Note: This is a reference cited in *AP 42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources.* AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the reference number, the AP42 chapter and section. The file name "ref02_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

SPE-AWMA(6713E)

PHOSPHORIC
MANUFACTUF

Gordon F. Pa

In the past 10 years, wet process pho
the source of perhaps 100% of the ne

Anhydrite: $CaSO_4$
Hemihydrate: $CaSO_4 \cdot \frac{1}{2}H_2O$
Dihydrate: $CaSO_4 \cdot 2H_2O$

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At present there is no commercial use of the anhydrite process, mainly because the required reaction temperature is high enough to cause severe corrosion difficulties. Processes in commercial use are listed in Table 1.

Straight dihydrate processes are the most popular today. Recently, some have been converted to a one-step hemihydrate process that has the advantage of producing phosphoric acid of a relatively high concentration and with lower impurity levels. Hemihydrate-dihydrate processes without intermediate filtration and hemihydrate-dihydrate processes with two separation steps are not used in the United States.

CHEMISTRY

Digestion is considered to take place in several stages.[2] First, tricalcium phosphate in the rock is attacked by phosphoric acid to form monocalcium phosphate. The monocalcium phosphate then reacts with sulfuric acid to yield additional phosphoric acid and gypsum. The overall reaction is as follows:

(1)

Simplified versions of these reactions are as follows:

(2)

(3)

Depending on the temperature and phosphoric acid strength maintained during digestion, dihydrate, hemihydrate or even the anhydrite of calcium sulfate may result.[2]

A number of minor reactions occur between fluorides, silica, and water in the scrubbing of gaseous fluorides from the digester. These reactions are discussed under "Air Pollution Control Measures."

AIR EMISSION CHARACTERISTICS

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Fluorides

In the digester, about 3–7% of the fluoride in the phosphate rock is evolved.[2,4,5] At the higher P_2O_5 concentrations and temperature of the hemihydrate and hemihydrate-dihydrate processes, more silicofluoride fumes are emitted from the attack tank than in the dihydrate process.[5] The digesters are vented to wet scrubbers for fluoride removal.

The relative quantities of fluorides in the filter acid and gypsum depend on the type of rock and the operating conditions.[6] The main factors appear to be the following.

1. The quantity of sodium or potassium salts present, which will precipitate insoluble fluorine compounds.
2. The reaction temperature at which digestion occurs (increasing temperature results in increasing gaseous fluorides).
3. The concentration of the product phosphoric acid.

Filter acid contains about 67% of the fluoride in the phosphate rock,[7] much of which is volatilized during evaporation. The gaseous fluorides are removed by scrubbing to prevent pollution. In some cases, salable products are produced[8] (fluosilicic acid, fluosilicates, cryolite, or aluminum fluoride). The amount of fluoride evolved during concentration from 30% to 54% P_2O_5 may be 70–80%[8] of that originally present in the acid. This is equivalent to 50% of the fluoride in the phosphate rock. In the production of superphosphoric acid (69–72% P_2O_5) by concentrating wet process acid, most of the fluoride is volatilized[8] so the acid contains only 0.2–0.3% as fluorine. The addition of reactive silica during evaporation enhances silicon tetrafluoride volatization and reduces fluoride content to about 0.1% as fluorine.

F

The evaporators used to concentrate phosphoric acid operate under a vacuum. The steam from the evaporated acid and the evolved fluorides goes to a total condenser where they are directly contacted with cool process water. The steam is condensed and the fluorides are absorbed in a large quantity of process water. Gaseous fluoride emissions from the condenser waters are negligible.

Wet process phosphoric acid[9] is defluorinated for use in animal feed products. The stripping of the fluoride from the acid is more easily attained when the fluoride is present in the silicon tetrafluoride form,[10] which is more volatile than hydrogen fluoride. Silicon dioxide is added as needed to the phosphoric acid to allow the chemical reactions necessary for producing silicon tetrafluoride. The various methods of defluorinating are as follows:

1. Air stripping by blowing air through hot 54% P_2O_5 acid (the exit air must be scrubbed).
1. Steam stripping 54% P_2O_5 phosphoric acid by circulating through a stripping column with steam blown countercurrent to the acid (exit steam must be condensed to remove fluorides).

3. Evaporation method by diluting 54% P_2O_5 acid and then reconcentrating the acid to 54%; uses conventional vacuum evaporation equipment.
4. Concentrating to superacid under vacuum will give a P/F (weight ratio) of 80 at 70% P_2O_5 acid. Reactive silica, such as diatomaceous earth, when added to the acid, allows it to be stripped of fluorides in the evaporator to a P/F ratio of 100 or higher.

