Scrubber Design for Phosphoric Acid Production Facility

Spring 1979

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SCRUBBER DESIGN FOR
PHOSPHORIC ACID PRODUCTION FACILITY

BY

EDWARD E. MAYER
B.S., Florida Technological University, 1974

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the degree of Master of Science in the Graduate Studies Program of the College of Engineering of University of Central Florida at Orlando, Florida

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ABSTRACT

This report is an examination of the practical design of a phosphoric acid production facility wet scrubber. It includes a brief background of the Florida Phosphate Industry, in addition to the rules and regulations affecting the emission of fluoride contaminants. The theoretical aspects of a packed absorption tower is discussed prior to the actual design of a cross-flow wet scrubber of the type typically found in the Florida Phosphate Industry.
ACKNOWLEDGMENTS

I am indebted to the faculty of the Environmental Engineering Department of the University of Central Florida for providing me with the basic background necessary to perform as an engineer.

I would also like to acknowledge the support and technical advice of the Engineering Staff of Agrico Chemical Company, South Pierce Chemical Works.

I include a special thanks to my wife, Diane, for her patience and many hours of typing.
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INTRODUCTION

The production of fertilizer products from the Florida Phosphate Industry is important not only to the economy of Florida, with 30,000 jobs, but to the United States and the world. Florida phosphate rock is relatively easy to mine and provides an inexpensive source of a much needed agricultural nutrient. This gigantic industry, which is primarily located in the backwoods of west-central Florida, impacts not only the economy but the ecology as well.

The purpose of this paper is to address one aspect of pollution control within the industry--fluoride emissions. A brief survey of the industry and the regulations governing fluoride emissions will be presented, followed by a discussion of the theoretical aspects of gaseous removal. This will hopefully provide the reader with a background on the problem. The remainder of the discussion will revolve around the practical design of a phosphoric acid production facility wet scrubber.

It is hoped that the result of this paper will be to provide an easy to follow manual on wet scrubber design suitable for use by interested students in environmental engineering.
I. AIR POLLUTION IN THE PHOSPHATE INDUSTRY

Phosphate Industry in Florida

Large deposits of pebble phosphate rock exist in a "shield-shaped" area, nearly 50 miles long and 40 miles wide, covering Polk, Hillsborough and Hardee Counties. Discovery of phosphate rock in the Peace River south of Fort Meade in the 1880's ushered in the industry. Approximately 70 percent of the nation's output and 30 percent of the world's usage come from the central Florida minefields.¹

The deposits were created ten to fifteen million years ago during the late Miocene Age. At this time water covered Florida, parts of Georgia and Alabama. Shoreline and ocean dwelling animal bones provided the calcium that, when leached and reacted with limestone, under pressure, provided phosphate rock.

Florida phosphate deposits consist of three types: land pebble, hard rock and soft rock. The land pebble, which accounts for 95 percent of the total Florida production, is centered in Polk and Hillsborough Counties.² Shoreline activity produced these dense deposits. Hard rock deposits are primarily located in northern Florida. Soft rock is from waste ponds of former hard rock operations.

The typical Florida phosphate company will have two types of operations: mining and chemical processing. The mining oper-
ation will consist of removing the rock from the ground and preparation for chemical processing. The preparation usually includes washing, sizing, drying and benefication.

The chemical processing complexes convert the phosphate rock into a form usable to plant life. The operation will usually consist of facilities to produce sulfuric acid, phosphoric acid, ammonium phosphates, and granular triple superphosphate. It is in the manufacturing of phosphates that fluoride is released as a pollutant.

Fluoride Contaminates

Phosphate rock in Florida has the approximate chemical formulation $3\text{Ca}_3\text{(PO}_4\text{)}_2 \cdot \text{CaF}_2$. This is a complex of tricalcium phosphate and calcium fluoride. The tricalcium phosphate is only slightly soluble and when combined with calcium fluoride is nearly insoluble in water. The compound has about 3.5 to 4.0 percent by weight of fluoride. Removal of fluorine is necessary in order to provide a non-toxic phosphate product.

The gaseous formation of fluorides, HF and SiF$_4$, is produced when heat or acid is applied to phosphate rock. Particulates of rock dust may also contain up to 4 percent fluoride. The particulates will be released in processing facilities such as drying, grinding, and material handling.

Fluoride is a cumulative poison and the degree of its toxicity is a function of both ingestion level and length of exposure. Fluoride ingestion causes a disturbed calcification of
growing teeth. Fluorides are also a protoplasmic poison.

Over the years there have been an increasing number of reports of injury to livestock and vegetation due to atmospheric pollution by fluorides. The importance of fluoride as an atmospheric pollutant was emphasized by a number of investigators at the U.S. Technical Conference on Air Pollution in 1950.4

When present in sufficient concentrations, fluorides in gaseous form are highly toxic to growing vegetation, humans, and animals. The President's Science Advisory Committee5 in its report to the President ranked investigations into the systemic effects on humans, animals, plants, and materials in the highest priority category along with sulfur dioxide, carbon monoxide, and carbon dioxide. The minutes of the Florida Air Pollution Control Commission6 have innumerable pages of testimony regarding the damages to vegetation, animals, and humans caused by fluoride emissions from the phosphate industry.

Rules and Regulations

The emission of fluorides from the phosphate industry is restricted by both the Environmental Protection Agency and the Florida Department of Environmental Regulation. Both agencies differentiate between existing and new point sources. In addition, non point sources are cited.

