

FLUORIDE REMOVAL FROM WET-PROCESS  
PHOSPHORIC ACID REACTOR GASES

By  
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## KEY TO MAIN ABBREVIATIONS

BPL - bone phosphate of lime, commonly used to express the content of tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , in phosphate rock, and used to express the grade of ore.

cfm - gas flow, cubic feet per minute.

gpm - liquid flow, gallons per minute.

HP - horsepower.

mg/std cu m - milligrams per standard cubic meter  
(standard conditions of 25°C and 760 mm mercury).

mv - millivolts.

ppb - parts per billion.

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FLUORIDE REMOVAL FROM WET-PROCESS  
PHOSPHORIC ACID REACTOR GASES

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Due, in part, to the growth of the phosphate fertilizer industry, fluoride pollution of the air has become an area of major concern. Since the state of Florida is the center of this industry in the United States, air pollution from the phosphate fertilizer industry is a major problem in certain areas of the state. Fluoride air pollution is a matter of great concern since even at very low levels it is known to produce detrimental effects on vegetation and animals.

Phosphate fertilizer manufacturing complexes normally have acid plants associated with them which produce the acid necessary to convert the highly insoluble fluorapatite in phosphate rock to a more readily available form of a nutrient phosphate. One of the most common methods of producing fertilizer grade phosphoric acid is via the wet-process phosphoric acid process.

In this process, the reaction between the phosphate rock, sulfuric acid, and recycled weak phosphoric acid releases fluoride gases which may be harmful to plants and animals if not closely controlled.

With this in mind, a research project was initiated to study the effects of operating variables upon certain types of air cleaning equipment and the efficiency of fluoride removal from wet-process phosphoric acid reactor gases.

For this study, a portable pilot plant was constructed on two semi-trailers, taken to a 650 tons/day wet-process phosphoric acid plant, and connected into the center compartment of the reactor tank. The air cleaning equipment used in this study included a 2600 cfm capacity cyclonic spray chamber, a 2600 cfm capacity venturi-cyclonic demister scrubber, a 350 cfm capacity baffle plate impingement column, and a 1000 cfm capacity variable throat venturi. The effects of liquid and gas flow rates and type of scrubbing liquid upon fluoride removal efficiency were studied. The types of scrubbing liquid used were well water and gypsum pond water.

In the case of scrubbing with well water, fluoride removal efficiencies of 63.2 to 96.1 percent, for less than 1.5 inches of  $H_2O$ , and for an energy input of less than 0.7 horsepower/1000 std cfm, are possible using the cyclonic spray chamber. Efficiencies of 88.3 to 99.5 percent, for less than 15 inches of  $H_2O$ , and for an

energy input of less than 3.7 horsepower/1000 std cfm, are possible using the venturi-cyclonic demister scrubber. Efficiencies of 90.1 to 99.0 percent, for less than 8.5 inches of  $H_2O$  pressure drop, and for an energy input of less than 1.0 horsepower/1000 std cfm, are possible using the baffle plate impingement column. Efficiencies of 92.9 to 97.8 percent, for less than 40.0 inches of  $H_2O$  pressure drop, and for an energy input of less than 4.3 horsepower/1000 std cfm, are possible using the variable throat venturi.

In all instances, scrubbing with gypsum pond water produced lower removal efficiencies than scrubbing with well water at approximately the same pressure drops and energy requirements.

The fluoride removal efficiencies developed by the equipment studied were not sufficiently high to meet the requirements necessary for emission control from this process. Two-stage scrubber installations are required if the fluorides from the reactor are to be brought under control. Since two-stage scrubber installations are necessary, gypsum pond water would be the preferable scrubbing liquid because the use of this liquid will not disturb the existing water balance established in the process.

## CHAPTER I

### INTRODUCTION

The emission of fluorides into the ambient air has long been a concern of many people and with the growth of certain industries fluoride pollution of the air has become more of a problem. The accepted threshold limit value for human exposure under industrial conditions is 3 ppm; however, atmospheric pollution would involve concentrations far below this level. Criteria for ambient fluoride levels are being prepared by the National Air Pollution Control Administration under provisions of the Clean Air Act of 1967. The American Industrial Hygiene Association has recommended the following air quality levels for gaseous fluorides, expressed as HF by volume:

4.5 ppb average for 12 hours

3.5 ppb average for 24 hours

2.0 ppb average for 1 week

1.0 ppb average for 1 month

There has been no demonstrated case of chronic fluorosis, or acute poisoning, resulting from humans breathing air containing these low concentrations of fluorine compounds.<sup>1</sup> Although some have suggested that fluorine compounds may have been the prime agents in the Meuse

Valley and Donora air pollution disasters, no evidence has been presented to substantiate these claims.<sup>2,3,4</sup>

Fluoride contaminants may be emitted to the ambient air in a wide variety of industrial processes in which fluorine compounds are manufactured, utilized, or are present as impurities in the process materials. The processes include but are not limited to:

Major sources

1. Phosphate fertilizer manufacturing
2. Aluminum manufacturing
3. Steel manufacturing

Minor sources

1. Brick and tile manufacturing
2. Enamel frit manufacturing
3. Manufacture of fluorine compounds
4. Power generation
5. Use of fluorine compounds as catalysts
6. Manufacture of motor fuels

Although the previously mentioned industries have been recognized as producing damage in some instances, numerous other industries may emit fluoride compounds to some extent in processing of minerals and ores. This is due to the wide distribution, frequently in small concentrations, of fluorine throughout the earth's crust. Recent estimates have placed fluorine as the thirteenth most abundant element in the earth's crust.<sup>5</sup>

Senrau<sup>1</sup> and Specht<sup>6</sup> consider the manufacture of phosphate fertilizers as the most important source of fluoride contamination of the atmosphere. Since Florida produces approximately 70 percent of the nation's phosphate rock, air pollution from this industry is a major problem in certain areas of the state. The objective of this research was to study fluoride emissions and their control from one of the processes involved in the phosphate fertilizer industry located in Florida and all discussion from this point on will be limited to this industry and its manufacturing processes.

The recovery of fluorine effluent, gaseous and particulate, from the phosphate industrial operations presents three equally demanding problems. First, level of recovery; second, operational dependability; and third, capital investment and operating costs. The recovery of gaseous fluorine compounds is, at present, most economically achieved by absorption in water or in other aqueous solutions. The design of a fluoride recovery system is not without many problems, some of which are:

1. Multiple contaminants within an effluent stream,
2. Low concentration of inlet gas and the extremely low concentration requirement for effluent.
3. Limitation in choice of scrubbing medium.

4. Low pressure drop requirements for the system.
5. Disposal of scrubbing solution.

In order to optimize the costs involved in constructing and maintaining recovery systems, the following steps are necessary:

1. Determination of optimum scrubbing solutions.
2. Determination of optimum scrubbing equipment configurations.
3. Determination of optimum liquid-gas ratios.

This research effort dealt with specific gas-liquid absorption processes utilizing four types of scrubbers and two scrubbing solutions. The types of scrubbers studied were:

1. Airetron Engineering Corporation modified low pressure drop venturi.
2. Airetron Engineering Corporation modified cyclonic spray chamber.
3. Peabody Engineering Company impingement baffle plate column.
4. American Air Filter Company variable throat venturi.

The scrubbing solutions studied were:

1. Gypsum pond water, pH 2, available at all plant sites.
2. Well water, pH 5 to 7, available at all

plant sites and lowest cost buffer for gypsum pond waters.

This study sought to answer the following questions:

1. What is the relationship between the operating variables and removal efficiency?
2. What are the mass transfer characteristics?
3. What are the optimum energy requirements?
4. What is the maximum fluoride removal?

The major independent variables studied for each system were:

1. Scrubbing solution.
2. Liquid and gas flow rates.

## CHAPTER II

### PHOSPHATE INDUSTRY IN FLORIDA

#### Phosphate Fertilizer Manufacturing Processes

Florida's phosphate industry had its start in the 1830's when phosphate pebbles and fossil bones were discovered in the Peace River south of Fort Meade.<sup>7</sup> Early mining efforts soon were shifted from the river bed to near Bartow and Mulberry, where land-locked phosphate of much higher grade could be obtained at far less cost. From this small beginning, the phosphate industry in Florida has grown to an industry which at the present time exceeds 40 million long tons a year or approximately 70 percent of the nations output.

The principal use of phosphate rock is in the production of fertilizer. Other products are phosphorus, phosphoric acid and ferrophosphate. By-products of the phosphate industry include gypsum, fluorine compounds, sulfur dioxide and carbon dioxide.

#### Geology

Two general types of phosphate ore deposits serve as sources of high-grade material. One is of igneous origin; the other sedimentary. Both have essentially the

same phosphate mineral, calcium phosphate of the apatite class of minerals.

