter vacuum pump, and the crossflow fume scrubber. The emission rates were reported as lbs H_2S per hour, and the production rate was reported as tons P_2O_5 input per day. From the handwritten calculations presented in this reference, it is assumed that this facility operates 24 hours a day, the emission factors for Unit No. 1 for the belt filter fume scrubber, belt filter vacuum pump, and the crossflow fume scrubber were calculated to be 0.0177, 0.0518, and 5.60 lb H_2S per ton P_2O_5 input, respectively. The emission factors for Unit 4 for the belt filter fume scrubber, belt filter vacuum pump, and the crossflow fume scrubber were calculated to be 0.00161, 0.000578, and 0.115 lb H_2S per ton P_2O_5 input, respectively. No explanation was provided in the report concerning the fact that the emissions from Unit No. 4 were significantly less than the emissions from Unit No. 1. Even though the emissions between units vary, the individual runs for each unit are consistent. Furthermore, this test was performed in accordance with EPA Reference Method 16 and contains all necessary documentation for validation, and is thus rated "A." Hydrogen sulfide emission factors were not reported in the previous version of Section 5.11 (February 1980.) Due to the fact that only two source tests from the same facility were received during this revision, H_2S emission factors were not developed. However, the data are presented in Table 4.2-1 and discussed in Section 4.2 of this background report for information purposes.

Reference 9: Stationary Source Sampling Report, Texasgulf Chemicals Company, Aurora, NC. Entropy Environmentalists, Inc., Research Triangle Park, NC. March 1987.

This source test was performed using EPA Reference Method 16 to determine the total reduced sulfur emissions reported as hydrogen sulfide (H₂S). Two units were tested, Unit No. 1 which processes calcined ore, and Unit No. 3 which processes uncalcined ore. Both units were tested at the same points: the fume scrubber exhaust, the vacuum pump exhaust, and the bird filter exhaust. The emission rates were reported as lbs H₂S per hour, and the production rate was reported as tons P₂O₅ input per hour. The emission factors for Unit No. 1 for the belt filter fume scrubber, vacuum pump, and the bird filter were calculated to be 1.97, 2.04, and 0.00714 lb H₂S per ton P₂O₅ input, respectively. The emission factors for Unit No. 3 for the belt filter fume scrubber, belt filter vacuum pump, and the crossflow fume scrubber were calculated to be 0.112, 0.0125, and 0.00090 lb H₂S per ton P₂O₅ input, respectively. No explanation was provided in the report concerning the fact that the emissions from Unit No. 3 were significantly less than the emissions from Unit No. 1. Even though the emissions between units vary, the individual runs for each unit are consistent. Furthermore, this test was performed in accordance with EPA Reference Method 16 and contains all necessary documentation for validation, and is thus rated "A." As previously stated, hydrogen sulfide emission factors were not reported in the previous version of Section 5.11 (February 1980.) Due to the fact that only two source tests from the same facility were received during this revision, H₂S emission factors were not developed. However, the data are presented in Table 4.3-1 and discussed in Section 4.3 of this background report for information purposes.

Reference 10: Source Test Report. FMC Corporation, Carteret, NJ. Princeton Testing Laboratory, Princeton, NJ. March 1991.

The process tested was a meta furnace (meta is a polymer of phosphoric acid). The control device is an acid mist eliminator. This type of furnace is rarely used in the phosphoric acid industry, and this is the only test report received on the meta furnace. The production rate is reported as pounds of phosphorous fed per hour. FMC has deemed the production rate confidential; therefore, the production rate and emission factors have been omitted in this report. The confidential information in the report has been placed in the PES and EPA Confidential Business Information (CBI) files. A modified EPA Method 5 was used to measure the phosphoric acid (H₃PO₄) mist from the acid mist eliminator. The average H₃PO₄ emission rate from the acid mist eliminator was calculated to be 0.000028 tons per hour. The previous version

of Section 5.11 (February 1980) did not include an emission rate for H_3PO_4 . Due to the fact that the production rates in this reference are considered confidential, a H_3PO_4 emission factor could not be developed for this revision. However, the emission rates are presented in Table 4.3-2 and discussed in Section 4.3 for information purposes. This test was performed in accordance with a modified EPA Method 5, contains all necessary documentation for validation, has consistent results, and is thus rated "A."

4.2 CRITERIA POLLUTANT EMISSIONS DATA

No data on emissions of volatile organic compounds, lead, nitrogen oxides, particulate or carbon monoxide were found nor expected for the phosphoric acid production process. H_3PO_4 mist is considered a particulate, but it is discussed as phosphoric acid in section 4.3 of this background report. The remaining criteria pollutant, sulfur dioxide, is discussed below.