The E.P.A. proposed standards of air pollution control performance for five affected facilities within the phosphate fertilizer industry on October 22, 1974, (39 FR 37602). The final
version of the standards was published on August 6, 1975, (40 FR 33152) with an effective date of August 4, 1975. These standards are promulgated under the authority of Section III (a), (b), and (c) of the Clean Air Act, and apply to new sources for which construction or modification commenced after the publication of proposed regulations; i.e., October 22, 1974.

Section III (d) of the Clean Air Act requires that the E.P.A. establish procedures under which states must develop emission standards for certain pollutants from which new source performance standards (NSPS) have been promulgated.

As required by the procedure, E.P.A. first defined designated pollutants, such as fluoride as a welfare-related or a health-related pollutant, and then established a guideline for existing sources which recommended a level of emission control for these sources. This guideline determined fluoride to be a welfare-related pollutant and was published in April, 1976.

Table 1 is a summary of the NSPS Standards promulgated by the E.P.A. for the phosphate fertilizer industry. The allowable emissions are an indication of the absolute amount of fluoride produced in the processes. More fluoride is released in the production of GTSP than the other processes. DAP manufacture is second, phos acid third, and the storage of GTSP last. The emission limitations in this table will be adhered to in the following pollution control equipment design.
<table>
<thead>
<tr>
<th>Source</th>
<th>NSPS Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Process Phosphoric Acid</td>
<td>0.02 lb F/ton P₂O₅</td>
</tr>
<tr>
<td>Granular Triple Superphosphate (GTSP)</td>
<td>0.15 lb F/ton P₂O₅</td>
</tr>
<tr>
<td>Diammonium Phosphate (DAP)</td>
<td>0.06 lb F/ton P₂O₅</td>
</tr>
<tr>
<td>Granular Triple Superphosphate</td>
<td>5.0 x 10⁻⁴ lb F/hr/ton stored</td>
</tr>
</tbody>
</table>


Florida's regulations for new sources follow the guidelines of the E.P.A. Existing sources fall under the ".4 Rule." This states that a facility cannot emit more than .4 pounds of fluoride per ton of P₂O₅ input into the wet phosphoric acid production unit.⁷

Controls are usually accomplished by the use of wet scrubbers. The scrubbers utilize the phenomenon of absorption to remove the fluoride that the processes will emit.
II. DESIGN OF WET SCRUBBERS

Basic Concepts of Mass Transfer

The object of a wet scrubber is to remove the gaseous pollutant from the air stream. This is accomplished through the phenomenon of absorption, which is the gas-liquid contacting process for gas separation, which utilizes the preferential solubility of the liquid phase.

The mechanism of absorption is illustrated in Figure 1. Molecular diffusion in a gas is rapid compared to molecular diffusion in a liquid because of the greater space between molecules in the gas. The more closely spaced molecules of a liquid inhibit this free motion, and the movement is predominantly by mechanical mixing which sweeps the absorbed molecules away from the gas-liquid interface.

The phenomenon of absorption is further explained through the two-film theory first proposed by Lewis and Whitman. This model as shown in Figure 2 presumes a mass transfer zone between phases comprised of two films, one gas and the other liquid. There is a concentration gradient that exists in the gas and liquid films. The gradient also exists outside the film because some mass transport occurs in the main body of the gas or liquid phase due to turbulence.

In the gas phase the concentration of the solute decreases
Fig. 1. Gas to Liquid Transfer Phenomenon

Fig. 2. The Two-Film Theory of Interphase Diffusion

from Pag (mean concentration in the bulk of the gas) to Pai (concentration of the gas at the interface). Resistance to diffusion across the interface is disregarded in the Lewis-Whitman model.

Mass transfer represents a flow of material from one phase to another across the interface. This flow encounters resistance, and a force is required to initiate and maintain the flow. This "driving force" is represented by mass flow rate (Na). An expression for mass transfer of solute A from the bulk of the moving gas stream toward the liquid-gas interface is given by:

\[ Na = Kg(Pag - Pai) + Ky(Yag - Yai) \]

Where Kg is the gas phase mass transfer coefficient based on partial pressure; Pag is the partial pressure of A in the bulk of the gas phase; Pai is the partial pressure of A in the gas phase at the interface; Ky is the gas phase mass transfer; Yag is the mole fraction of A in the bulk of the gas phase; and Yai is the mole fraction of A in the phase at the interface.

Resistance to mass transfer can either be in the gas phase, liquid phase, or both. When the resistance is primarily in the gas phase, which characterizes the majority of absorption problems in air pollution, the situation is said to be "gas film controlling."

**Theoretical Design of a Packed Absorption Tower**

A packed tower is a tower that is filled with one of many available packing materials. The packing is designed so as to expose a large surface area. When this packing surface is wet by
the solvent, it presents a large area of liquid film for contacting the solute gas.

Usually the flow through a packed column is countercurrent, with the liquid introduced at the top to trickle down through the packing while gas is introduced at the bottom to pass upward through the packing. This results in highest possible efficiency, since, as the solute concentration in the gas stream decreases as it rises through the tower, there is constantly fresher solvent available for contact. This gives maximum driving force for the diffusion process throughout the entire column.

The general design procedure for a packed tower consists of a number of steps which one must examine. These include:
1. Solvent selection
2. Mass balance
3. Equilibrium data evaluation (liquid flow rate and number of transfer units)
4. Calculation of column diameter
5. Estimation of column height
6. Determination of pressure drop through the column

**Solvent Selection**

The first design consideration is the determination of the scrubbing liquid. The type of solvent depends primarily on the pollutant gas. Water is the most common and usually the least expensive. Some acid gases may require a base liquid such as limewater or some base gases may require an acid wash such as
weak phosphoric acid.