The igneous deposits are not so extensive in number or as easily and economically processed as the sedimentary deposits.<sup>8</sup> This type of deposit accounts for approximately 10 percent of the world's production from mines located in Russia, South Africa and South America.<sup>9</sup>

The major phosphate deposits of the world are sedimentary in origin and nearly all are calcium phosphate. There are two types of sedimentary phosphate deposits -- guano and pellet. Hutchinson<sup>10</sup> has discussed the guano type in some detail in his work. The pellet deposits are the major deposits in the world. They furnish over 80 percent of the world's phosphate demands at the present time. According to Emigh<sup>9</sup> they exist in many parts of the world and new deposits are periodically being discovered. A recent discussion of the geology of these deposits is given by Emigh.<sup>9</sup>

Recognizing that there is little phosphate in sea water, past theories have tried to establish how sufficient quantities of phosphate in solution could be concentrated in any one place to furnish the large amounts now present in the phosphate deposits. Some of the theories that have been postulated are:

1. Accumulation of remains of organisms due to local destruction of sea life.

2. Chemical precipitation.
3. Phosphatization of animal excrement.

Emigh<sup>9</sup> indicates the most accepted theory at this date is the one postulating chemical precipitation.

The phosphate deposits in Florida are divided into three types: land pebble, hard rock and soft rock. The land pebble phosphate deposits, centered in Polk and Hillsborough counties, account for more than 95 percent of the total Florida production.<sup>11</sup> These deposits are apparently ancient placer deposits concentrated by wave action along a former shoreline or shorelines.

The hard rock deposits occur in a narrow belt extending southward from northern Florida through the western half of the peninsula and parallel to its axis for about 100 miles to a point about halfway down the state. In this type of deposit the phosphate has apparently replaced other types of rock and occurs as fragmentary rock, boulders, plate rock, pebbles, and soft phosphatic clay.

Soft rock phosphate production is from the waste ponds of former hard rock operations and from colloidal clay deposited at the margins of the land-pebble phosphate area. The deposits currently being mined yield phosphate rock containing from 65 to 80 percent BPL. BPL denotes bone phosphate of lime,  $\text{Ca}_3(\text{PO}_4)_2$ , and is used as an expression of the grade of deposit.

## Mining

In the land pebble area of Florida, phosphate is covered over by deposits of quartz sand known as the overburden ranging in thickness from 5 to 50 feet, averaging about 15 feet. The phosphate ore-bearing material known as "matrix" consists of approximately 30 to 60 percent phosphate rock, 15 to 40 percent clay and colloidal phosphate, and 10 to 25 percent quartz sand, is found beneath the overburden.

In mining, the overburden is removed by drag-lines. After the overburden is stripped off, the matrix is removed and deposited into a pit where it is sluiced into a sump. The slurry formed during the sluicing operation is pumped from the sump to the flotation washer plant. Figure 1 depicts the flow of the phosphater rock from the mine through shipment.

## Washing and Flotation

At the washing and flotation plant, the slurry of water, phosphate, quartz sand, and clay passes through two processing stages, washing and flotation. Figure 2 describes the flow of rock through the washer and flotation plant.

Phosphatic material is scrubbed, washed, and screened. The screening separates the material into two sizes, less than and larger than 1 mm. Material not passing a 14-mesh screen comprises pebble rock

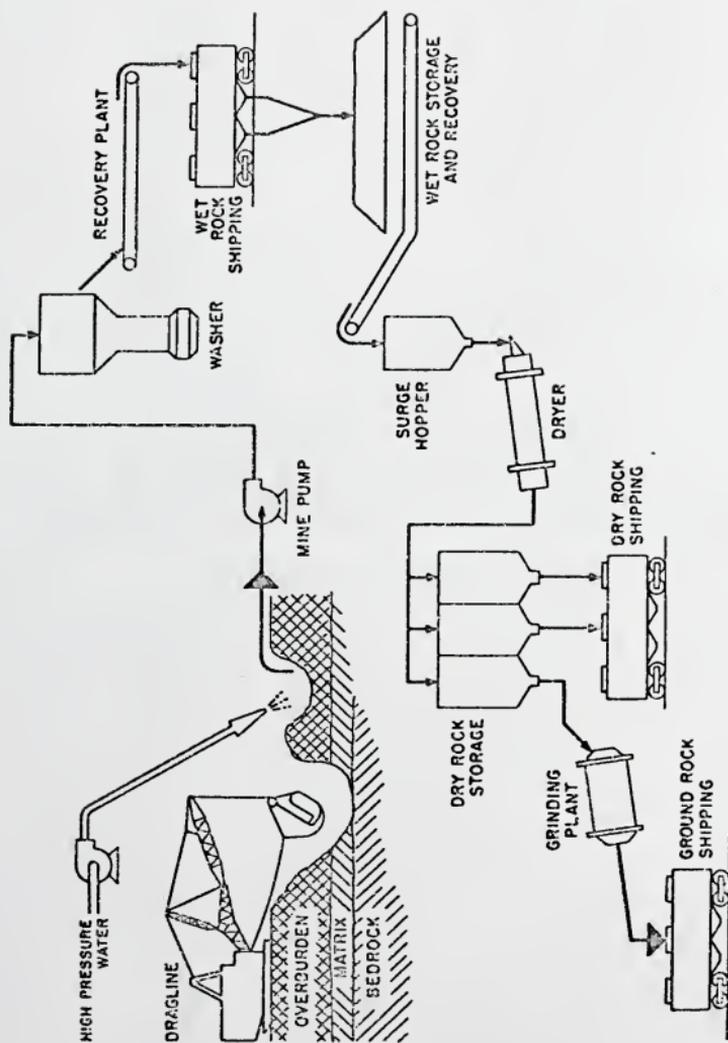


Figure 1: Typical Phosphate Rock Processing Facility

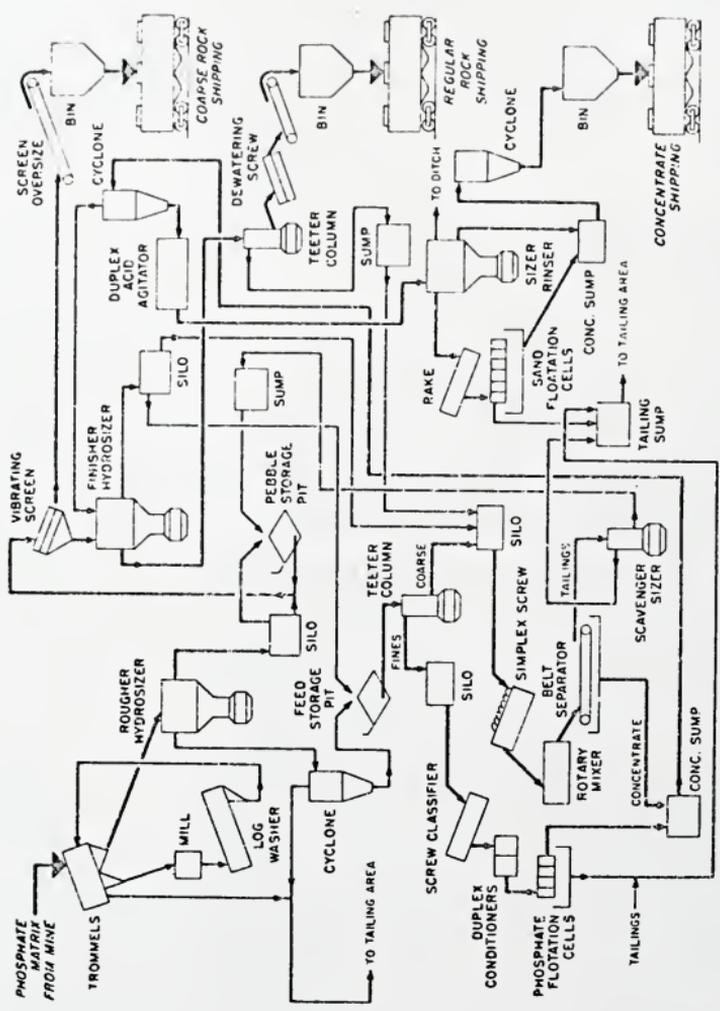


Figure 2: Washer and Flotation Plant Flow Diagram

which is more or less free from quartz sand and clay when delivered to loading bins for shipment. The smaller material is sent to feed storage bins for further processing in the flotation plant.

In the flotation plant reagents are used to separate the quartz sand from the phosphatic material. Reagents used in the process are caustic soda, fuel oil, and a mixture of fatty and resin acids known as tall oil. The caustic soda cleans the phosphate particles and regulates the pH so that the tall oil can be properly absorbed. The phosphate rock particles then take on a film of oil and when agitated float to the top of the water while the sand sinks to the bottom.