Acid used in animal feed products must have a minimum P/F of 100. If there is fluoride in the limestone used for feed-grade dicalcium phosphate, the acid P/F must be about 125. Fifty-four percent P_2O_5 acid has a P/F of about 15; 30% P_2O_5 acid is hard to defluorinate.

Particulates

In the older plants, dry ground phosphate rock is generally used. It is transported to the phosphoric acid plant digester by conveyor belt, screw conveyor, and/or airveying systems. The handling of the dry ground rock results in the generation of fugitive dust which is collected by ventilation ductwork and removed by bag collectors which discharge the dust to the rock feed bin. In addition to the gaseous fluoride in the digester vent, there is usually a small amount of rock dust generated by the mechanically handling of the rock.[11] This dust is removed in the wet scrubber designed for the removal of fluorides.

In newer plants, there are no particulate emissions since wet rock grinding is used.[12] The rock is ground as a slurry in a ball mill to about 65% solids. The advantages of wet rock grinding are a 30–40% reduction in horsepower in the grinding area, elimination of the rock dryer, elimination of atmospheric pollution by dust, and a savings in the cost of fuel for drying. Many older plants have been converted to wet rock grinding to realize these significant environmental and cost benefits.

Gypsum Stacks and Process Water Ponds

The gypsum stacks and process water ponds are an integral part of a typical phosphoric acid plant.[13] The gypsum stacks serve primarily as storage for stacking of the by-product gypsum. Adjoining these stacks are process water ponds that provide surge volume for wet and dry weather conditions to avoid water treatment and water discharge and to conserve on fresh water makeup. The water in the ponds, commonly called "pond water," is recirculated for process cooling, recovery of P_2O_5 and sulfate values, control of effluents, scrubbing of process emissions, process makeup water, and hydraulic transport of by-product gypsum. The tops of the gypsum stacks are frequently used for supplemental cooling of the pond water. During the manufacturing process, the pond water comes in direct contact with raw

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materials, intermediate products, by-products, waste products, or finished products. The cooling ponds, including the cooling water on top of the gypsum stacks, also serve as surge equalization ponds for the rainfall runoff from the gypsum stacks.

Pond water is used mainly in the phosphoric acid processes to wash the filter cake, in scrubbers, in barometric condensers, and for slurrying waste gypsum. After settling of gypsum solids in the gypsum stack, the pond water is allowed to cool by natural evaporation and is recirculated. Pond water is acidic, has a pH of about 1.5–2.0, and contains weak sulfuric, phosphoric, and fluosilicic anion components. Phosphate analysis, reported as P_2O_5, varies from about 1% to 2% P_2O_5. Fluoride analysis, reported as percent of fluorine, varies from about 1% to 1.8% ~~fluorine~~ F

Hydrogen fluoride (HF) and silicon fluoride (SiF_4) are prevented from escaping from the facility into the atmosphere by the use of wet scrubbers. These recycle pond water as the scrubbing medium.[13] In the scrubbers, HF and SiF_4 are removed from the air, forming H_2SiF_6.

Low-level fluoride emissions occur from the pond water on top of the gypsum stack and pond water cooling ponds. Measurements of these levels are extremely difficult to correlate because of changing air velocity and direction and the concentration variation of the fluorides along the elevation over the pond water surface. Estimations based on fluoride vapor pressure are also difficult to make because of the wide variations in pond water composition and the lack of available data.[14]

The U.S. Environmental Protection Agency, in discussing the verification of predicted fluoride emissions, made the following statement[13]: "Based on our findings concerning the emissions of fluoride from gypsum ponds, it was concluded that no investigator had as yet established the fluoride emission rate from gypsum ponds."

Cooling towers are mentioned for cooling condenser pond water[15] rather than a pond water cooling pond. However, if a cooling tower is used, surge equalization provisions must also be considered to avoid excessive treatment and the discharge of treated water. Cooling towers are used for cooling gypsum pond water in four U.S. locations instead of pond water cooling ponds. Fluoride emissions from the cooling towers are a function of the fluoride vapor pressure of the pond water. The fluoride emissions are low, but must meet limits of the state regulatory authorities.

EMISSION FACTORS

Emission factors for wet phosphoric acid production are shown in Table 2. These were obtained from Table 5.11-1 of AP-42 dated February 1980 with modifications as shown.