Mass transfer involves the transfer of pollutant gas to a liquid. This contaminated liquid must be disposed of, and therefore, may present the controlling factor in solvent selection.

Mass Balance

Figure 3 is a general schematic of an absorption tower indicating the gas and liquid flow. The input value of the pollutant gas, $Y_1$, is combined with the total gas flow, $G$, to produce inlet concentration. The output pollutant, $Y_2$, mixed with the air flow produces the tower exit concentrations. The liquid input solvent flow will contain pollutant amount, $X_1$. The liquid will absorb the pollutant species and exit the tower as $X_2$.

Equilibrium Data Evaluation

For a given gas-liquid system, with constant temperature and variable gas partial pressure, the gas concentration in the liquid changes to an equilibrium concentration at each partial pressure. If the system consists of a soluble gas to be removed, an insoluble carrier gas, and a solvent, then as the amount of soluble gas in the system increases, the equilibrium concentration of the soluble gas in the liquid increases but not proportionally.

Figure 4 is a typical equilibrium curve. The $Y$ axis is the partial pressure of the gas while the $X$ axis is a liquid mole ratio of pollutant concentration in solvent.

The operating line of the packed tower must be above the
Fig. 3. General Schematic of an Absorption Tower

Fig. 4. Typical Equilibrium Curve and Operating Line

equilibrium curve. The slope of this line may be determined by the following equation: \[ \frac{L_m}{G_m} = \frac{\Delta Y}{\Delta X} \]

If the slope of the operating line is known by the inlet-outlet concentrations with a minimum operation assumed, then the liquid flow rate can be estimated.

A transfer unit is a measure of the difference of the mass transfer operation, and is a function of the solute gas in the gas and liquid streams.

A number of transfer units needed in a system may be determined graphically or mathematically. The graphical method entails drawing horizontal and vertical lines "step wise" between the operating line and the equilibrium line.

Mathematically the number of transfer units, NTU, is approximately equal to the total change in concentration divided by the average driving force.

If an assumption is made that the equilibrium line is straight, the following equation can be used: \[ NTU = \frac{Y_1 - Y^*}{Y_2 - Y^*} \]

\( Y^* = \) equilibrium concentration

The assumption that the equilibrium line is straight is not valid in most situations and the curvature correction factor "CF" is given by Buonicore and Theodore. \[ \text{12} \]
Column Diameter

The area of packed section is based upon the flooding correlation as indicated in Figure 5. The value of the superficial gas mass flow rate, $G'$, may be determined by use of this graph. The packing factor, $F$, may be found in most texts dealing with tower design or from the packing manufacturer.

Once the superficial gas mass flow rate has been calculated, a simple ratio of $G$ over $G'$ will produce the required column diameter.

Column Height

The relationship for the height of $(Z)$ of the column may be expressed as:

$$Z = H_{og} \times NTU$$

In this equation $H_{og}$ is the height of a transfer unit. It is generally a combination of the height for gas transfer, $(H_{g})$, and liquid transfer units $(H_{l})$. These use experimentally derived factors based on the type of packing and the gas and liquid flow rates as indicated below:

$$H_{g} = \frac{\alpha (G')^8}{(L')^\gamma (Sc)^{0.5}}$$

and

$$H_{l} = \phi \left( \frac{L'}{\mu L} \right)^\eta (Sc)^{0.5}$$

where

$\alpha$, $\beta$, $\gamma$, $\phi$, and $\eta$ are packing constant found in most
Fig. 5. Generalized Pressure Drop Correlation

texts on tower design or from packing manufacturers

\[ \mu L = \text{viscosity of liquid, lb/hr ft} \]

\[ L' = \text{superficial liquid flow rate, lb/hr/ft}^2 \]

\[ Sc = \text{Schmidt number} \]

The terms, \( H_g \) and \( H_l \), are combined in the following equation to produce the height of a transfer unit.\(^{15} \)

\[ H_{og} = H_g + \left( \frac{mG_m}{L_m} \right) H_l \]

where

\[ m = \text{slope of the equilibrium curve} \]

\[ G_m = \text{gas rate, lb-moles/hr} \]

\[ L_m = \text{liquid rate, lb-moles/hr} \]

**Pressure Drop Through Packing**

The pressure drop through the packing may be determined by the following empirical correlation:\(^{16} \)

\[ \frac{\Delta P}{Z} = m(10^{-8}) \left( 10^n L'/\rho_L \right) \left( \frac{G'}{\rho_G} \right)^2 \]

where

\[ \frac{\Delta P}{Z} = \text{pressure drop per foot of packing} \]

\[ m \text{ and } n = \text{packing constants found in texts or obtained from packing manufacturers} \]

\[ \rho_L, \rho_G = \text{density of liquid and gas} \]

**Practical Considerations for Fluoride Wet Scrubbers**

The removal of gaseous fluorides in wet scrubbers in the
phosphate industry is an absorption process in which the gaseous fluorides, (HF or SiF₄), in the vent air from the various processes are dissolved in a liquid. In the typical situation the scrubbing solvent is a water solution containing weak fluosilicic and phosphoric acids plus non-volatile dissolved inorganic compounds and is commonly called contaminated pond water.

Fluoride gaseous concentrations in equilibrium with the pond water are extremely low and on the order of $5 \times 10^{-6}$ lb moles F⁻ per lb moles air. Figures 6 and 7 are typical equilibrium curves for fluoride in fluosilicic acid solutions (H₂SiF₄). It must be noted, however, that each phosphate processing plant will have its own equilibrium curve for each individual pond. It should also be mentioned that vapor-liquid equilibrium data may tend to indicate that scrubbing below acceptable regulatory levels is impossible. This is not true in actual practice. Based on stack sampling data at the New Wales Processing Plant in Polk County, it was concluded that actual scrubbing can lower emission levels below the equilibrium point.¹⁷ This is most likely the result of the fluorine in the contaminated water pond not existing in a completely soluble state but may be largely suspended in the water phase. A suspended solid will not contribute to vapor pressure.