### Beneficiation

Various grades of rock are blended on a conveyor belt to meet specific manufacturing and sales requirements. The rock is fed into either rotary or fluidized bed dryers. Dried rock is then conveyed to grinders for final sizing before shipment to fertilizer plants for the manufacturing of triple superphosphate and phosphatic fertilizer mixtures, phosphoric acid, or to produce elemental phosphorus. Figure 3 illustrates the rock flow in a typical beneficiation facility.

### Acid Manufacturing

Most phosphate manufacturing facilities have sulfuric and phosphoric acid manufacturing plants

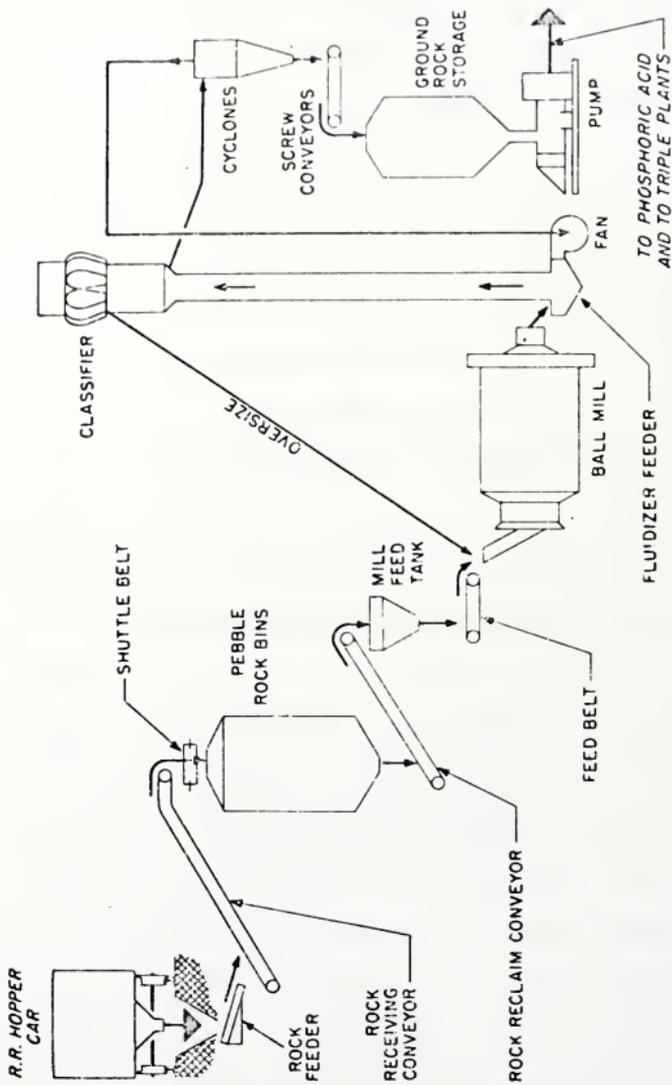


Figure 3: Typical Phosphate Rock Benefication Flow Diagram

associated with them. Figure 4 illustrates the acid flow in a typical acid-fertilizer manufacturing complex.

Sulfuric acid is manufactured by the conventional Contact Sulfuric Acid process.<sup>12</sup> In this operation elemental sulfur is burned in a combustion chamber to form sulfur dioxide gas. The sulfur dioxide is then passed through a series of converters, charged with catalysts; there it interacts with air to form sulfur trioxide gas. This gas passes on to the absorption tower, where it interacts with water and weak sulfuric acid to form the strong product sulfuric acid. Figure 5 is a typical flow diagram of a Contact Sulfuric Acid process.

In the manufacture of phosphoric acid by the Wet-Process Phosphoric Acid process,<sup>12</sup> ground phosphate rock is mixed with the strong sulfuric acid in a reactor to form weak phosphoric acid and gypsum. The weak phosphoric acid is separated from the gypsum in the filtering step, and the gypsum is pumped to ponds for storage. The clean phosphoric acid is then concentrated to 54 percent  $P_2O_5$  strength in vacuum evaporators. The 54 percent strength acid is then stored for use in fertilizer manufacture or for further concentrating to make superphosphoric acid. Figure 6 is a flow diagram depicting a typical phosphoric acid process.