Sulfur dioxide.

One source test (Reference 7) was received containing emission data for sulfur dioxide (SO_2). This facility produces phosphoric acid for fertilizers from raw ore. The crossflow scrubbers were tested for SO_2 emissions at four different units. EPA Reference Method 6 was used to determine the SO_2 emissions. Units 1, 2, and 4 processed calcined ore; Unit No. 3 processed uncalcined ore. The production rate was reported as tons P_2O_5 input per day and SO_2 emission rates were reported as pounds per day. Assuming the facility operates 24 hours per day, the SO_2 emission factors were calculated to be 0.139, 0.143, 0.327, and 0.103 kg (SO_2) per Mg (P_2O_5) input for Units 1, 2, 3, and 4, respectively. The previous version of Section 5.11 (February 1980) did not include emission factors for SO_2 . Due to the fact that this was the only source test received, SO_2 emission factors were not developed for this revision. However, the data are presented in Table 4.2-1 below for information purposes. This test was performed in accordance with EPA Reference Method 6, contains all necessary documentation for validation, has consistent results, and is thus rated "A."

**TABLE 4.2-1 (METRIC UNITS)
SULFUR DIOXIDE**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Crossflow scrubber						
7 Unit No. 1 Calcined Ore	B	6	1	39.1	2.93	0.0749
			2	38.8	2.64	0.0680
			3	38.8	2.54	0.0655
			Average	38.9	2.70	0.0695
Control device: Crossflow scrubber						
7 Unit No. 2 Calcined Ore	B	6	1	34.1	2.94	0.0865
			2	34.2	2.22	0.0650
			3	34.5	2.19	0.0635
			Average	34.3	2.45	0.0715
Control device: Crossflow scrubber						
7 Unit No. 3 Uncalcined Ore	B	6	1	44.0	8.35	0.190
			2	39.8	5.62	0.142
			3	37.6	5.94	0.159
			Average	40.5	6.67	0.164
Control device: Crossflow scrubber						
7 Unit No. 4 Calcined Ore	B	6	1	29.0	1.52	0.0525
			2	28.1	1.32	0.0471
			3	28.0	1.53	0.0545
			Average	28.4	1.46	0.0515

^aUnits in Mg (P₂O₅) input per hr.

^bUnits in kg (SO₂) per hr.

^cUnits in kg (SO₂) per Mg (P₂O₅) input.

**TABLE 4.2-1 (ENGLISH UNITS)
SULFUR DIOXIDE**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Crossflow scrubber						
7 Unit No. 1 Calcined Ore	B	6	1	43.1	6.47	0.150
			2	42.8	5.81	0.136
			3	42.8	5.61	0.131
			Average	42.9	5.96	0.139
Control device: Crossflow scrubber						
7 Unit No. 2 Calcined Ore	B	6	1	37.6	6.49	0.173
			2	37.7	4.90	0.130
			3	38.0	4.82	0.127
			Average	37.8	5.41	0.143
Control device: Crossflow scrubber						
7 Unit No. 3 Uncalcined Ore	B	6	1	48.5	18.4	0.380
			2	43.9	12.4	0.284
			3	41.5	13.1	0.317
			Average	44.6	14.7	0.327
Control device: Crossflow scrubber						
7 Unit No. 4 Calcined Ore	B	6	1	32.0	3.34	0.105
			2	31.0	2.92	0.0941
			3	30.9	3.37	0.109
			Average	31.3	3.21	0.103

^aUnits in tons (P₂O₅) input per hr.

^bUnits in lb (SO₂) per hr.

^cUnits in lb (SO₂) per ton (P₂O₅) input.

4.3 NONCRITERIA POLLUTANT EMISSIONS DATA

Hazardous Air Pollutants.

Hazardous air pollutants (HAPs) are defined in Title III of the 1990 Clean Air Act Amendments. Hydrogen sulfide (H₂S) is classified as a HAP and may be emitted from the phosphoric acid manufacturing process. Two source tests (References 8 and 9) were received during this revision of Section 5.11 that document H₂S emissions from the manufacture of phosphoric acid. Both tests were performed in accordance with EPA Reference Method 16 and contain all necessary documentation for validation, and are thus rated "A." Hydrogen sulfide emission factors were not reported in the previous version of Section 5.11 (February 1980.) Due to the fact that only two source tests from the same facility were received during this revision, H₂S emission factors were not developed. However, the data are presented in Table 4.3-1 for information purposes.