Figure 8 is a typical wet scrubber used in the phosphate industry. It is of the cross-flow design and is very versatile. It can be used for tail-gas scrubbing of phosphoric acid, diammonium phosphate, monoammonium phosphate, granular triple superphosphate,
Fig. 6. Equilibrium Curve for Low Concentration of F

Fig. 7. Equilibrium Curve for High Concentration of F

Fig. 8. Typical Cross-Flow Scrubber

GTSP storage, and animal feed ingredients plant exhaust gases.

Tail-gas scrubbers in the phosphate industry are generally designed to remove fluorine, traces of ammonia, particulate mist, and water vapor. Non-dusty air enters the scrubber at one end and discharges at the other end. The air is contacted stage-wise with acidic pond water from the plant's contaminated water pond. A series of sprays is used to cool the fumes, condense the water vapor and begin the scrubbing operation. The final scrubbing takes place in the packed section with pond water entering at the top and on the face. The air leaving the wet packed section is generally 90° - 120° F, saturated. A final demisting pad or packed section is used to reduce pond water mist entrainment to the atmosphere. A variation of this design, used on phos acid plant scrubbers, is to vent low fluorine gases into the scrubber after the spray section.

Cross-flow scrubbers are generally used where gas absorption is combined with particulate removal. In cross-flow scrubbers, the liquid flows vertically down while the gas passes horizontally through the irrigated packed bed. These scrubbers offer reduced pressure drops and use lower pump recycle flows than the typical packed tower under the same inlet conditions.18
III. DESIGN OF A PHOSPHORIC ACID PLANT
FLUORIDE CONTROL SYSTEM

Phosphoric Acid Production Process

Phosphoric acid is used in the production of superphosphate, ammonium phosphate, and mixed granular fertilizers.

The most common method of phosphoric acid production in the phosphate industry is the dihydrate or "wet process." This is basically the extraction of phosphoric acid from phosphate rock by means of adding the rock to sulfuric acid, filtering the "slurry," and concentrating the phosphoric acid to desired strengths. It is described as the dihydrate process because the gypsum byproduct that is formed is substantially all in the hydrate form.

There are several variations of the dihydrate process in current use by the phosphate fertilizer industry. The Dorr-Oliver, St. Gohain, Prayon, and Chemico processes are all used. There is little design difference among the different process types. They consist of three major steps: reaction, filtration, and evaporation. Figure 9 is a process flow diagram for the production of wet phosphoric acid. The chemical formula for the reaction is as follows:

\[ \text{(M = minor miscellaneous elements present in small amounts)} \]
\[
H_2SO_4 + Ca_{10}(PO_4)_{6}F_2CaCO_3 + SiO_2 + M_2O + FePO_4 + AlPO_4 + H_2O =
\]

Sulfuric Acid + Phosphate Rock

\[
H_2SiF_6 + H_3PO_4 + FePO_4 + AlPO_4 + M_2SiF_6 + CO_2 + CaSO_4 2H_2O
\]

Hydro-Fluorosilicic Acid + Phosphoric Acid + Post Precipitates + Insol. Carbon + Gypsum + Silica-Dioxide + Fluorides

This reaction is the combination of sulfuric acid and phosphate rock. This takes place in the digestion system over a period of approximately eight hours. The reaction itself is very rapid, however, the proper formation of gypsum crystals takes time.

The desired products are the phosphoric acid and the hydrofluorosilicic acid. The post precipitates and insoluble silica-fluorides are undesirable but do not present much of a byproduct problem. The main problem is to separate the calcium and the sulfate.

The forming of gypsum crystals and filtrations is the most practical method of removing the calcium and sulfate ions. The best filtration is obtained with large gypsum crystals. These are produced if there is a slight excess of sulfate ions in the crystallizing solution.

The operation to remove the gypsum crystals is carried out on a series of filter surfaces. Belt or rotary type horizontal tilting pan filters are superior to other types and are widely used in almost all new plants.20

The filter is a continuous circulation unit, horizontally
circling in a counter-clockwise direction. There are usually 24 pans that provide different filtering functions. Dewatering of the filter cake and washing out the phosphoric acid-rich liquor is the function of the filter. See Figure 10.

The gypsum is removed and stored on a pile. The weak acid which is about 30% $P_2O_5$ is concentrated to about 54% $P_2O_5$. Multi-stage vacuum evaporators are used for this concentrating.

**Sources of Air Pollution**

The reactor in wet process phosphoric acid manufacture is the primary source of emissions. This usually accounts for 90% of the fluorides entering the control system. The digestion of phosphate rock in the reactor is the mechanism that releases both $SiF_4$ and HF.

The filter is the second most important source of fluoride emission, since most of the fluorides are emitted where the feed acid and wash liquor are introduced to the filter.

There are other minor sources of fluoride emissions that could include vents from sumps, clarifiers, and acid tanks. The gypsum pond may also evolve fluorides because of the vapor pressure of the fluoride. The rate of evolution of fluoride will vary with temperature, concentration, absolute pressure, and exposed area of the liquid surface.

