In the past 10 years, wet process phosphoric acid is manufactured.
Anhydrite: \( \text{CaSO}_4 \)
Hemihydrate: \( \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} \)
Dihydrate: \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)

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

Fluorides

In the digester, about 3–7% of the fluoride in the phosphate rock is evolved. At the higher P₂O₅ concentrations and temperature of the hemihydrate and hemihydratedihydrate processes, more silicofluoride fumes are emitted from the attack tank than in the dihydrate process. 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. 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, much of which is volatilized during evaporation. The gaseous fluorides are removed by scrubbing to prevent pollution. In some cases, salable products are produced (fluosilicic acid, fluosilicates, cryolite, or aluminum fluoride). The amount of fluoride evolved during concentration from 30% to 54% P₂O₅ may be 70–80% 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% P₂O₅) by concentrating wet process acid, most of the fluoride is volatilized so the acid contains only 0.2–0.3% as fluoride. The addition of reactive silica during evaporation enhances silicon tetrafluoride volatilization and reduces fluoride content to about 0.1% as fluorine.

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 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, 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% P₂O₅ acid (the exit air must be scrubbed).
2. Steam stripping 54% P₂O₅ 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% P₂O₅ 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% P₂O₅ 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 P₂O₅ acid has a P/F of about 15; 30% P₂O₅ 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 P₂O₅ 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
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 slunying 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 P₂O₅, varies from about 1% to 2% P₂O₅. Fluoride analysis, reported as percent of fluorine, varies from about 1% to 1.8% fluoride.

Hydrogen fluoride (HF) and silicon fluoride (SiF₄) are prevented from escaping from the facility into the atmosphere by the use of wet scrubbers. These recycle pond water as the scrubbing medium. In the scrubbers, HF and SiF₄ are removed from the air, forming H₂SiF₆.

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.

The U.S. Environmental Protection Agency, in discussing the verification of predicted fluoride emissions, made the following statement: “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 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.
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. 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.

\[ \text{(4)} \]

\[ \text{(5)} \]

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

\[ \text{(6)} \]

High temperature drives the reaction to the right, increasing the vapor pressure of both the HF and SiF₄, and increases the relative significance of SiF₄ as the fluorine-containing species. 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.

\[
(7)
\]

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.\textsuperscript{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 estimated 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,\textsuperscript{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 in 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

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

\[ N_{eq} = \ln \left( \frac{y_1}{y_2} \right) \]

**Scrubbers**

Scrubbing systems used in phosphoric acid plants are venturi, wet cyclonic, and semi-cross-flow\textsuperscript{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, this feature improves the operating of the scrubber. Figure 3 shows a two-stage cyclonic scrubber recently installed on a phosphoric acid reactor.

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.

**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.

**Florida**

Florida rules\textsuperscript{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.\textsuperscript{20} Florida has no ambient air or vegetation fluoride rules.

**Texas**

Texas fluoride rules\textsuperscript{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 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 and are limited to 0.30 lb/ton P₂O₅ fed to the phosphate rock calciner. There are no standards for ambient air or vegetation.

Louisiana
Louisiana has also adopted by reference 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 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.

References


22. Wyoming Air Quality Standards and Regulations, Section 11, Fluorides, Ambient Air and Forage Standards for Fluorides, Department of Environmental Quality, Division of Air Quality, April 17, 1986.


Bibliography

V. Sauchelli, Chemistry and Technology of Fertilizers, Rheinhold, New York, 1960, pp 192-250.

TABLE 1. Commercial Wet Processes in Use

<table>
<thead>
<tr>
<th>Crystal Form(s)</th>
<th>Number of Separation Steps</th>
<th>Usual Concentration of Acid, % P₂O₅</th>
<th>Reactor Temperature, °C</th>
<th>Recrystallizer Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydrate</td>
<td>1</td>
<td>25-32</td>
<td>70-85</td>
<td></td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>1</td>
<td>40-50</td>
<td>85-100</td>
<td></td>
</tr>
<tr>
<td>Hemihydrate-dihydrate</td>
<td>2</td>
<td>25-30</td>
<td>90-100</td>
<td>50-60</td>
</tr>
<tr>
<td>Hemihydrate-dihydrate</td>
<td>2</td>
<td>40-50</td>
<td>90-100</td>
<td>50-65</td>
</tr>
<tr>
<td>Dihydrate-hemihydrate</td>
<td>2</td>
<td>35-38</td>
<td>65-70</td>
<td>90-100</td>
</tr>
</tbody>
</table>

*Filtration of centrifuging steps.

TABLE 2. Emission Factors for Wet Process Phosphoric Acid Production

<table>
<thead>
<tr>
<th>Source</th>
<th>Fluorides</th>
<th>lb/ton*</th>
<th>kg/MT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet process, uncontrolled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor, dihydrate</td>
<td></td>
<td>13</td>
<td>6.5</td>
</tr>
<tr>
<td>Reactor, hemihydrate</td>
<td></td>
<td>27-54</td>
<td>14-27</td>
</tr>
<tr>
<td>Evaporation, 30-54% P₂O₅</td>
<td></td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Evaporation, 54-70% P₂O₅</td>
<td></td>
<td>41</td>
<td>21</td>
</tr>
<tr>
<td>Gypsum settling and cooling ponds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Typical controlled emissions*</td>
<td></td>
<td>0.02-0.07</td>
<td>0.01-0.04</td>
</tr>
</tbody>
</table>