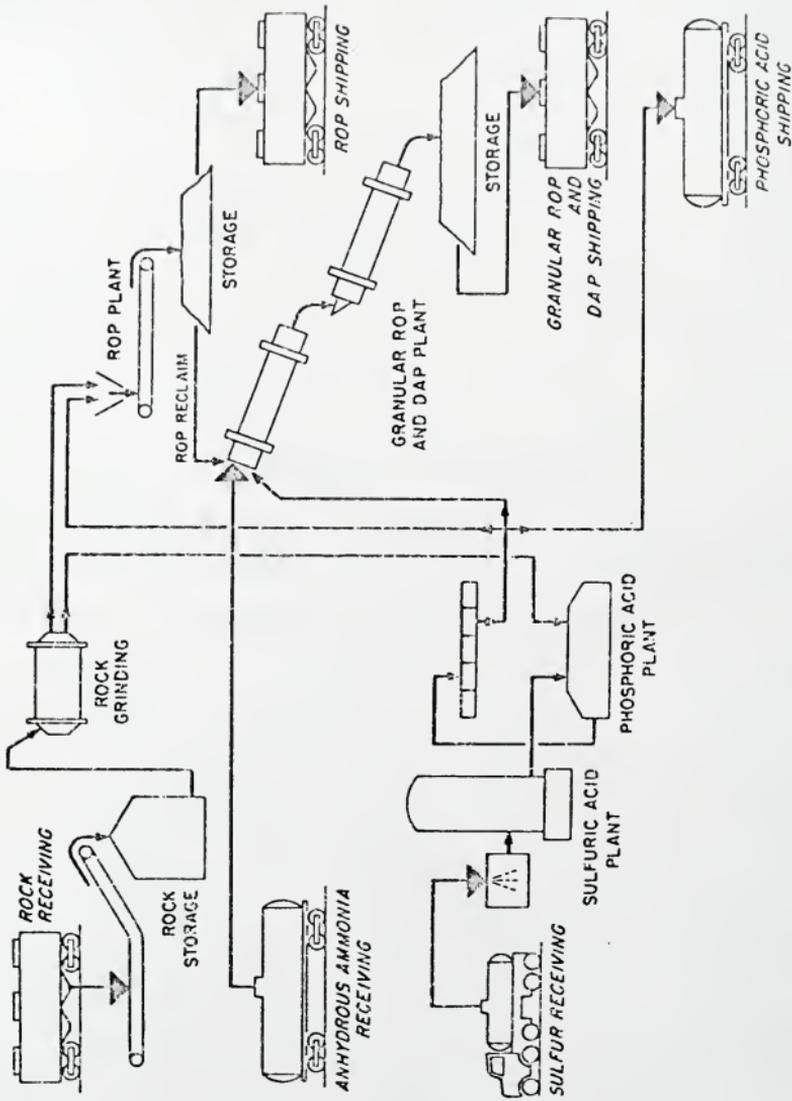


Figure 4: Typical Acid-Fertilizer Manufacturing Complex Flow Diagram

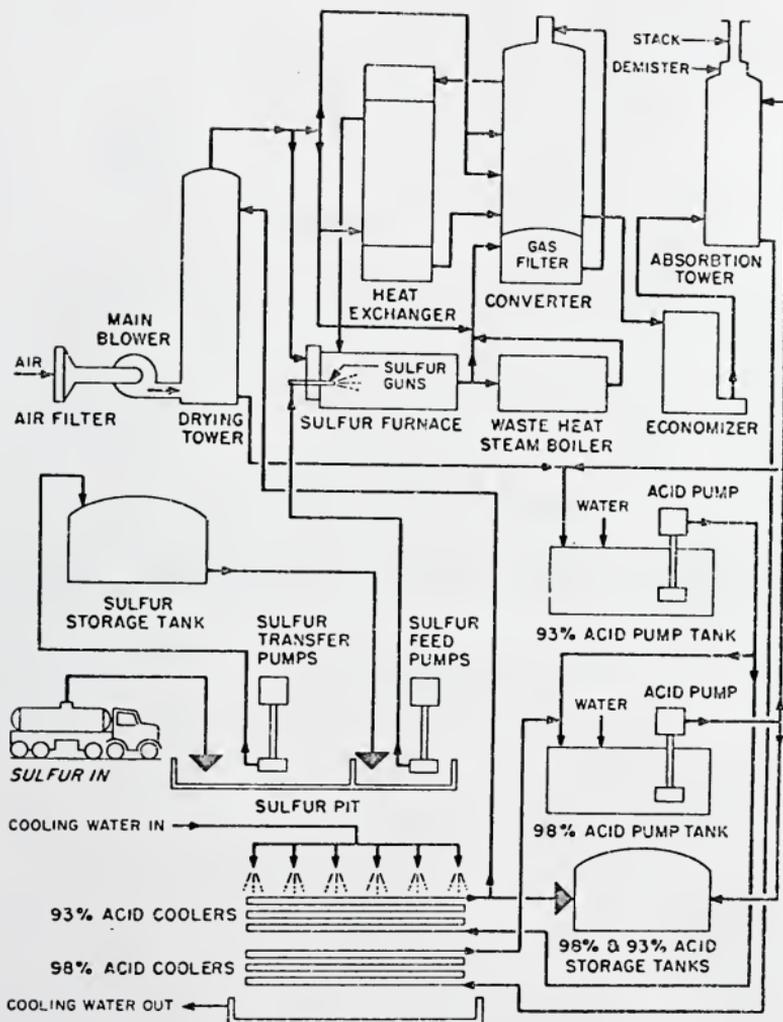


Figure 5: Typical Contact Sulfuric Acid Process Flow Diagram

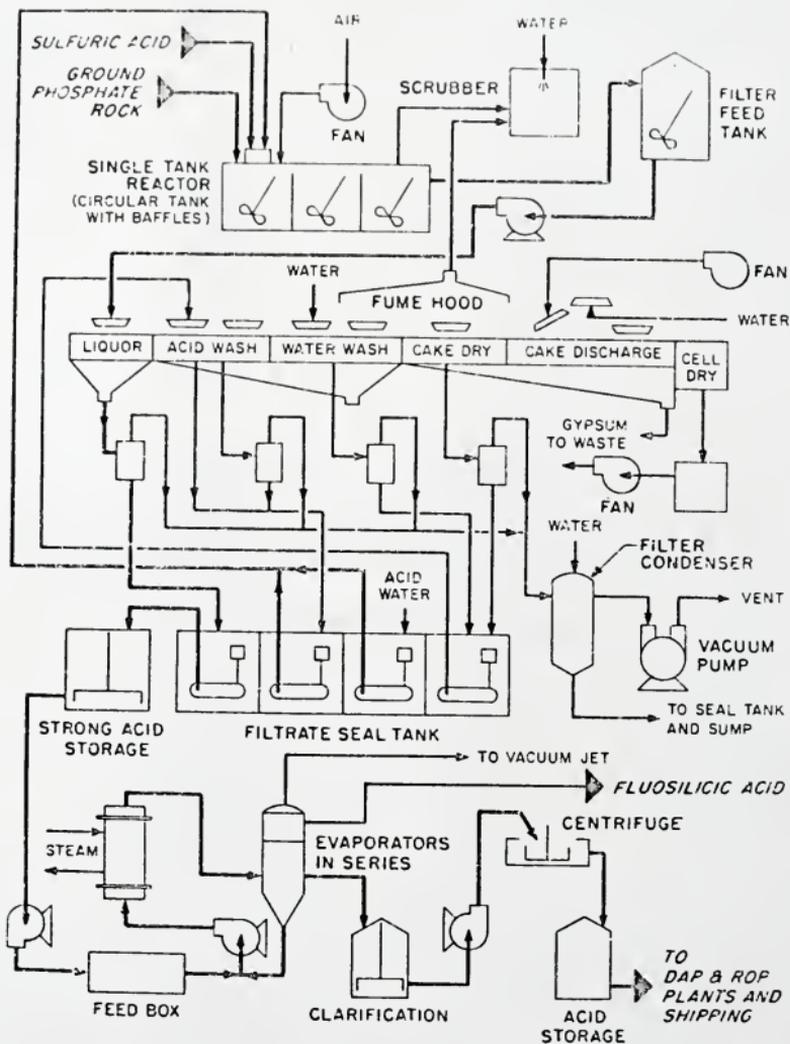


Figure 6: Typical Wet-Process Phosphoric Acid Flow Diagram

## Fertilizer Manufacturing

Triple superphosphate (TSP) is manufactured by reacting phosphate rock with phosphoric acid in a cone-type continuous mixer. The cone discharges to a series of enclosed moving belts called the "Den," where the mixture completes its chemical reaction and solidifies. From these belts the triple superphosphate is sent to the storage pile, where after further "curing" it is ready for shipment. At this stage it is called run-of pile (ROP) triple superphosphate. Figure 7 illustrates a typical triple superphosphate plant.

Granular TSP is made from ROP triple superphosphate.<sup>9,12</sup> In this process ROP with a small amount of water is rolled in a granulating drum to form small round pellets. These are dried in a rotary or fluidized bed dryer, cooled, screened to size and sent to finished product storage.

Diammonium phosphate (DAP) is made by reacting phosphoric acid and anhydrous ammonia in a reactor, to form a hot liquid DAP.<sup>9,12</sup> This liquid is pumped to a granulator where it mixes with recycled material and solidifies. It is then dried, cooled, screened to size and sent to storage. Figure 8 illustrates a typical diammonium phosphate plant.

## Elemental Phosphorous Manufacturing

At present there are only two elemental phosphorous manufacturing facilities in Florida.<sup>6</sup> Elemental