**Design Procedure**

The typical pollution control device for a phosphoric acid
Fig. 10. Bird-Prayon Tilting Pan Vacuum Filter

production facility is a cross-flow wet scrubber similar to the one shown in Figure 8. The design of the scrubber will consist of:

1. Sizing the fume collection hoods
2. Sizing the ducting system
3. Material balance
4. Determining the amount of water needed for cooling in the spray chamber
5. Determining the amount of mass transfer accomplished in the spray chamber
6. Determining the number of transfer units needed in the packing
7. Calculating the area of the packing
8. Calculating the depth of the packing
9. Determining the total pressure drop in the entire system
10. Specifying the fan, stack and construction details

The emphasis will be primarily on practical design considerations as practiced by the phosphate industry.

Fume Collection Hood

Figure 11 is a layout of a typical phos acid plant indicating the position of the filter and the reactor.

The filter is approximately 60 feet in diameter with 8 foot wide by 14 foot long tray sections. The venting of the filter will occur at the point of acid wash. Two filter trays will be vented. This constitutes a surface area of approximately 224 ft².

A canopy hood will be used to enclose the vented area. The hood will be enclosed on two sides and will be 4 feet above the top
Fig. 11. Typical Layout of Phos Acid Plant Indicating Position of Scrubber
of the filter. Industrial Ventilation\textsuperscript{21} gives the following relationships to determine flow for a canopy hood:

\[ Q = (W + L)HV \]

where

- \( Q \) = flow, CFM
- \( W \) and \( L \) = sides, ft
- \( H \) = height of hood above surface, ft
- \( V \) = velocity, FPM

When a velocity of 200 FPM is assumed and the length of 2 trays is 28 feet, the width of a tray is 8 feet and the height is 4 feet, the flow will be 28,000 ACFM. This design should be for 30,000. Figure 12 indicates the approximate design of the hood.

The ductwork from the filter will have a flow of 30,000 ACFM. A duct diameter of 48 inches will be assumed. This will produce a velocity of 2,388 FPM.

The reactor vessel will be fully enclosed. Assorted openings in the top of the vessel will allow fumes to escape, therefore, it should be vented. The evolution of carbonate and fluoride within the reactor could be predicted using chemical equilibrium data. A survey of actual installations indicate that volumes of between 15,000 and 20,000 ACFM will be sufficient to maintain a negative pressure within the reactor.

A design velocity of 2,500 FPM within a circular 36 inch duct will be assumed. This will produce a volume of 17,675 ACFM. The system connecting the hood to the scrubber will have
four 90° elbows and approximately 100 feet of ductwork. Table 2 is the calculations for the friction losses and the required pressures.

The losses encountered in the short reactor duct will be assumed to be minimal and, therefore, omitted.

Material Balance

Figure 13 is a diagram of the proposed scrubber indicating the various known and unknown inputs into the system. The input concentrations are typical of those found in the industry.

The first step in establishing a material balance will be to convert all flows into molar concentrations. (Assume molecular weight of F⁻ to be 19 with a density of 0.062 lb ft⁻³).

1. Reactor flow = 17,675 ACFM @ 180° F

$$17,675 \text{ ft}^3 \times 60 \text{ min} \times 0.062 \text{ lb} = 65,751 \text{ lb} \times 1 = 2,267 \text{ lb moles moles hr}$$

Input pollutant = 120 lb moles F⁻ x 1 = 6.32 lb moles F⁻ hr

2. Filter flow = 30,000 ACFM @ 90° F (with density of 0.072 lb ft⁻³)

$$30,000 \text{ ft}^3 \times 60 \text{ min} \times 0.072 \text{ lb} = 129,600 \text{ lb} \times 1 = 4,470 \text{ lb moles moles hr}$$

Input pollutant = 30 lb F⁻ x 1 = 1.57 lb moles F⁻ hr

3. Determine input pollutant concentrations

Reactor = 6.32 lb moles F⁻ x \(\frac{1}{2,267 \text{ lb moles hr-air}}\) = 2.78 x 10⁻³ moles F⁻ moles air
### TABLE 2

PRESSURE DROPS IN FILTER DUCT

<table>
<thead>
<tr>
<th>Point</th>
<th>Restriction</th>
<th>Loss, Inches of Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Hood Entry</td>
<td>.09</td>
</tr>
<tr>
<td>A - B</td>
<td>10' L</td>
<td>.01</td>
</tr>
<tr>
<td>B'</td>
<td>90 EL</td>
<td>.10</td>
</tr>
<tr>
<td>C - D</td>
<td>15' L</td>
<td>.01</td>
</tr>
<tr>
<td>D'</td>
<td>90 EL</td>
<td>.10</td>
</tr>
<tr>
<td>E - F</td>
<td>15' L</td>
<td>.01</td>
</tr>
<tr>
<td>F'</td>
<td>90 EL</td>
<td>.10</td>
</tr>
<tr>
<td>G - H</td>
<td>60' L</td>
<td>.06</td>
</tr>
<tr>
<td>H'</td>
<td>90 EL</td>
<td>.10</td>
</tr>
</tbody>
</table>

Sp = Loss + Vp = .58" + .36" = .94" of H₂O
Fig. 13. Known Inputs into Scrubber
4. Determine output pollutant concentration. Assume the plant produces 26 tons of $P_2O_5$ per hour using the E.P.A. restriction of 0.02 lb $F^{-}$ tons $P_2O_5$.

$$0.02 \frac{lb \ F^-}{tons \ P_2O_5} \times 26 \ tons \ P_2O_5 \times \frac{1}{19} = 0.027 \ lb \ moles \ F^- \ hr-F^{-}$$