Global Warming Gases

Pollutants such as methane (CH₄), carbon dioxide (CO₂), and nitrous oxide (N₂O) have been found to contribute to overall global warming. No data on emissions of these pollutants were found for the phosphoric acid process.

Stratospheric Ozone-Depleting Gases

Chlorofluorocarbons, halons, carbon tetrachloride, methyl chloroform and hydrofluorocarbons have been found to contribute to stratospheric ozone depletion. No data on emissions of these pollutants were found nor expected for the phosphoric acid process.

Phosphoric Acid

One source test reporting phosphoric acid (H₃PO₄) mist emissions was received during this revision. The data are presented in Table 4.3-2. Only the emission factors are reported; the production rate is considered confidential by the manufacturer. The process tested was a meta furnace (meta is a polymer of phosphoric acid). The control device is an acid mist eliminator. This type of furnace is rarely used in the phosphoric acid industry and this is the only test report received on the meta furnace. The H₃PO₄ emission factor from the acid mist eliminator was calculated to be 0.280 lb per ton. The previous version of Section 5.11 (February 1980) did not include a H₃PO₄ emission factor. Due to the fact this was the only thermal process source test received, a H₃PO₄ emission factor was not developed for this revision.

**TABLE 4.3-1 (METRIC UNITS)
TOTAL REDUCED SULFUR (as H₂S)**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Belt filter fume scrubber						
8 Unit No. 1 Calcined Ore	A	16A	1	14.42	0.146	0.0102
			2	13.7	0.126	0.0092
			3	14.71	0.107	0.0073
			Average	14.27	0.127	0.0089
Control device: Belt filter vacuum pump						
8 Unit No. 1 Calcined Ore	A	16A	1	14.91	0.413	0.0277
			2	15.12	0.372	0.0246
			3	15.63	0.397	0.025
			Average	15.22	0.394	0.0259
Control device: Crossflow fume scrubber						
8 Unit No. 1 Calcined Ore	A	16A	1	36.91	105.2	2.85
			2	37.12	102.5	2.76
			3	36.93	102.8	2.78
			Average	36.99	103.5	2.80
Control device: Belt filter fume scrubber						
8 Unit No. 4 Uncalcined Ore	A	16A	1	13.16	0.0077	0.00059
			2	13.19	0.0078	0.00059
			3	13.37	0.0165	0.00123
			Average	13.24	0.0107	0.00081
Control device: Belt filter vacuum pump						
8 Unit No. 4 Uncalcined Ore	A	16A	1	13.34	0.0045	0.00034
			2	14.62	0.0041	0.00028
			3	15.59	0.0036	0.00023
			Average	14.18	0.0041	0.00029
Control device: Crossflow fume scrubber						
8 Unit No. 4 Uncalcined Ore	A	16A	1	33.57	2.29	0.068
			2	33.67	1.78	0.053
			3	33.95	1.77	0.057
			Average	33.73	1.95	0.058

^aUnits in Mg (P₂O₅) input per hr.

^bUnits in kg (H₂S) per hr.

^cUnits in kg (H₂S) per Mg (P₂O₅) input.

TABLE 4.3-1 (METRIC UNITS) (continued)
TOTAL REDUCED SULFUR (as H₂S)

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Fume filter						
9 Unit No. 1 Calcined Ore	A	16A	1	27.18	27.94	1.02
			2	27.17	26.3	0.97
			3	27.32	26.24	0.96
			Average	27.23	26.83	0.985
Control device: Vacuum pump						
9 Unit No. 1 Calcined Ore	A	16A	1	26.94	29.87	1.11
			2	27.35	28.15	1.03
			3	27.58	25.45	0.92
			Average	27.29	27.82	1.02
Control device: Bird filter						
9 Unit No. 1 Calcined Ore	A	16A	1	25.21	0.064	0.0025
			2	25.35	0.177	0.007
			3	25.45	0.03	0.0012
			Average	25.34	0.09	0.0036
Control device: Fume scrubber						
9 Unit No. 3 Uncalcined Ore	A	16A	1	48.8	2.91	0.059
			2	48.77	2.283	0.047
			3	48.8	3.025	0.062
			Average	48.8	2.74	0.056
Control device: Vacuum pump						
9 Unit No. 3 Uncalcined Ore	A	16A	1	37.96	0.14	0.0037
			2	38.7	0.31	0.008
			3	38.44	0.269	0.007
			Average	38.37	0.24	0.0062
Control device: Bird filter						
9 Unit No. 3 Uncalcined Ore	A	16A	1	49.09	0.0146	0.0003
			2	39.44	0.0132	0.00034
			3	48.85	0.0205	0.00042
			Average	45.8	0.0161	0.0004

^aUnits in Mg (P₂O₅) input per hr.