*References 7 and 8. Pounds of fluoride (as gaseous fluoride) per ton of P₂O₅ produced.
*Site specific. Acres of cooling pond required: ranges from 0.10 acre per daily ton P₂O₅ 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]

"AP-42, Compilation of Emission Factors, U.S. Environmental Protection Agency, Table 5.11-1, February 1980."
### TABLE 3. Fluoride Emission Limits

<table>
<thead>
<tr>
<th>Regulator</th>
<th>Facility</th>
<th>Emission Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Federal EPA</td>
<td>Wet process phosphoric acid</td>
<td>10.0 g/metric ton P₂O₅&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Superphosphoric acid</td>
<td>5.0 g/metric ton P₂O₅&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Florida</td>
<td>Wet process phosphoric acid</td>
<td>Same as EPA</td>
</tr>
<tr>
<td></td>
<td>Superphosphoric acid</td>
<td>Same as EPA</td>
</tr>
<tr>
<td>Wyoming</td>
<td>Wet process phosphoric acid</td>
<td>Same as EPA</td>
</tr>
<tr>
<td></td>
<td>Superphosphoric acid</td>
<td>Same as EPA</td>
</tr>
<tr>
<td>Idaho</td>
<td>Total plant</td>
<td>0.30 lb F/ton P₂O₅&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Louisiana</td>
<td>Wet process phosphoric acid</td>
<td>Same as EPA</td>
</tr>
<tr>
<td></td>
<td>Superphosphoric acid</td>
<td>Same as EPA</td>
</tr>
<tr>
<td>Texas</td>
<td>Individual stacks</td>
<td>Calculated from Sutton</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total property limited to 6 ppb fluoride (as HF) difference upwind and downwind concentration&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

North Carolina Wet process phosphoric acid Same as EPA
Superphosphoric acid Same as EPA

<sup>a</sup>40 CFR 60.200 Subpart T.
<sup>b</sup>40 CFR 60.000 Subpart U.
<sup>c</sup>Total fluorides from reactors, filters, evaporators, hot wells.
<sup>d</sup>Total fluorides from evaporators, hot wells, acid sumps, cooling tanks.
<sup>e</sup>Total fluoride emissions in gaseous and particulate form, expressed as (F), per ton of P₂O₅ input, to the calciner operations, calculated at the maximum feed rate.
<sup>f</sup>Total inorganic fluorides from three consecutive hours, by volume.

### TABLE 4. Fluoride Ambient Air and Vegetation Limits

<table>
<thead>
<tr>
<th>Regulator</th>
<th>Ambient Air Limits</th>
<th>Vegetation Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time period ppb F&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Time period ppm F&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Texas</td>
<td>12 hours 4.5</td>
<td>12 months 40</td>
</tr>
<tr>
<td></td>
<td>24 hours 3.5</td>
<td>3 months 60</td>
</tr>
<tr>
<td></td>
<td>7 days 2.0</td>
<td>2 months 80</td>
</tr>
<tr>
<td></td>
<td>30 days 1.0</td>
<td></td>
</tr>
<tr>
<td>Idaho</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Louisiana</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Florida</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>North Carolina</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Wyoming</td>
<td>Regional standard</td>
<td>Time period ppm F&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Time period µg/m³&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1 year 30</td>
</tr>
<tr>
<td></td>
<td>12 hours 10.0</td>
<td>60 days 60</td>
</tr>
<tr>
<td></td>
<td>24 hours 4.0</td>
<td>30 days 80</td>
</tr>
<tr>
<td></td>
<td>7 days 1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 days 1.2</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Average gaseous fluorides (calculated as HF) by volume.
<sup>b</sup>Average inorganic fluoride, by weight in forage based on samples once a month for consecutive calendar months. Total of absorbed and deposited fluoride.
<sup>c</sup>Calculated as HF, maximum allowable for averaging time. See rule for specific areas.
<sup>d</sup>In forage for animal consumption. Maximum allowable, measured as fluoride, dry basis.
C₆₀P₆₃F₂₅CaCO₃ + 11H₂SO₄ = 6H₃PO₄ + 11CaSO₄·nH₂O + 2HF + CO₂ + H₂O  (1)

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

Ca₃(PO₄)₂ + 4H₃PO₄ = 3CaH₂(PO₄)₂ (2)
Tricalcium Phosphoric Monocalcium
phosphate acid phosphate

(3CaH₂(PO₄)₂ + 3H₂SO₄ + 6H₂O = (CaSO₄·2H₂O + 6H₃PO₄)  (3)
Monocalcium Sulfuric Water Gypsum Phosphoric
phosphate acid acid

CaF₂ + H₂SO₄ = CaSO₄ + 2HF  (4)
Calcium Sulfuric Calcium Hydrogen
fluoride acid sulfate fluoride

or

2HF + SiF₄ = H₂SiF₆  (5)
Hydrogen Silicon Fluosilicic
fluoride tetrafluoride acid

H₂SiF₆ = 2HF + SiF₄  (6)
Fluosilicic Hydrogen Silicon
acid fluoride tetrafluoride

3SiF₄ + 4H₂O = Si(OH)₄ + 2H₂SiF₆  (7)
Silicon Water Silicic Fluosilicic
tetrafluoride acid acid