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AIR POLLUTION CONTROL MEASURES

Fluorides

Gaseous fluoride compounds are removed from the vent air of the digester, filter, and various tanks. Wet scrubbers have been used exclusively for this service in the United States.

Wet scrubbing combines the ability to remove particulates (rock dust) from gas streams by impaction of the particulates on the surface of liquid droplets and the ability to absorb gaseous constituents into the liquid phase.[16] Both of these functions are limited by the characteristics of the scrubbing liquor, the properties of the materials to be removed, and sometimes by the two in combination. In the phosphoric acid plant wet scrubbers, the pond water and the fluoride-containing gases from the wet process phosphoric acid plant reactor can produce a gelatinous silica precipitate. This plugs the packing in the scrubbers and limits the types of scrubbing equipment that can be used.

The basic chemistry of the compounds of fluoride, silica, and water must be considered to characterize the application. In the reactor, the fluoride contained in the fluorapatite or fluorspar goes into solution accordingly to the following reactions.[16]

(4)

(5)

A vapor equilibrium is set up between the reactants in equation 5, which may be regarded as the reverse of the following equation.

(6)

High temperature drives the reaction to the right, increasing the vapor pressure of both the HF and SiF_4, and increases the relative significance of SiF_4 as the fluorine-containing species.[16] These vapor pressures set the lower limit of fluoride concentration in the gas phase leaving the scrubber.

In addition to the reactions given, hydrolysis of SiF_4 occurs when the concentration of this component is higher than the equilibrium values, according to the following reaction.

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(7)

Reaction 7 occurs as the temperature of a gas stream is reduced in the presence of water and leads to the formation of gelatinous deposits of polymeric silica, which plug scrubber packings. This problem limits the use of conventional packed countercurrent absorbers in this service, as well as other contacting devices that have small gas passages that might plug up.

Transfer Unit Concept

Removal of fluorine compounds from effluent gases is achieved by absorption in water. With the decrease of allowable emissions in the past few years, scrubber efficiencies in the range of 99+% are required.[17] Scrubber emissions are now expressed as pounds per hour of fluorides emitted. If once-through or neutralized water can be used, at least 4.6 transfer units are required to achieve this efficiency. If recycled pond water is used, the number of transfer units required for the same efficiency has been as many as eight units in several installations. This depends on the partial pressure of fluorides in the incoming water. The number of transfer units required is established for these lean systems as shown in the following.

It is first assumed that enough absorbing liquid is used to prevent the concentration of fluoride in the liquid from varying significantly as a result of the absorption. Then,[17]

$$N_{og} = \ln[y_1 - a)/(y_2 - a)]$$

where: N_{og} = number of transfer units required

y_1 = inlet concentration of fluorine-containing compound to gas phase

y_2 = outlet concentration of fluorine-containing compound in gas phase

a = concentration of fluorine-containing compounds in gas phase in equilibrium with scrubbing liquid

1N

All concentrations are expressed in the same units, which may be volume percent, mole percent, or partial pressure. For very dilute systems, little accuracy is lost by expressing concentrations in weight percent or weight per unit volume.

In those cases where the vapor pressure of fluorides in the scrubbing liquid, inlet and outlet, is negligible, then

12.65

$$N_{og} = \ln[y_1/y_2]$$

Scrubbers

Scrubbing systems used in phosphoric acid plants are venturis, wet cyclonic, and semi–cross-flow[18] scrubbers.

Figure 2 is an artist's sketch of a cyclonic scrubber with outside wall-mounted spray boxes. This design feature allows the spray nozzles, which are mounted in a number of boxes, to be cleaned or replaced while the scrubber is in operation. Since the nozzles tend to plug the silica, this feature improves the operating of the scrubber. Figure 3 shows a two-stage cyclonic scrubber recently installed on a phosphoric acid reactor.

WITH

F2&3 ?

In the current design of semi–cross-flow scrubbers, pond water is sprayed countercurrent to the gas stream in several rows of spray headers in the front of the scrubber. Then spray headers are used to spray cocurrent with the gas stream onto two or more Kimre tower packing sections (multiple woven pads) in series followed by a dry Kimre tower packing for drift elimination. Several older spray cross-flow packed scrubbers have been modified because of plugging of the initial type of tower packing used. In some plants, the packing was removed and the scrubber converted by installing Kimre tower packing. In other plants, the Kimre tower packing was installed prior to the initial tower packing and a dry Kimre tower packing installed before the fan suction for drift elimination. Figure 4 presents a sketch of a phosphoric acid scrubber showing these changes.