^bUnits in kg (H₂S) per hr.

^cUnits in kg (H₂S) per Mg (P₂O₅) input.

**TABLE 4.3-1 (ENGLISH UNITS)
TOTAL REDUCED SULFUR (as H₂S)**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Belt filter fume scrubber						
8 Unit No. 1 Calcined Ore	A	16A	1	15.89	0.323	0.0203
			2	15.1	0.278	0.0184
			3	16.21	0.235	0.0145
			Average	15.73	0.280	0.0177
Control device: Belt filter vacuum pump						
8 Unit No. 1 Calcined Ore	A	16A	1	16.44	0.911	0.0554
			2	16.67	0.820	0.0491
			3	17.23	0.875	0.0508
			Average	16.78	0.869	0.0518
Control device: Crossflow fume scrubber						
8 Unit No. 1 Calcined Ore	A	16A	1	40.69	231.9	5.70
			2	40.92	225.9	5.52
			3	40.71	226.6	5.57
			Average	40.77	228.1	5.60
Control device: Belt filter fume scrubber						
8 Unit No. 4 Uncalcined Ore	A	16A	1	14.51	0.0169	0.00117
			2	14.54	0.0173	0.00119
			3	14.74	0.0363	0.00246
			Average	14.6	0.0235	0.00161
Control device: Belt filter vacuum pump						
8 Unit No. 4 Uncalcined Ore	A	16A	1	14.70	0.010	0.000680
			2	16.12	0.009	0.000558
			3	16.08	0.008	0.000497
			Average	15.63	0.009	0.000578
Control device: Crossflow fume scrubber						
8 Unit No. 4 Uncalcined Ore	A	16A	1	37.01	5.04	0.136
			2	37.12	3.93	0.106
			3	37.42	3.90	0.104
			Average	37.18	4.29	0.115

^aUnits in tons (P₂O₅) input per hr.

^bUnits in lb (H₂S) per hr.

^cUnits in lb (H₂S) per ton (P₂O₅) input.

TABLE 4.3-1 (ENGLISH UNITS) (continued)
TOTAL REDUCED SULFUR (as H₂S)

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Fume filter						
9 Unit No. 1 Calcined Ore	A	16A	1	29.98	61.60	2.05
			2	29.95	57.98	1.94
			3	30.12	57.86	1.92
			Average	30.02	59.15	1.97
Control device: Vacuum pump						
9 Unit No. 1 Calcined Ore	A	16A	1	29.7	65.85	2.22
			2	30.15	62.02	2.06
			3	30.4	56.11	1.85
			Average	30.08	61.33	2.04
Control device: Bird filter						
9 Unit No. 1 Calcined Ore	A	16A	1	27.79	0.140	0.00502
			2	27.94	0.391	0.0140
			3	28.05	0.067	0.00240
			Average	27.93	0.1993	0.00714
Control device: Fume scrubber						
9 Unit No. 3 Uncalcined Ore	A	16A	1	53.79	6.416	0.119
			2	53.76	5.032	0.0936
			3	53.79	6.669	0.124
			Average	53.78	6.039	0.112
Control device: Vacuum pump						
9 Unit No. 3 Uncalcined Ore	A	16A	1	41.84	0.308	0.00737
			2	42.66	0.684	0.0160
			3	42.37	0.592	0.0140
			Average	42.29	0.528	0.0125
Control device: Bird filter						
9 Unit No. 3 Uncalcined Ore	A	16A	1	54.11	0.0321	0.00059
			2	43.48	0.0290	0.00067
			3	53.85	0.0451	0.00084
			Average	50.48	0.0354	0.00090

^aUnits in tons (P₂O₅) input per hr.

^bUnits in lb (H₂S) per hr.

^cUnits in lb (H₂S) per ton (P₂O₅) input.

**TABLE 4.3-2 (METRIC UNITS)
PHOSPHORIC ACID**

Reference Number	Test Rating	Test Method	Run #	Production Rate	Emission Rate ^a	Emission Factor
Control device: Acid mist eliminator						
10	A	5	1	b	.0345	b
			2	b	.0159	b
			3	b	.0258	b
			Average	b	.0254	b

^aUnits in kg (H₃PO₄) per hour.

^bConfidential phosphorus feed rate.