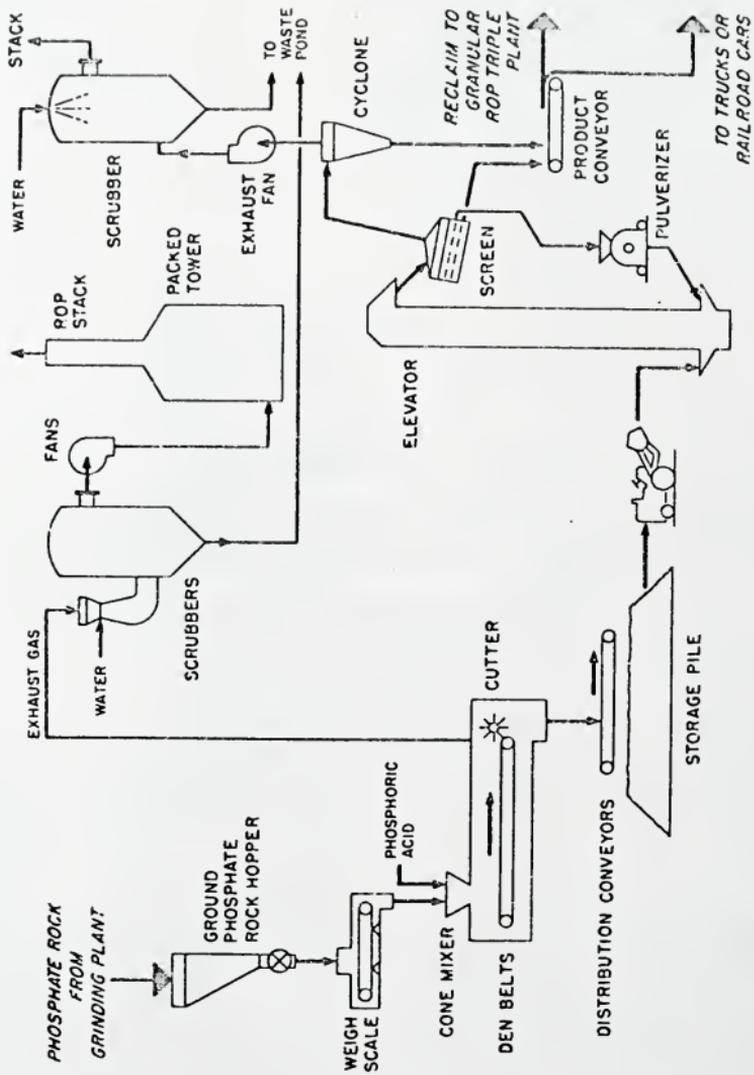


Figure 7: Typical Triple-Superphosphate Facility Flow Diagram

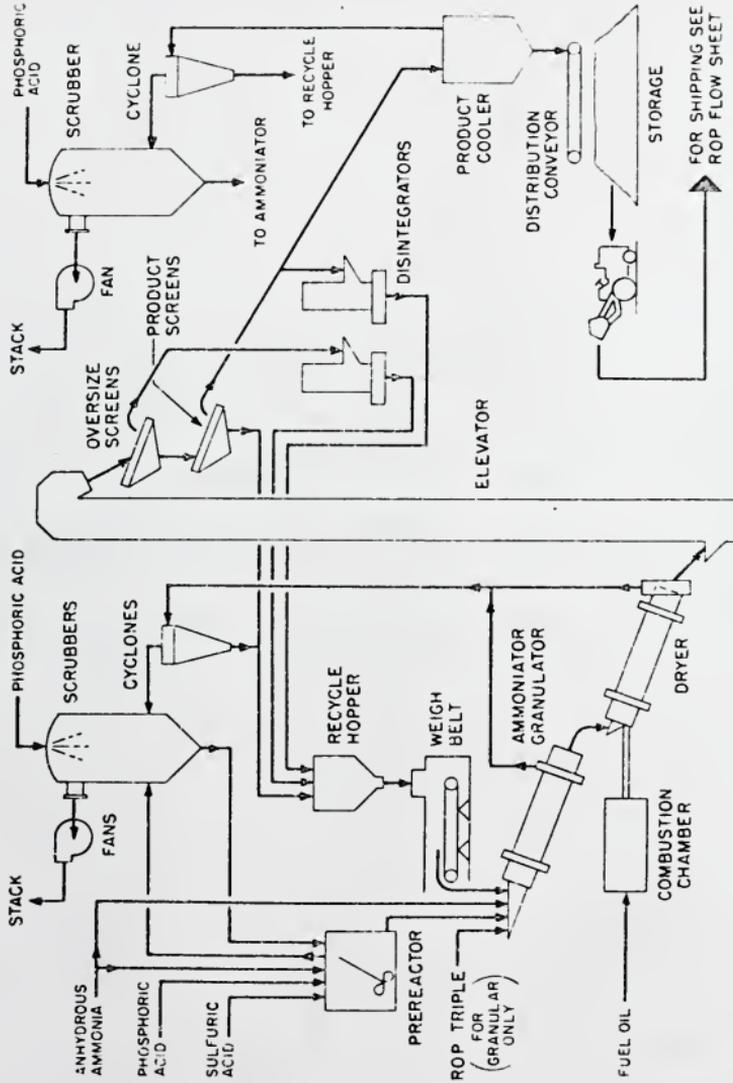


Figure 8: Typical Diammonium Phosphate Facility Flow Diagram

phosphorous is manufactured at these facilities by the electrothermal process.<sup>12</sup> In this process the phosphate rock is mixed with coke which acts as a reducing agent and silica which acts as a flux and conveyed to electric furnaces. As the furnace charge is melted the elemental phosphorus is released from the rock and passes off as a vapor. The vapor is condensed and collected as a liquid in pans under water below the condenser pipes. The elemental phosphorus is then stored under water because of its instability and is ready for use or sale. Figure 9 illustrates a typical elemental phosphorous plant.

#### Air Pollution Associated With the Phosphate Industry

Florida phosphate rock is a non-crystalline phosphorite consisting principally of fluorapatite (a complex of tricalcium phosphate and calcium fluoride) having the approximate formulation  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ .<sup>13</sup> The tricalcium phosphate is only slightly soluble and when combined with calcium fluoride is nearly insoluble in water. The fluorine represents 3.5 to 4.0 percent by weight of the total compound. In order to make the phosphate available to plants or animals and at the same time non-toxic, the fluoride must be removed.

The release of fluorides from the phosphate rock is usually accomplished by treatment with heat or acid. Unfortunately, this treatment produces fluorides in the

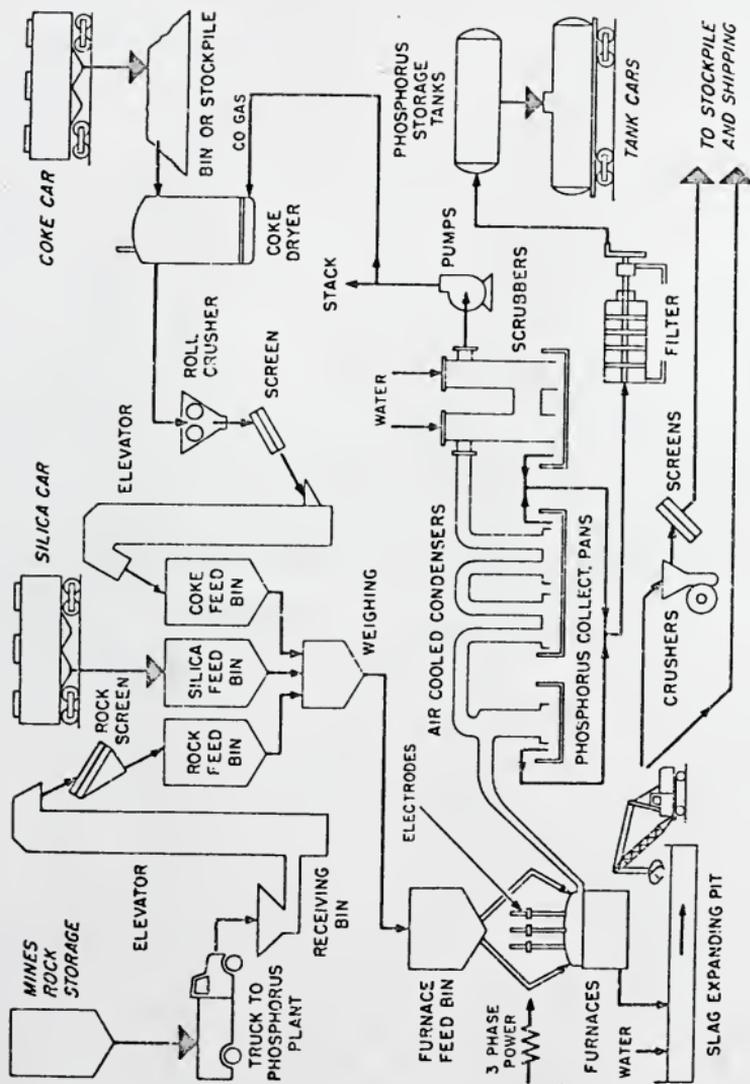


Figure 9: Typical Elemental Phosphorus Facility Flow Diagram

form of HF,  $\text{SiF}_4$ , and  $\text{H}_2\text{SiF}_6$ . In addition to the gases and vapors released from some of the chemical processes, insoluble dust containing upwards of 4 percent fluoride may be discharged from other processing facilities such as drying, grinding and material handling.

Generally in the presence of reactive silica from the rock, fluoride is released as gaseous silicon tetrafluoride ( $\text{SiF}_4$ ), which readily is hydrolyzed in the presence of water to  $\text{H}_2\text{SiF}_6$ . Silicon tetrafluoride evolution is not restricted to any one process in manufacture of fertilizer. It is normally given off in the processes of (1) acidulation, (2) concentration by evaporation, and (3) calcination when silica and water are present.

Specht and Calaceto<sup>6</sup> have reported the fluoride evolutions from fertilizer processes given in Table 1.

TABLE 1  
FLUORIDE EVOLUTION  
ACCORDING TO SPECHT AND CALACETO

<u>Process</u>	<u>g F<sup>-</sup>/std cu m*</u>
Acidulation	
Batch	10.6 - 20.6
Continuous	2.1 - 5.3
Triple superphosphate	
Granular	1.8 - 3.6
Phosphoric acid	
Digestion (Acidulation)	0.3 - 1.2
Superphosphoric	7.0 - 17.5

\* Standard conditions not stated

Huffstutler<sup>14,15</sup> reported fluoride emissions "that are probably in the form of silicon tetrafluoride" as noted in Table 2.

TABLE 2  
FLUORIDE EMISSIONS  
ACCORDING TO HUFFSTUTLER

<u>Process</u>	<u>gm F<sup>-</sup>/hr</u>
Phosphoric acid plant	1.8 - 79.5
Phosphoric acid reactor	1.2 - 6.3
Run-of-pile triple superphosphate	23.4 - 331.5
Diammonium phosphate	8.5 - 39.0
<u>Granular triple superphosphate</u>	<u>4.2 - 102.6</u>

Sherwin<sup>16</sup> has reported an evolution of 540 mg SiF<sub>4</sub>/std cu ft from a 28 ton per hour superphosphate manufacturing plant using phosphate rock from Morocco.

### Fluoride Toxicity

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.<sup>17</sup>

When present in sufficient concentrations, fluorides in gaseous form are highly toxic to growing vegetation, humans and animals. The President's Science Advisory Committee<sup>18</sup> 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<sup>19</sup> Commission have innumerable pages of testimony regarding the damages to vegetation, animals and humans caused by fluoride emissions from the phosphate industry. The International Clean Air Conference<sup>20</sup> meeting in London, England discussed the damage done to fruit, vegetation, gladiolus, and cattle in the Florida phosphate belt due to the toxicity of the fluoride emissions. The President's Science Advisory Committee<sup>21</sup> pointed out the severity of the fluoride damage in Southern Florida in its statement regarding the effects of phosphate fertilizer effluents on citrus, vegetables, flower crops and cattle. Largent<sup>22</sup> has compiled a detailed review of the reported effects of fluorides, from all sources, on vegetation, animals and humans.

#### Vegetation Damage

Florida's phosphate belt unfortunately is located in the same general area that for years has been used for raising citrus, truck crops and gladiolus among other vegetation.