Design of Spray Chamber

The spray chamber serves the dual purpose of providing some pollutant gaseous diffusion and cooling the gas stream. The design of the spray chamber will consist of estimating the amount of pond water needed to cool the reactor gas and determining the number of transfer units. The procedure is as follows:

1. Determine operating conditions.

Input Data (See Figure 13)

1) Volume of inlet gas - 17,675 ACFM
2) Moisture of inlet gas, % by volume - 45%
3) Temperature of inlet pond water - 90° F

Output Data

1) Temperature of outlet pond water - 115° F
2) Temperature of outlet gas - 110° F
3) Moisture of outlet gas, by volume - 9%

2. Determine amount of input dry gas.

$$17,675 \ ft^3 \times 0.062 \ lb \ ft^3 \ min \times 60 \ min \times (1 - .45) = 36,163 \ lb \ dry \ air \ hr^{-}$$
3. Determine amount of heat needed to be removed. All enthalpy values are from Perry's Chemical Engineering Handbook.

- **ha** = enthalpy of dry air
- **has** = enthalpy of saturated air

Inlet ratio of weight of water to weight of air at 180° F is

\[
.45 \times 17,675 \text{ ft}^3/\text{min} = 50.28 \text{ ft}^3/\text{lb} \text{ water vapor}
\]

\[
158 \text{ lb water vapor} \times 60 \text{ min/hr} = 36,163 \text{ lb dry air} = 26.3\% \text{ water vapor/dry air}
\]

Enthalpy of dry inlet gas at 180° F

\[
ha = 43.3 \frac{\text{BTU}}{\text{lb dry air}}
\]

Enthalpy of saturated inlet gas at 180° F

\[
has = 748.5 \times \frac{.658}{.263} = 298 \frac{\text{BTU}}{\text{lb dry air}}
\]

Total enthalpy = 43.3 + 298 = 342 \frac{\text{BTU}}{\text{lb dry air}}

4. Determine outlet gas volume. Assume gas is saturated with 9% moisture.

\[
36,163 \text{ lb dry air} \times 14,359 \text{ ft}^3/\text{h} = 519,264 \text{ ft}^3/\text{hr} \times \frac{1}{.91} = 570,620 \text{ ft}^3/\text{hr}
\]

5. Determine enthalpy of exit air stream.

\[
hs = \text{total enthalpy} = 92.34 \frac{\text{BTU}}{\text{lb dry air}}
\]

6. Difference in input and output enthalpy

\[
342 \frac{\text{BTU}}{\text{lb dry air}} - 92.34 \frac{\text{BTU}}{\text{lb dry air}} = 249.66 \frac{\text{BTU}}{\text{lb dry air}}
\]
7. Enthalpy of pond water.

At outlet temperature 115° F \( h_w = \frac{83 \text{ BTU}}{\text{lb}} \)

At inlet temperature 90° F \( h_w = \frac{53 \text{ BTU}}{\text{lb}} \)

\( \Delta h_w = \frac{25 \text{ BTU}}{\text{lb}} \)

8. Amount of heat removed per hour.

\[
249.66 \frac{\text{BTU}}{\text{lb dry air}} \times 36,163 \frac{\text{lb dry air}}{\text{hr}} = 9.028 \times 10^6 \frac{\text{BTU}}{\text{hr}}
\]

9. Amount of water needed

\[
9.028 \times 10^6 \frac{\text{BTU}}{\text{hr}} \times \frac{1}{\frac{25 \text{ BTU}}{\text{lb}}} \times \frac{1}{\frac{500 \text{ lb}}{\text{GPM}}} = 722 \text{ GPM}
\]

The spray chamber will primarily be used for cooling of the gases, however, some mass transfer will take place. The efficiency of fluoride spray chambers was determined by John Craig at the University of Florida in 1970. Figure 14 indicates the number of transfer units that can be expected from a ratio of liquid to gas.

With a design of 800 GPM and approximately 8.05 m standard cubic feet of gas, a ratio of 100 exists. This would indicate that the maximum of 3 transfer units would be possible within the spray chamber. For design purposes only, one transfer unit will be assumed. This will be done for conservative design practice. It is common for the sprays to plug up with silica and not function properly. Additionally, the temperature and F\(^{-}\) concentration in the pond water will vary with time, therefore, the efficiency of
Fig. 14. Effect of Liquid/Gas Ratio on NTU for Spray Chamber Using Gypsum Pond Water

the chamber will change.

**Design of Packed Section**

**Number of Transfer Units**

In order to size the packed section, it will first be necessary to determine the number of transfer units needed to provide required efficiency.

1. Determine output from spray chamber.

The previously defined relationship of

\[
NTU = \left(\frac{Y_1 - Y^*}{Y_2 - Y^*}\right) CF
\]

is utilized to determine the output from the spray chamber.

\[
Y_1 = 2.78 \times 10^{-3} \text{ moles } F^- \text{ (input)}
\]

\[
Y_2 = \text{Unknown (output)}
\]

\[
Y^* = 2.0 \times 10^{-6} \text{ moles } F^- \text{ (equilibrium)}
\]

CF = 1.0 for low concentration values

NTU = 1 from spray chamber

therefore

\[
1 = \left(\frac{2.78 \times 10^{-3} - 2.0 \times 10^{-6}}{Y_2 - 2.0 \times 10^{-6}}\right) 1.0
\]

\[
Y_2 = 1.1 \times 10^{-3} \text{ moles } F^- \text{ moles air}
\]

2. Determine reduced flow of air due to temperature change of 180° F to 110° F from reactor.

\[
17,675 \frac{ft^3}{min} \times \frac{570}{640} \frac{R}{R} \times \frac{0.069 \text{ lb}}{ft^3} \times 60 \frac{min}{hr} \times \frac{1}{29} \frac{lb}{hr} = 2,247 \frac{lb \text{ moles}}{hr}
\]
3. Determine concentration of $F^-$ into packed section from reactor.