**TABLE 4.3-2 (ENGLISH UNITS)
PHOSPHORIC ACID**

Reference Number	Test Rating	Test Method	Run #	Production Rate	Emission Rate ^a	Emission Factor
Control device: Acid mist eliminator						
10	A	5	1	b	.000038	b
			2	b	.000018	b
			3	b	.000029	b
			Average	b	.000028	b

^aUnits in tons (H₃PO₄) per hour.

^bConfidential phosphorus feed rate.

Fluoride

During this revision, six new source tests were received documenting gaseous fluoride emissions. Unfortunately, the only data contained in these tests were reported as controlled. Ideally, uncontrolled emissions data are used for emission factor development. However, due to the fact that the emission factors in the previous revision are based only on a material balance, coupled with assumptions from 20 year old documents (e.g., "half of [the fluorine] may be volatilized in the processing"), PES has used the controlled data to develop new uncontrolled emission factors by applying a nominal control efficiency to "back-calculate" from the controlled factors. The data from the six source tests are reported in Table 4.3-2.

PES also received Reference 11, the phosphoric acid manufacturing chapter of the new draft Air Pollution Engineering Manual (AP-40). This draft chapter omitted the fluoride emission factor, citing a 1978 EPA document (Reference 12), Evaluation of Emissions and Control Techniques for Reducing Fluoride Emission from Gypsum Ponds in the Phosphoric Acid Industry, which states:

"Based on our findings concerning the emissions of fluoride from gypsum ponds, it was concluded that no investigator had as yet established experimentally the fluoride emission from gypsum ponds."

Based on information in References 11 and 12, PES has omitted the fluoride emission factor from gypsum settling and cooling ponds in this revision.

Of the six source tests received, References 1, 2, and 3 are source tests conducted on the same unit (IMC, Inc.). Therefore, the average controlled reactor emission factors from these three source tests were averaged together as follows:

$$(0.00254 + 0.0054 + 0.00191)/3 = 0.0033 \text{ kg/Mg P}_2\text{O}_5 \text{ input}$$

Similarly, References 4 and 5 are also source tests from the same unit (Seminole); therefore, the controlled reactor emission factors were averaged together as follows:

$$(0.00249 + 0.00398)/2 = 0.00324 \text{ kg/Mg P}_2\text{O}_5 \text{ input}$$

Reference 6 (Texasgulf) provided controlled reactor emission factors from four different units; therefore, these average emission factors were not averaged together. The final controlled

emission factor from the reactor was calculated by averaging the average IMC and Seminole emission factors with the four average Texasgulf unit emission factors as follows:

$$[0.0033 + 0.00324 + 0.00234 + 0.000826 + 0.00117 + 0.000489]/6 = 0.0019 \text{ kg/Mg P}_2\text{O}_5 \text{ input}$$

Assuming a control efficiency of 99 percent (as reported in Reference 4 and 5), the estimated uncontrolled emission factor from the reactor was calculated as follows:

$$[0.0019 \text{ kg/Mg P}_2\text{O}_5 \text{ input}/(1-.99)] = 0.19 \text{ kg/Mg P}_2\text{O}_5 \text{ input.}$$

The controlled reactor emission factor was derived from "A" rated source tests from three different facilities, and is therefore rated "A." However, because the data were reported as controlled, and the uncontrolled emission factors were calculated from a nominal control efficiency, the uncontrolled emission factor is rated "B."

Reference 6 (Texasgulf) provided controlled emission factors from the evaporator from one unit of 0.0000217 kg per Mg P₂O₅ input, which was used as the controlled emission factor from the evaporator. The uncontrolled factor was calculated as shown above by estimating a 99 percent efficiency of the venturi scrubber, resulting in an uncontrolled emission factor from the evaporator of 0.00217 kg per Mg P₂O₅ input. Because the controlled emission factor was derived from a single "A" rated source test, the emission factor was rated "B." However, because the data were reported as controlled, and the uncontrolled emission factor was calculated from a nominal control efficiency, the uncontrolled emission factor is rated "C."

Reference 6 (Texasgulf) also provided controlled emission factors from the belt filter of 0.000090 and 0.000555 kg per Mg P₂O₅ input. The controlled emission factor from a belt filter was calculated from the average as follows:

$$[(0.000090 + 0.000555)/2] = 0.00032 \text{ kg per Mg P}_2\text{O}_5 \text{ input}$$

The uncontrolled emission factor from the belt filter was estimated by applying a 99 percent efficiency as follows:

$$[0.00032 \text{ kg/Mg P}_2\text{O}_5 \text{ input}/(1-.99)] = 0.032 \text{ kg/Mg P}_2\text{O}_5 \text{ input.}$$

Because the controlled emission factor was derived from only two "A" rated source tests from the same facility, the emission factor was rated "B." However, because the data were reported as controlled, and the uncontrolled emission factor was calculated from a nominal control efficiency, the uncontrolled emission factor is rated "C."