The leading agricultural industry in Florida involves the growing and processing of citrus. Heavy concentrations of citrus groves are found in the Polk-

Hillsborough area within a relatively short distance of the phosphate area. Citrus damage which has been attributed to gaseous fluorides includes defoliation of trees, reduction of yield, reduction of growth, leaf burn and severe chlorosis.

Citrus trees have formations of flushes of leaves periodically through the year which renders the plants continuously susceptible to atmospheric fluoride pollution. Studies at low concentrations and long periods of exposure have been used to determine leaf injury, growth, productivity, and physiological effects in chronic situations.<sup>23,24,25,26</sup> These studies indicate that for a mean concentration of atmospheric fluoride of 10 mg/cu m for 2 months to 2 mg/cu m for 12 months significant injury occurs.

Relatively high concentrations and short exposure periods have been used to simulate a fumigation situation. Acute effects of leaf injury and defoliation have occurred at 8,000 mg/cu m for 15 minutes to 400 mg/cu m for 2 hours.<sup>25</sup> Leonard<sup>27</sup> reported on controlled experiments using HF for fumigation of citrus but Taylor<sup>28</sup> in testimony before the Florida Air Pollution Control Commission indicated that "data concerning yield and leaf-fluoride content is sufficiently scarce and contradictory that it offers little scientific basis for establishing a threshold limit of fluoride in foliage." Weinstein and McCune<sup>29</sup> at the same hearing indicated

that fluoride would affect plants differently at different levels due to:

1. A critical stage in the development of the plant occurs in which yield is most likely to be affected. The stage is usually during the flowering period.
2. The age of the foliage affects the sensitivity. Younger foliage is consistently more sensitive to fluoride than older foliage.
3. Dilution by growth and losses to the soil decrease the fluoride level in a plant with time.
4. Some fluoride in the plant will be converted to an inactive state in time.
5. Some investigations have shown that intermittent fumigations may be less effective than continuous exposures since plants show a recovery process during low-fluoride periods.

Winter truck crops such as tomatoes, lettuce, corn, endive, cabbage and other vegetables are also produced in the Polk-Hillsborough County area. Although vegetation of this type is fairly resistant to fluoride damage, damage from fluoride air pollution has been alleged more than once.<sup>19</sup>

A relatively large body of data is available on the effects of atmospheric fluoride on tomato plants. McCune<sup>30</sup> has summarized the available data in the form of Figure 10. Line a represents his criterion with respect to the presence or absence of foliar markings. Line b represents the times and concentrations that are known to have produced economic damage, namely a reduction in the quantity or quality of the crop.

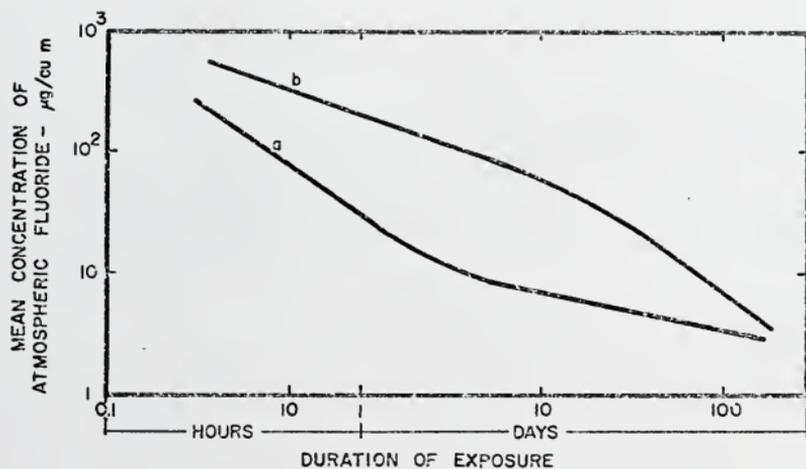


Figure 10: Relation of Concentration and Duration of Exposure to Effects of Atmospheric Fluoride on Tomato Plants.

Benedict<sup>31</sup> has reported that as long as leaves of alfalfa, orchard grass, endive, chard, spinach, and romaine lettuce did not develop markings attributed to fluorides, fumigations of four months at 100 mg/cu m of HF showed no significant effect on the growth of these plants.

McCune<sup>30</sup> in his summary of available data on the effects of atmospheric fluoride on corn indicates that the data are scarce on chronic exposures but in the available data no significant reductions in growth or yield were found in the limited range of concentrations and exposure times.

Gladiolus is one of the more susceptible plants to atmospheric fluoride damage. McCune<sup>30</sup> reports on the considerable data available on experiments concerning both chronic and acute fluoride damage. In general, atmospheric fluoride levels above 6 mg/cu m for 1 day to 1 mg/cu m for 10 days would cause permanent injury to the gladiolus leaf.

#### Cattle Damage

Cattle have been raised in the Polk-Hillsborough County area for many years. In recent years veterinarians have diagnosed fluorosis in some of the cattle raised in this area.<sup>19</sup> In most cases, the diagnosis is chronic fluoride poisoning and not acute poisoning indicating a long exposure to fluoride.

Cattle develop fluorosis by feeding on pastures contaminated by fluorides hence the mode of entry into the animals is through the digestive system. Up to a certain level fluorides are excreted, and when this level is exceeded fluoride is then deposited in their bones due to the affinity of fluorine for calcium.<sup>31</sup>

In order to combat fluorosis in domestic animals, the Florida Air Pollution Control Commission<sup>32</sup> set the standard of a maximum of 40 ppm of soluble fluoride (dry weight basis) for acceptable forage or grass that is to be used for cattle. They stated that grasses containing more than 40 ppm F will, "if consistently used as feed or forage over a substantial period of time, produce harmful effects." However, Hobbs and Merriman<sup>33</sup> have reported that cattle grazing on pastures with up to 44 ppm F and cattle consuming hay averaging up to 66 ppm F showed no significant damage during 10 years of testing. Hendrickson<sup>34</sup> has reported that reduced milk production, a decrease in the reproduction process, and a reduction in appetite will result from fluorosis. Evidence published by the National Research Council<sup>35</sup> indicated that the tolerance level for lactating dairy cows lies between 30 and 50 ppm F. But Suttie and Phillips<sup>36</sup> have indicated that mature cattle could tolerate 50 ppm F for 3 years and show no adverse effects.

Largent<sup>22</sup> in his text Fluorosis devotes an entire chapter on the chronic effects of fluoride intoxication on animals. In general, the typical effects of chronic fluoride poisoning on cattle are:

1. Incipient dental changes
2. Staining, with detectable wearing of teeth
3. Decreased consumption of food
4. Loss of body weight

5. Decrease in calf production
6. Decrease in milk and butter fat production
7. Overgrowth at joints

Largent also discusses the effects of both chronic and acute poisoning on rats, sheep, poultry, swine, rabbits, and household pets.

The toxicity of fluoride appears to be greater in forage contaminated with gaseous effluents such as silicon tetrafluoride rather than with phosphate dust. Thirty to 50 ppm (by weight) of soluble fluoride compounds in the total diet of dairy cattle may cause deleterious effects, while it takes 60 to 100 ppm of insoluble fluorides to produce the same effect.<sup>37</sup>

Lewis,<sup>38</sup> while taking the phosphate industry to task, brings out an interesting statistic regarding the damage that fluorosis can cause. He states that in 1954 Polk County was the largest cattle producing county in Florida with 120,000 head. In 1965, there were 90,000 head of cattle and the number continues to decrease and he states "it is not unusual to come upon cattle crawling across pastureland on their knees, starved from their inability to chew,"

#### Human Health Damage

Fluorides that are highly reactive chemically will be irritating to exposed areas of the human body when they are present in the air in sufficient quantities.

Normally, exposures to such highly reactive fluorides is limited to occupational exposure. Less is known about the effects on humans of inhaled fluorides that are not surface irritants and whose action depends upon their absorption from the lungs by the blood.

The fact the cattle grazing in an area have had health effects does not mean that people living in the same area would have the same effects. Cattle obtain most of their fluoride from the forage and water rather than from the air. The California State Department of Public Health<sup>39</sup> has estimated that 1.0 to 1.2 milligrams per day of fluoride is the optimum ingestion for the control of cavities in children.

The mean concentration of fluoride found in the air of communities ranges from 0.003 ppm in Charlestown to 0.018 ppm in Baltimore.<sup>40</sup> The maximum concentration in most cities is about 0.025 ppm with a high of 0.08 ppm being reported in Baltimore. Thomas<sup>41</sup> reported a value of 0.29 ppm in the vicinity of a superphosphate plant.

Largent<sup>42,43</sup> has observed the following effects when hydrogen fluoride was inhaled by man under laboratory conditions:

1. At concentrations less than 5 ppm, no local and immediate systemic effects. A sizable portion of the inhaled dose was promptly excreted.