$$2,247 \, \text{lb moles} \times 1.1 \times 10^{-3} \, \text{moles F}^- = 2.47 \, \text{lb moles F}^- \, \text{hr moles air}^{-1}$$

$$2.47 \, \text{lb moles F}^- \, \text{hr} + 1.57 \, \text{lb moles F}^- \, \text{hr} \text{ from filter} = 4.04 \, \text{lb moles F}^- \, \text{hr}$$

4.04 lb moles $F^-$ into packed section

There is a combined air flow of $2,247 + 4,470 = 6,717 \, \text{lb moles air, hr}$ therefore, the inlet concentration of $F^-$ into the packed section is:

$$Y_1 = 4.04 \, \text{lb moles F}^- \, \text{hr} \times 6.717 \, \text{lb moles air}^{-1} = 6.0 \times 10^{-4} \, \text{moles F}^- \, \text{moles air}^{-1}$$

4. Determine NTU.

$$NTU = (\ln \frac{6.0 \times 10^{-4} - 2.0 \times 10^{-6}}{4.10 \times 10^{-6} - 2.0 \times 10^{-6}}) \times 1.0$$

$$NTU = 5.6$$

Design for 6 transfer units.

Amount of Scrubbing Liquid Needed

The slope of the equilibrium line as indicated in Figure 6 is approximately .04. The minimum amount of liquid needed can be determined by:

$$\frac{L_m}{G_m} = .04$$

where

$L_m = \text{liquid flow rate}$

$G_m = \text{gas flow rate (6,717 lb moles air)}$\, \text{hr}^{-1}$

therefore
6,717 \text{ lb moles air} \times 0.04 = 269 \text{ lb moles liquid hr} \\
269 \text{ lb moles hr} \times 19 = 5,111 \text{ lb} = 85 \text{ lb min} = \text{approximately 10 gal min}

This figure of 10 GPM represents the theoretical amount of water needed to perform the necessary mass transfer. The actual amount of water needed should be a much greater volume due to several factors:

1. The method assumes perfect mass transfer. The reaction of H\textsubscript{2}O and SiF\textsubscript{4} will result in a silica shell forming on the water film. This will impede the diffusion process.

2. The formation of silica in the packed section requires water flushing for removal. Low volumes of water would result in the plugging of the packing with solids.

3. The lower the amount of water used, the smaller the area of the packing. A relatively small packed section coupled with high volumes of gas would produce high velocities. This would result in low water-gas contact time. Also, the high velocity would strip water droplets off the packing, resulting in a demisting problem.

A survey of several companies utilizing the cross-flow packed section indicates an approximate water to gas flow ratio of 15 to 20 GPM per 1000 ACFM.\textsuperscript{23} Assuming a ratio of 17.5, the resulting amount of water usage for 40,000 ACFM would be 700 GPM. High amounts of water usage is not a problem due to the fact that water is recycled. In the Florida Phosphate Industry the only
cost due to water use is that of pumping.

**Area of Packing**

The area of the packing is based on the flooding correlation in Figure 5. The relationship of the gas flow rate, \( G \), divided by the superficial gas flow rate, \( G' \), will produce the area.

1. Determine the density of liquid and gas. Assume the density of the pond water to be that of pure water (62.4 lb/ft\(^3\)).

For the gas:

\[
p_G = \frac{PM}{RT}
\]

\[
P = 14.7 \text{ lb/ft}^2
\]

\[
R = 10.73 \text{ psia - ft}^3/\text{lb mole °R}
\]

\[
T = 90 + 460 = 550°\text{R}
\]

\[
M = 29.0 \text{ (Assume molar mass of air)}
\]

\[
p_G = \frac{14.7(29.0)}{10.73(570)} = 0.070 \text{ lb/ft}^3
\]

2. Determine the ordinate for flooding.

\[
\frac{L}{G} (\frac{p_L}{p_G})^{0.5} = \frac{352,800 \text{ lb/hr}}{188,181 \text{ lb/hr}} \frac{0.07 \text{ lb}}{62.4 \text{ lb/ft}^3} = 0.063
\]

From Figure 5, the ordinate for flooding is .16.

3. Calculate the superficial gas flow rate, \( G' \).

Assume that the packing material is \( \frac{1}{2} \)" intalox saddles. The packing factor "F" is 52. Assume the viscosity to be that of water, 1 centipose.
\[ \frac{0.063}{g \rho G_\text{p}} = \left( \frac{(G')^2 F (\mu_L)^{0.2}}{g \rho G_\text{p} \rho_L} \right) \rho_W \]

\[ 0.063 = \left( \frac{(G')^2 52 (1.0)^2}{32.2 (0.07) (62.4)} \right) \times 1 \]

\[ G' = \frac{0.659 \text{ lb}}{\text{s-ft}^2} \]

Assume the rate to be 60% flooding

\[ \frac{0.659 \text{ lb}}{\text{s-ft}^2} \times 0.60 = \frac{0.396 \text{ lb}}{\text{s-ft}^2} \]

4. Determine area of packing.

\[ A = \frac{G}{G'} = \frac{188,181 \text{ lb}}{3,600 \text{ sec} \times \frac{\text{lb}}{\text{hr}}} = 132 \text{ ft}^2 \]

This packing dimension of 8 x 16.5 is similar to that found in actual use.

**Width of Packing Bed**

The width of the packing in a cross-flow scrubber may be estimated by using the same procedure as that of a counter current scrubber.