F4 ?

REGULATIONS

Fluorides

Emission standards for fluorides in the states with operating phosphoric acid plants are summarized in Table 3. Ambient air and vegetation standards are shown in Table 4.

T3&4 ?

Florida

Florida rules[19] state that discharges to the atmosphere from wet process phosphoric acid plants shall not contain total fluorides in excess of 10 grams per metric ton (0.020 lb/ton) of equivalent P_2O_5 feed and 5 grams per metric ton (0.010 lb/ton) for superphosphoric acid plants. These were adopted by reference to the federal EPA rules.[20] Florida has no ambient air or vegetation fluoride rules.

Texas

Texas fluoride rules[21] limit inorganic fluoride emissions, calculated as HF to 6 ppb by volume average ambient air difference between upwind level and downwind level for the property (measured at the property lines). Allowable fluoride emissions for point sources must be calculated by

Sutton's equation for dispersion from stacks. The equation has been modified to consider the critical wind speed and to correspond to a three-hour air sample. The equation contains terms for stack velocity, exit stack diameter, and stack height.

Texas also has ambient air fluoride standards for 12-hour, 24-hour, 7-day, and 30-day periods, including background, as shown in Table 3. Vegetation fluoride levels have been set for samples taken once a month for various consecutive monthly periods, as shown in Table 3.

Wyoming

Wyoming has also adopted the EPA fluoride emissions standards by reference[22] for wet process phosphoric acid plants and superphosphoric plants. Ambient air standards for Wyoming provide statewide values that vary with sampling times. More restrictive standards are used for the areas that contain phosphoric acid and superphosphoric acid plants (Table 3). Vegetation standards vary with sampling time, as shown in Table 3.

Idaho

Idaho fluoride emissions are based on the entire fertilizer complex[23] and are limited to 0.30 lb/ton P_2O_5 fed to the phosphate rock calciner. There are no standards for ambient air or vegetation.

Louisiana

Louisiana has also adopted by reference[24] the federal EPA rules for emissions of fluorides from wet process phosphoric acid plants and superphosphoric acid plants. Louisiana has no ambient air or vegetation fluoride standards.

North Carolina

North Carolina has also adopted by reference[25] the EPA rules for emissions of fluorides from wet process phosphoric acid plants and superphosphoric acid plants. North Carolina has no ambient air or vegetation fluoride standards.

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LIMITS

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KEY WORDS ?

LEFT OUT

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TABLE 1. Commercial Wet Processes in Use

Crystal Form(s)	Number of Separation Steps[a]	Usual Concentration of Acid, % P_2O_5	Usual Temperature, °C: Reactor	Usual Temperature, °C: Recrystallizer
Dihydrate	1	26–32	70–85	
Hemihydrate	1	40–50	85–100	
Hemihydrate-dihydrate	1	26–30	90–100	50–60
Hemihydrate-dihydrate	2	40–50	90–100	50–65
Dihydrate-hemihydrate	2	35–38	65–70	90–100

[a]Filtration of centrifuging steps.

TABLE 2. Emission Factors for Wet Process Phosphoric Acid Production

Source	Fluorides: lb/ton[a]	Fluorides: kg/MT
Wet process, uncontrolled		
Reactor, dihydrate	13	6.5
Reactor, hemihydrate	27–54	14–27
Evaporation, 30–54% P_2O_5	100	50
Evaporation, 54–70% P_2O_5	41	21
Gypsum settling and cooling ponds	[b]	[b]
Typical controlled emissions[c]	0.02–0.07	0.01–0.04

[a]References 7 and 8. Pounds of fluoride (as gaseous fluoride) per ton of P_2O_5 produced.

[b]Site specific. Acres of cooling pond required: ranges from 0.10 acre per daily ton P_2O_5 produced in the summer in the southeastern United States to zero in the colder locations in the winter months when the cooling ponds are frozen. Also, EPA 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."[13]

[c]AP-42, Compilation of Emission Factors, U.S. Environmental Protection Agency, Table 5.11-1, February 1980.