2. At 10 ppm, many exposed persons complained of discomfort.
3. At 30 ppm, all exposed persons complained about environment.
4. At 60 ppm, definite irritation of conjunction and nasal passages and discomfort of pharynx and trachea.

Derryberry<sup>44</sup> reported on a study of a large group of men exposed to a phosphate fertilizer plant for periods of up to 25 years and the few suggestions of toxicity "were not found to be formidable in light of the fact that other factors may have been responsible."

A Florida State Board of Health study of school children in Polk County found no evidence of fluorosis in their teeth. The same conclusion was reached by the Bureau of Dental Health and the National Institute of Dental Research after they toured schools in Polk County.<sup>45</sup>

While individual cases of temporary illness have been well documented by physicians and civic organizations<sup>19</sup> in the Polk-Hillsborough area, it appears that to date there have been no permanent human defects directly attributable to the phosphate industry in this area.<sup>34,46</sup>

### Governmental Controls

Perhaps the occurrence of illnesses alleged to be caused by the emissions from the phosphate processing industry gave the impetus to the formation of the Polk-Hillsborough Air Pollution Control District. Perhaps it was the economic loss to the area such as \$1,000,000 damage to new citrus groves, loss of 1,500,000 boxes of fruit per year, or a reduction of citrus property value of \$20,000,000 in the Polk-Hillsborough Area.<sup>47</sup> Perhaps, it was the decline in cattle production in the two county area.

For whatever the reason or combination of reasons, the Polk Air Pollution Control District was formed in March 1958 to handle complaints regarding air pollution, mainly from the phosphate industry, in the county. The district was formed under the 1957 Florida Air Pollution Control Act which established an air pollution control commission in the State Board of Health. The district was created with the understanding that it would permit an "orderly study of air pollution in the county, and that members of agricultural, livestock, industrial, and political interests would be considered and the cooperation of those interests encouraged."

Hillsborough County Air Pollution Control District was formed in July, 1959.<sup>48</sup> The two control districts were merged into the Polk-Hillsborough Air

Pollution Control District in June, 1960.<sup>49</sup> It was hoped that the merger would provide greater efficiencies and better control for the areas involved.

The Polk-Hillsborough Control District did not live up to its expectations due to a number of reasons including: lack of proper legal counsel; delays in taking lawful action due to the procedure of conference, conciliation, and persuasion; inadequate funding; a defeatist attitude where the commission felt "hamstrung"<sup>50</sup> due to not enough direction, responsibility, and authority from the legislature regarding its desires; pressures from the industry; and lack of adequate and properly trained personnel.

In 1967, the enabling legislation for the act forming this district was repealed and the Florida Air and Water Pollution Control Act was passed. One of the purposes of this act was to strengthen the pollution control agencies in the state. The act had been enacted with the hopes of eliminating some of the major problems associated with Florida Air Pollution Act. It gave the control commission powers which if used properly would provide the incentive for positive action in controlling air polluting industries.

On June 30, 1969 the Florida Air Pollution Control Commission was out due to governmental reorganization. On July 1, 1969 the Florida Department of Air and Water Pollution Control was created and it is under this

department that all present surveillance of the phosphate industry takes place. The requirements of the department regarding fluoride emissions are "the unit emissions of fluoride expressed as pounds of fluoride per ton of  $P_2O_5$  or equivalent produced, shall not exceed 0.4 pounds," taking into consideration the latest technology, existing pollution levels, the lowest value attained by other plants, and location. This requirement necessitates that some method of fluoride recovery be utilized.

CHAPTER III  
WET-PROCESS PHOSPHORIC ACID

Most wet-process phosphoric acid produced at the present time is used in fertilizer production since the acid meets the critical requirements of cost and grade. Until quite recently, the general availability of sulfuric acid gave the wet-process acid a favorable economic position and since the fertilizer industry can use a relatively impure phosphoric acid, the wet-process phosphoric acid process is used in Florida instead of the furnace process. This chapter will be confined to the process of producing fertilizer grade, orthophosphoric acid ( $H_3PO_4$ ).

History

Prior to 1900

The development of wet-process phosphoric acid manufacture is closely related with the early production of chemical fertilizers.

Chinese farmers are said to have used calcined bones some 2,000 years ago,<sup>51</sup> and Fritish<sup>52</sup> has stated that bones have been applied for centuries to the vineyards in southern France. Guano, a fertilizing material consisting almost wholly of the excreta of sea birds,

was used by the Incas as early as 200 B.C. Bird guano, bones, and other organic substances formed the basis for the early fertilizer industry and during the 19th century the use of these materials was limited only by their availability.<sup>53</sup>

Brandt prepared elemental phosphorus from urine in 1669, and Boyle made phosphoric acid from phosphorus in 1698. Gahn in 1769 first associated these materials with bones. Scheele in 1775 prepared elemental phosphorus from bones by treatment with mineral acids and reduction with heated charcoal. In 1840, phosphorus was recognized as the major component of bone manure. Justus von Liebig, in 1840, proposed that bones be dissolved in sulfuric acid to make the phosphorus content more available to crops.<sup>54</sup> J. B. Lawes was issued a patent in 1842 for making superphosphate from "bones and other phosphoritic substances" and sulfuric acid by "setting free such phosphoric acid as will hold in solution the undecomposed phosphate of lime." Lawes modified his patent, and confined his claim to apatite, phosphorite, and other substances containing phosphoric acid. Lawes essentially founded the mineral superphosphate industry.

In 1851, Albright and Wilson Ltd., at present England's largest producer of phosphoric acid, was formed at Oldbury, England.<sup>55</sup> In 1870, a plant was established in Germany to manufacture an improved grade

of superphosphate by reacting low-grade rock with phosphoric acid in place of the sulfuric acid that had been used to date. By 1900, at least 12 European companies were manufacturing phosphoric acid for fertilizer process use by batch operations from low-grade ores.<sup>56</sup>

Commercial fertilizer operations in the United States predate those of Europe. William Davidson erected the first sulfuric acid plant in 1832 to acidulate bones and oyster shells.<sup>57</sup> The first triple superphosphate plant was built by the American Phosphate and Chemical Company in 1890 at Baltimore, Maryland. This plant was built using knowledge gained in 1867 when phosphate rock from South Carolina was used in the acidulation process in place of bones and oyster shells.<sup>58</sup>

#### 1900 to 1930

In the United States wet-process phosphoric acid production was insignificant prior to 1900, and the total production, which was mainly concentrated in the Baltimore area, did not exceed 2000 tons/year. The leaders in the industry in the period from 1900 to 1915 were Stauffer Chemical Company, Virginia-Carolina Company (now a division of Mobil Oil Company) and American Agricultural Chemical Company (now a division of Continental Oil Company). These companies and many other smaller concerns were acidulating bones to make the acid in the 1900 to 1905 period, and then switched over to the use

of phosphate rock in the 1905 to 1915 period. The process was a batch operation in which digestion of low-grade rock took place in wooden tanks of 1 to 2 tons/batch and the resulting slurry was filtered on lead-lined, wooden filtering pans.<sup>59</sup> The filtrate, containing 10 to 15 percent  $P_2O_5$ , was concentrated in rock or lead-lined pans.

In 1915, the continuous process was introduced into the phosphoric acid industry by the Dorr Company. By 1924, this process made possible an acid containing 22 to 23 percent  $P_2O_5$ , as compared with the 10 to 15 percent with the batch process. Briefly, the process consisted of the reaction of a phosphate rock-phosphoric acid mixture in a series of primary digestion tanks with sulfuric acid (66.6 or 77.7 percent  $H_2SO_4$ ). Agitation of the slurry produced was maintained and after the slurry left the last tank it was washed counter-currently in thickeners. The overflow from the primary thickener normally analyzed 22 to 23 percent  $P_2O_5$ . The calcium sulfate dihydrate which settled in the primary thickener was washed in the remaining thickeners to remove the entrained acid.<sup>60</sup>

In the period 1916 to 1929, Dorr built strong acid plants for some 31 companies in the United States and Europe. The smallest of these plants processed 25 tons of rock per day. During this same period, the Chemical Construction Company (Chemico) built wet phos-

phoric acid plants for U. S. Export Chemical Corporation (now U. S. Phosphoric Chemical Corporation) and American Cyanamid.

### 1930 to 1968

During the 1930 to 1940 period, Nordengren and associates in Sweden developed strong acid processes that produced a calcium sulfate hemihydrate and a very strong acid, 40 to 50 percent  $P_2O_5$ . However, after experience was gained with this process, the conclusion was reached that the economies in producing the strong acid did not justify the complications involved in the filtration of the slurry.<sup>61</sup> However, Nordengren and his associates performed basic studies to determine the conditions under which the anhydrite ( $CaSO_4$ ), hemihydrate ( $CaSO_4 \cdot \frac{1}{2}H_2O$ ), and dihydrate ( $CaSO_4 \cdot 2H_2O$ ) were formed in phosphoric acid slurries and established the relationship between crystal filterability and acid concentrations for each of these crystal forms. Dorr and other companies in the United States were also working on producing an acid in the 40 to 50 percent  $P_2O_5$  range; however, due to the same type of problems encountered by Nordengren, they were not able to produce a high strength acid economically.