Reference 6 (Texasgulf) also provided controlled emission factors from the belt filter vacuum pump from four units. The controlled emission factor from a belt filter vacuum pump was calculated from the average as follows:

$$[(0.000215 + 0.000010 + 0.000020 + 0.000045)/4] = 0.000073 \text{ kg per Mg P}_2\text{O}_5 \text{ input}$$

The uncontrolled emission factor from the belt filter vacuum pump was estimated by applying a 99 percent efficiency as follows:

$$[0.000073 \text{ kg/Mg P}_2\text{O}_5 \text{ input}/(1-.99)] = 0.0073 \text{ kg/Mg P}_2\text{O}_5 \text{ input.}$$

Because the controlled emission factor was derived from four "A" rated source tests from the same facility, the emission factor was rated "B." However, because the data were reported as controlled, and the uncontrolled emission factor was calculated from a nominal control efficiency, the uncontrolled emission factor is rated "C."

**TABLE 4.3-3 (METRIC UNITS)
FLUORIDE**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Wet scrubber						
1 IMC 8/90 Reactor	A	13B	1	62.5	0.15	2.33
			2	62.5	0.14	2.18
			3	62.5	0.19	3.05
			Average	62.5	0.16	2.54
Control device: Wet scrubber						
2 IMC 2/91 Reactor	A	13B	1	56.8	0.29	5.11
			2	56.8	0.30	5.35
			3	56.8	0.33	5.75
			Average	56.8	0.31	5.4
Control device: Wet scrubber						
3 IMC 8/91 Reactor	A	13B	1	64.0	0.12	1.91
			2	64.0	0.16	2.48
			3	64.0	0.091	1.42
			Average	64.0	0.12	1.91
Control device: Crossflow packed scrubber (99% efficiency)						
4 Seminole 9/90 Reactor	A	13B	1	31.0	0.082	2.63
			2	31.0	0.054	1.76
			3	31.0	0.091	2.93
			Average	31.0	0.077	2.49
Control device: Crossflow packed scrubber (99% efficiency)						
5 Seminole 5/91 Reactor	A	13B	1	31.9	0.19	5.95
			2	32.0	0.10	3.26
			3	31.9	0.082	2.56
			Average	31.9	0.13	3.98

^aUnits in Mg (P₂O₅) input per hr.

^bUnits in kg (fluoride) per hr.

^cUnits in kg (fluoride) x 10⁻³ per Mg (P₂O₅) input.

TABLE 4.3-3 (METRIC UNITS) (continued)
FLUORIDE

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #1 Reactor	A	13B	1	37.3	0.074	1.98
			2	36.8	0.092	2.50
			3	36.3	0.091	2.51
			Average	36.8	0.086	2.34
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #2 Reactor	A	13B	1	36.2	0.036	0.994
			2	36.2	0.018	0.497
			3	36.4	0.036	0.989
			Average	36.3	0.030	0.826
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #3 Reactor	A	13B	1	37.6	0.038	1.01
			2	37.6	0.038	1.01
			3	37.8	0.057	1.51
			Average	37.6	0.044	1.17
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #4 Reactor	A	13B	1	40.2	0.02	0.498
			2	40.3	0.02	0.496
			3	42.2	0.021	0.498
			Average	40.9	0.02	0.489
Control device: Venturi scrubber						
6 Texasgulf 12/87 Unit #1 Evaporator	A	13B	1	105	0.0026	0.0248
			2	105	0.0021	0.020
			3	108	0.0022	0.0204
			Average	106	0.0023	0.0217

^aUnits in Mg (P₂O₅) input per hr.

^bUnits in kg (fluoride) per hr.

^cUnits in kg (fluoride) x 10⁻³ per Mg (P₂O₅) input.