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TABLE 3. Fluroide Emission Limits

Regulator	Facility	Emission Limits
Federal EPA	Wet process phosphoric acid[a]	10.0 g/metric ton P_2O_5[c] (0.02 lb/ton)
	Superphosphoric acid[b]	5.0 g/metric ton P_2O_5[d] (0.01 lb/ton)
Florida	Wet process phosphoric acid	Same as EPA
	Superphosphoric acid	Same as EPA
Wyoming	Wet process phosphoric acid	Same as EPA
	Superphosphoric acid	Same as EPA
Idaho	Total plant	0.30 lb F/ton P_2O_5[e]
Louisiana	Wet process phosphoric acid	Same as EPA
	Superphosphoric acid	Same as EPA
Texas	Individual stacks	Calculated from Sutton See Rule
		Total property limited to 6 ppb fluoride (as HF) difference upwind and downwind concentration[f]
North Carolina	Wet process phosphoric acid	Same as EPA
	Superphosphoric acid	Same as EPA

[a]40 CFR 60.200 Subpart T.
[b]40 CFR 60.000 Subpart U.
[c]Total fluorides from reactors, filters, evaporators, hot wells.
[d]Total fluorides from evaporators, hot wells, acid sumps, cooling tanks.
[e]Total fluoride emissions in gaseous and particulate form, expressed as (F), per ton of P_2O_5 input, to the calciner operations, calculated at the maximum feed rate.
[f]Total inorganic fluorides from three consecutive hours, by volume.

TABLE 4. Fluoride Ambient Air and Vegetation Limits

Regulator	Ambient Air Limits		Vegetation Limits	
Texas	Time period	ppb F[a]	Time period	ppm F[b]
	12 hours	4.5	12 months	40
	24 hours	3.5	3 months	60
	7 days	2.0	2 months	80
	30 days	1.0		
Idaho	None	None		
Louisiana	None	None		
Florida	None	None		
North Carolina	None	None		
Wyoming	Regional standard		Time period	ppm[d]
	Time period	$\mu g/m^3$[c]	1 year	30
			60 days	60
	12 hours	10.0	30 days	80
	24 hours	4.0		
	7 days	1.8		
	30 days	1.2		

[a]Average gaseous fluorides (calculated as HF) by volume.
[b]Average inorganic fluoride, by weight in forage based on samples once a month for consecutive calendar months. Total of absorbed and deposited fluoride.
[c]Calculated as HF, maximum allowable for averaging time. See rule for specific areas.
[d]In forage for animal consumption. Maximum allowable, measured as fluoride, dry basis.

FIGURE 1. Diagram of Wet Process Phosphoric Acid Plant (Ap-42, *Compilation of Air Pollution Factors* U.S. Environmental Protection Agency, revised February 1980, p 5.41-1.)
FIGURE 2. Artist's Sketch of Cyclonic Scrubber with Wall-Mounted Spray Boxes Showing Flows of Internal Gases and Scrubbing Liquid
FIGURE 3. Two-stage Cyclonic Scrubber Installed on a Wet Process Phosphoric Acid Reactor (Hydronics Engineering Corp., Midland Park, NJ.)
FIGURE 4. Phosphoric Acid Fluoride Scrubber After Changes (Kimre, Inc., Perrine, FL.)

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(HYDRONICS ENGINEERING CORP., MIDLAND PARK, N.J.)

SEE ATTACHED PAGE

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$$Ca_{10}(PO_4)_6F_2CaCO_3 + 11H_2SO_4 = 6H_3PO_4 + 11CaSO_4 \cdot nH_2O + 2HF + CO_2 + H_2O \quad (1)$$

Fluorapatite, Sulfuric acid, Phosphoric acid, Gypsum, Hydrogen fluoride, Carbon dioxide, Water

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2 \quad (2)$$

Tricalcium phosphate, Phosphoric acid, Monocalcium phosphate

$$3CaH_4(PO_4)_2 + 3H_2SO_4 + 6H_2O = CaSO_4 \cdot 2H_2O + 6H_3PO_4 \quad (3)$$

Monocalcium phosphate, Sulfuric acid, Water, Gypsum, Phosphoric acid

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF \quad (4)$$

Calcium fluoride, Sulfuric acid, Calcium sulfate, Hydrogen fluoride

or

$$2HF + SiF4 = H_2SiF_6 \quad (5)$$

Hydrogen fluoride, Silicon tetrafluoride, Fluosilicic acid

$$H_2SiF_6 = 2HF + SiF_4 \quad (6)$$

Fluosilicic acid, Hydrogen fluoride, Silicon tetrafluoride

$$3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6 \quad (7)$$

Silicon tetrafluoride, Water, Silicic acid, Fluosilicic acid