1. Evaluate the height of a transfer unit in terms of the gas phase.

\[ H_{\text{TG}} = \frac{a(G')^\beta}{(L')^\gamma} \]

\[ a = 5.0 \]

\[ \beta = 0.30 \]

\[ \gamma = 0.50 \]
\[ G' = 1,426 \text{ lb/hr-ft}^2 \]
\[ L' = 2,673 \text{ lb/hr-ft}^2 \]
\[ Sc = 1.24 \text{ (for SiF}_4\text{)} \]

\[ H_{TG} = \frac{5.0 \times (1,426)^{-30}}{(2,673)^{0.5}} (1.24)^{0.5} \]

\[ H_{TG} = 1.1 \]

2. Evaluate the height of a transfer unit in terms of liquid phase.

\( H_{TL} \) may be considered to be zero due to the fact that the absorption of gaseous fluorides has been shown by Whynes\textsuperscript{24} to be gas film controlling. The rate of absorption is controlled by the rate at which the gaseous fluorides reach the liquid-gas interface.

3. Determine the height of the packing.

\[ H_{OG} = H_{TG} + \left( \frac{mGm}{Lm} \right) H_{TL} \]

\[ H_{OG} = 1.1 + 0 \]

\[ H_{OG} = 1.1 \]

\[ Z = H_{OG} + NTU \]

\[ Z = 1.1 \times 6 \]

\[ Z = 6.6 \text{ ft} \]

Design for 6 feet which is a common width of packing used in actual phos acid scrubbers.

Pressure Drop

The pressure drop can be calculated by utilizing the following equation:
\[ \frac{\Delta P}{Z} = m(10^{-8}) \left( \frac{10nL'}{p_L} \right) \left( \frac{G'}{p_G} \right)^2 \]

\( m = 5.66 \) for 1\( \frac{1}{2} \)" intalox saddles

\( n = .00225 \) for 1" intalox saddles

\( \rho = 62.4 \text{ lb/ft}^3 \)

\( \rho_G = .07 \text{ lb/ft}^3 \)

\( L' = 2,673 \text{ lb/hr-ft}^2 \)

\( G' = 1,426 \text{ lb/hr-ft}^2 \)

\[ \frac{\Delta P}{Z} = 5.66 \left( 10^{-8} \right) \left( 10 \cdot .00225 \right) \left( 2,673 \right) \left( 1,426 \right)^2 \]

\[ \frac{\Delta P}{Z} = \frac{62.4}{.07} \]

\[ \frac{\Delta P}{Z} = 2.05 \text{ lb per ft}^2 \times .192 \text{ in H}_2\text{O} = .39 \text{ in H}_2\text{O} \]

For 6 feet of packing there will be a drop of 2.36 inches of H\(_2\)O. The normal drop under working conditions should be about 3 inches. The formation of silica will tend to plug the packing and, therefore, over design will be necessary.

**Design Details**

The action of gas passing through a wet packed section will result in the formation of water droplets. A mist eliminator will be needed to stop the particles from entering the fan and exiting the stack. The screen should be capable of removing droplet sizes greater than 0.5 microns. Several manufacturers produce units that can remove mist droplets of that size. The pressure drop should not be greater than 0.5 inches of water for the unit.

The fan selection for the scrubbing unit will consist of a
centrifugal fan that will be required to produce a flow of 48,000 ACFM with a static pressure drop of 5 inches of water.

The materials of scrubber shell construction can be either rubber-lined steel, FRP, or stainless steel. The most economical at the present time is rubber-lined steel. All internal piping and packing support grids should be made of stainless steel.

The length of the scrubber will be 31 feet. The scrubber will be 3 feet high by 17 feet wide. The packing will have 6 inch wide supports all around.

Figure 15 indicates the approximate layout of the scrubber. Four rows of sprays will be used for the spray chamber. Each row will have 36 sprays for a total of 144.

The packing will have 4 rows of sprays with 6 sprays for a total of 24. In addition, the face of the packing will have 36 sprays.

The typical phos acid scrubber stack in Florida is approximately 100 feet high. The material of construction should be rubber-lined steel. Sampling portholes should be provided at a minimum distance of 3 diameters from the stack exit.
Fig. 15. Phos Acid Scrubber
SUMMARY

The control of gaseous fluoride emissions from a phosphoric acid production facility is most commonly controlled by the use of a cross-flow wet scrubber. The typical fluoride inputs from both the reactor and filter will be approximately 150 lb/hr F⁻. A maximum output of .48 lb/hr F⁻ is needed to meet E.P.A. New Source Performance Standards. A 99.68% reduction in emissions will be required.

The design of the scrubber necessary to meet the reduction consists of the following steps:

1. Size of ductwork
2. Determine the material balance
3. Calculate the liquid flow
4. Determine the packing area and depth
5. Calculate the pressure drop

The scrubber as designed in the text will be 9 feet high, 17 feet wide and 31 feet long. It will utilize approximately 1,500 GPM of pond water for scrubbing and cooling. It will have 792 ft³ of packing with a total pressure drop of 5 inches of water.
FOOTNOTES


6Florida Air Pollution Control Commission, Minutes of the Florida Air Pollution Control Commission (Tallahassee, Florida: n.p., 1957-1967).

7Florida, Department of Environmental Regulation, Air Pollution (Tallahassee, Florida: n.p., 1972), Chapter 17-2.


9Ibid., p. 263.

10Ibid., p. 275.

11Ibid., p. 280.


14Ibid., p. 284.

15Ibid.

16Ibid., p. 272.