**TABLE 4.3-3 (METRIC UNITS) (continued)
FLUORIDE**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Cyclonic scrubber						
6 Texasgulf 12/87 Units #1 & 2 Belt Filter	A	13B	1	74.7	0.00599	0.080
			2	74.7	0.00671	0.090
			3	74.7	0.00708	0.095
			Average	74.7	0.00671	0.090
Control device: Cyclonic scrubber						
6 Texasgulf 12/87 Units #3 & 4 Belt Filter	A	13B	1	72.3	0.0303	0.420
			2	72.9	0.0635	0.870
			3	73.8	0.0273	0.370
			Average	73.0	0.0406	0.555
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #1 Belt Filter Vacuum Pump		13B	1	36.1	0.00848	0.235
			2	36.1	0.00776	0.215
			3	35.7	0.00694	0.080
			Average	35.9	0.00771	0.215
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #2 Belt Filter Vacuum Pump	A	13B	1	41.3	0.000413	0.010
			2	40.2	0.000404	0.010
			3	40.2	0.000404	0.010
			Average	40.6	0.000404	0.010
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #3 Belt Filter Vacuum Pump	A	13B	1	41.7	0.000835	0.020
			2	41.4	0.000826	0.020
			3	33.8	0.000508	0.015
			Average	39.0	0.000780	0.020
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #4 Belt Filter Vacuum Pump	A	13B	1	36.7	0.00166	0.045
			2	34.8	0.00157	0.045
			3	34.6	0.00156	0.045
			Average	35.4	0.00159	0.045

^aUnits in Mg (P₂O₅) input per hr.

^bUnits in kg (fluoride) per hr.

^cUnits in kg (fluoride) x 10⁻³ per Mg (P₂O₅) input.

**TABLE 4.3-3 (ENGLISH UNITS)
FLUORIDE**

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Wet scrubber						
1 IMC 8/90 Reactor	A	13B	1	68.9	0.32	4.65
			2	68.9	0.30	4.36
			3	68.9	0.42	6.10
			Average	68.9	0.35	5.08
Control device: Wet scrubber						
2 IMC 2/91 Reactor	A	13B	1	62.6	0.64	10.2
			2	62.6	0.67	10.7
			3	62.6	0.72	11.5
			Average	62.6	0.677	10.8
Control device: Wet scrubber						
3 IMC 8/91 Reactor	A	13B	1	70.6	0.27	3.82
			2	70.6	0.35	4.96
			3	70.6	0.20	2.83
			Average	70.6	0.27	3.82
Control device: Crossflow packed scrubber (99% efficiency)						
4 Seminole 9/90 Reactor	A	13B	1	34.2	0.18	5.26
			2	34.2	0.12	3.51
			3	34.2	0.20	5.85
			Average	34.2	0.17	4.97
Control device: Crossflow packed scrubber (99% efficiency)						
5 Seminole 5/91 Reactor	A	13B	1	35.2	0.42	11.9
			2	35.2	0.23	6.51
			3	35.2	0.18	5.11
			Average	35.2	0.28	7.95

^aUnits in ton (P₂O₅) input per hr.

^bUnits in lb (fluoride) per hr.

^cUnits in lb (fluoride) x 10⁻³ per ton (P₂O₅) input.

TABLE 4.3-3 (ENGLISH UNITS) (continued)
FLUORIDE

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #1 Reactor	A	13B	1	41.125	0.164	3.96
			2	40.542	0.203	5.00
			3	40.0	0.20	5.02
			Average	40.556	0.191	4.68
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #2 Reactor	A	13B	1	39.917	0.08	1.99
			2	39.958	0.04	0.994
			3	40.083	0.08	1.98
			Average	39.986	0.068	1.65
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #3 Reactor	A	13B	1	41.458	0.083	2.02
			2	41.417	0.083	2.02
			3	41.625	0.125	3.02
			Average	41.50	0.095	2.34
Control device: Crossflow scrubber						
6 Texasgulf 12/87 Unit #4 Reactor	A	13B	1	44.333	0.044	0.966
			2	44.458	0.044	0.992
			3	46.542	0.046	0.996
			Average	45.111	0.045	0.978
Control device: Badger evaporator venturi scrubber						
6 Texasgulf 12/87 Unit #1 Evaporator	A	13B	1	115.50	0.0058	0.0496
			2	115.625	0.0046	0.040
			3	119.047	0.0048	0.041
			Average	116.724	0.0047	0.0434

^aUnits in ton (P₂O₅) input per hr.

^bUnits in lb (fluoride) per hr.

^cUnits in lb (fluoride) x 10⁻³ per ton (P₂O₅) input.

TABLE 4.3-3 (ENGLISH UNITS) (continued)
FLUORIDE

Reference Number	Test Rating	Test Method	Run #	Production Rate ^a	Emission Rate ^b	Emission Factor ^c
Control device: Cyclonic scrubber						
6 Texasgulf 12/87 Units #1 & 2 Belt Filter	A	13B	1	82.3	0.0132	0.16
			2	82.3	0.0148	0.18
			3	82.3	0.0156	0.19
			Average	82.3	0.0148	0.18
Control device: Cyclonic scrubber						
6 Texasgulf 12/87 Unit #3 & 4 Belt Filter	A	13B	1	79.7	0.0669	0.84
			2	80.4	0.1400	1.74
			3	81.4	0.0602	0.74
			Average	80.5	0.0894	1.11
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #1 Belt Filter Vacuum Pump	A	13B	1	39.8	0.0187	0.47
			2	39.8	0.0171	0.43
			3	39.3	0.0153	0.39
			Average	39.6	0.0170	0.43
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #2 Belt Filter Vacuum Pump	A	13B	1	45.5	0.00091	0.02
			2	44.3	0.00089	0.02
			3	44.3	0.00089	0.02
			Average	44.7	0.00089	0.02
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #3 Belt Filter Vacuum Pump	A	13B	1	46.0	0.00184	0.04
			2	45.6	0.00182	0.04
			3	37.3	0.00112	0.03
			Average	43.0	0.00172	0.04
Control device: Scrubber (type unspecified)						
6 Texasgulf 12/87 Unit #4 Belt Filter Vacuum Pump	A	13B	1	40.5	0.00365	0.09
			2	38.4	0.00346	0.09
			3	38.1	0.00343	0.09
			Average	39.0	0.00351	0.09

^aUnits in ton (P₂O₅) input per hr.

^bUnits in lb (fluoride) per hr.

^cUnits in lb (fluoride) x 10⁻³ per ton (P₂O₅) input.

4.4 DATA GAP ANALYSIS

For this revision, six new source tests were used to develop new wet process fluoride emission factors. These source tests only contained controlled emissions data. Ideally, uncontrolled emissions data are used for emission factor development. However, because the emission factors in the previous version were based on a material balance and assumptions from 20-year-old documents, the new controlled data were used for this revision to develop controlled and uncontrolled emission factors. A nominal efficiency was applied to the controlled emission factors to "back-calculate" the uncontrolled emission factors. The controlled factors were rated "A" and "B", while the uncontrolled factors were rated "B" and "C." Source testing to obtain uncontrolled emissions data would improve the confidence level of the uncontrolled emission factors.

Emissions data were also obtained documenting sulfur dioxide (SO₂) and hydrogen sulfide (H₂S, a HAP) emissions from wet process phosphoric acid manufacturing. However, the data received were insufficient for emission factor development. More source testing is necessary to obtain sufficient emissions documentation from which to develop emission factors for these pollutants.

Only one source test received during this revision documented emissions from a thermal process facility. This single test, which documents phosphoric acid mist (H₃PO₄) emissions, was insufficient for new emission factor development. Therefore, the thermal process emission factors were presented unchanged and unverified from the previous revision (February 1980). The controlled thermal process particulate emission factors were developed from the 1970 unpublished U.S. Public Health Service report Control Techniques for Fluoride Emissions. As discussed in Chapter 4.0 of this background report, this document was not contained in the background file; therefore, the controlled thermal process particulate emission factors could not be verified. As a result, the emission factor ratings have been downgraded from "B" to "E." Source testing of the thermal process phosphoric acid manufacturing would provide data from which to develop "A" rated emission factors.

**TABLE 4.4-1.
LIST OF CONVERSION FACTORS**

Multiply:	by:	To obtain:
mg/dscm	4.37 E-4	gr/dscf
m ²	10.764	ft ²
m ³	35.31	ft ³
m	3.281	ft
kg	2.2046	lb
kPa	1.45 x 10 ⁻¹	psia
kg/Mg	2.0	lb/ton
Mg	1.1023	ton

Temperature conversion equations:

Fahrenheit to Celsius:

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

Celsius to Fahrenheit:

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

4.5 REFERENCES FOR CHAPTER 4

1. Summary of Emission Measurements - East Phos Acid. International Minerals and Chemical Corporation, New Wales Operations, Polk County, FL. August 1990.
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6. Stationary Source Sampling Report. Texasgulf Chemicals Company, Aurora, NC. Entropy Environmentalists, Inc., Research Triangle Park, NC. December 1987.
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11. Gordon F. Palm, Phosphoric Acid Manufacturing, unpublished draft Air Pollution Engineering Manual (AP-40), Air & Waste Management Association, Pittsburgh, PA, January 1992.
12. 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, Research Triangle Park, NC, 1978.

APPENDIX A.

AP-42 SECTION 5.11

[Not presented here. See instead current AP-42 Section 8.9.]