During the same period, Dorr built the largest wet phosphoric acid plant up to that time for Consolidated Mining and Smelting Company at Trail, British Columbia.

The plant consisted of three trains, each having a processing capacity of 150 tons/day of phosphate rock. This plant was probably the major contribution of Dorr Company during this period since it involved (1) the recycle of gypsum slurry for better control of crystal growth, thus giving larger crystals and improved filterability, and (2) the separation and countercurrent washing of the gypsum on continuous filters. The product acid from the filters contained 30 to 32 percent  $P_2O_5$ . This process gained the name of the Dorr Strong Acid Process since it produced the highest strength commercial acid to that date. The acid produced was already strong enough for the production of ammonium or sodium phosphates but it was not used in the manufacture of triple superphosphate or food grade calcium phosphate since a concentrated acid was required for these products. This process produced a dihydrate gypsum and was the one used for many other plants throughout the world.

In the 1940 to 1950 period, processes yielding calcium sulfate anhydrite were studied by Davison Chemical Company; however, none of these processes were ever commercialized.<sup>62</sup> Tennessee Valley Authority (TVA) also began work on a process producing an anhydrite at their Muscle Shoals, Alabama facility.

In the 1950 to 1968 period, interest was renewed in the hemihydrate process of Nordengen and commercial installations have been built in Japan. Better recovery

of  $P_2O_5$  has been obtained and the by-product gypsum is of better quality in the hemihydrate process. An acid containing 40 percent or more of  $P_2O_5$  has been obtained using this process in large-scale tests.<sup>63</sup>

During this same period, due to a shortage of sulfur, interest was developed in substitution of hydrochloric acid for sulfuric acid. The Israel Mining Company developed a process using solvent extraction to separate the phosphoric acid from the calcium chloride formed. Small commercial plants have been built in Israel and Japan using this process. Other companies have used nitric acid as a replacement for sulfuric acid.<sup>64</sup>

The major process used at the present time is the dihydrate process and most large commercial plants constructed today utilize this process with the latest improvements which include (1) slurry recycle, (2) single-tank reactor, and (3) tilting-pan filter. The capacity of the largest single-train plant in Florida is a nominal 1500 tons  $P_2O_5$ /day. According to Slack,<sup>65</sup> as of 1968 this plant is also the largest single-train plant in the world. The Occidental Chemical Corporation plant at which all experimentation for this study took place had a nominal 650 tons  $P_2O_5$ /day capacity.

#### Fundamental Principles of the Dihydrate Process

The primary objective in the phosphate fertilizer industry is to convert the fluorapatite in phosphate rock

to a form available to plants. The fluorapatite is quite insoluble and is not normally used as a fertilizer in its natural state because it has little value as a supplier of nutrient phosphate. The most widely used method for making the nutrient phosphate available is treatment with a mineral acid such as sulfuric, phosphoric, nitric, or hydrochloric.

Since phosphoric acid can be readily manufactured at fertilizer plants, it is normally used to treat phosphate rock for production of triple superphosphate and in the reaction with ammonia to make ammonium phosphates. The growing importance of both of these products makes phosphoric acid a very important intermediate in the fertilizer industry.

Production of phosphoric acid by the wet-process involves the steps of (1) dissolving phosphate rock in sulfuric acid, (2) holding the acidulate slurry until the calcium sulfate crystals grow to adequate size, (3) separating the acid and calcium sulfate by filtration, and (4) concentrating the acid to the desired level. The principal difference in processes for manufacturing phosphoric acid is the degree of hydration of the calcium sulfate, which can be changed by altering the temperature and the  $P_2O_5$  concentration of the acidulate slurry. The dihydrate,  $CaSO_4 \cdot 2H_2O$ , is precipitated under conditions of low temperature and concentration (see Figure 11). Because of these two reasons, the

amount of wet-process acid produced by methods other than the dihydrate process is not significant.<sup>66</sup>

### Raw Materials

The two major raw materials in wet-process phosphoric acid manufacture are phosphate rock and sulfuric acid. The phosphate rock fed to the process is as high in grade as economically feasible, usually ranging from 30 to 35 percent  $P_2O_5$ . The sulfuric acid normally is 66° Be (93 to 98 percent).

The phosphate rock used exists principally in the form of a fluorapatite, which is a broad term given to a relatively complex mineral whose properties can vary widely, depending upon origin. Slack<sup>65,66</sup> normally uses the chemical formula  $Ca_{10}(PO_4)_6F_2$  in his descriptions of the process, while Waggaman<sup>61</sup> and Sauchelli<sup>67</sup> use  $3Ca_3(PO_4)_2 \cdot CaF_2$  in their descriptions of the process. Phosphate rock used for production of acid by the wet-process varies from about 65 to 85 BPL, depending upon the origin and extent of beneficiation. All rocks contain varying amounts of other compounds, either physically mixed or substituted in the mineral itself. Table 3 gives a typical analysis of Florida phosphate rock. Table 4 gives a typical analysis of the rock used by Occidental at their White Springs plant.

TABLE 3

TYPICAL COMPOSITION OF COMMERCIAL GRADES  
OF FLORIDA PHOSPHATE ROCK<sup>62,a</sup>

	<u>Specified BPL Range</u>		
	<u>68/66</u>	<u>72/70</u>	<u>77/76</u>
BPL	68.15	72.14	77.12
P <sub>2</sub> O <sub>5</sub> equiv.	31.18	33.00	35.28
H <sub>2</sub> O	1.3	1.0	1.0
Fe <sub>2</sub> O <sub>3</sub>	1.33	1.07	0.84
Al <sub>2</sub> O <sub>3</sub>	1.76	0.83	0.56
Organic	2.18	1.76	1.70
SiO <sub>2</sub>	9.48	6.46	2.02
CO <sub>2</sub>	3.48	2.87	2.98
F <sub>2</sub>	3.60	3.62	3.89
CaO	45.05	48.10	51.53
SO <sub>3</sub>	1.05	1.11	0.66

a Dry basis

TABLE 4

TYPICAL COMPOSITION OF OCCIDENTAL  
PHOSPHATE ROCK<sup>a</sup>

BPL	74.00
P <sub>2</sub> O <sub>5</sub>	33.80
Fe <sub>2</sub> O <sub>3</sub>	0.49
Al <sub>2</sub> O <sub>3</sub>	1.49
SiO <sub>2</sub>	4.30
CO <sub>2</sub>	4.72
F <sub>2</sub>	3.93
CaO	50.0
SO <sub>3</sub>	1.32
C	0.28
MgO	0.31

TABLE 4 CONTINUED

Na <sub>2</sub> O	0.69
K <sub>2</sub> O	0.10
<hr/>	
a	Process Report, P. Flanagan, 9/27/68, Occidental Chemical Company, White Springs Plant.

While the performance of a given rock cannot be completely predicated from the chemical analysis,<sup>68</sup> it is possible to draw certain general conclusions. Normally, a preferred rock is the one that yields phosphoric acid at the lowest cost; therefore, the primary consideration is the price of the rock per unit of P<sub>2</sub>O<sub>5</sub>. Other items which may affect production include:

1. CaO to P<sub>2</sub>O<sub>5</sub> ratio. This ratio eventually determines the amount of H<sub>2</sub>SO<sub>4</sub> used per unit of P<sub>2</sub>O<sub>5</sub> produced. A low CaO to P<sub>2</sub>O<sub>5</sub> ratio is desired since the cost of H<sub>2</sub>SO<sub>4</sub> is a major factor in the production cost of phosphoric acid.
2. Fluorine. Most companies do not consider this an item of significance, however, high values may increase the air pollution generated in the process and may increase plant corrosion.
3. Iron and aluminum. They are major problems in acid manufacture and are normally removed

by beneficiation to a major extent.

Residual amounts dilute the phosphate content, may interfere with crystal growth, cause sludge to form in the product acid, and in general may cause a poor acid for use in making fertilizer products.

4. Carbonates. A high carbonate content is accompanied by a high CaO to  $P_2O_5$  ratio reducing the grade of rock ( $P_2O_5$  content) and causing foaming during acidulation.
5. Magnesium and potassium. Normally both give rise to complexes that lead to sludge problems when the acid is concentrated.
6. Silica. Silica is partially attacked by the fluorine released during digestion. Normally, it is not considered a problem.
7. Sulfur compounds. Sulfur, if present as sulfates, can usually be credited against  $H_2SO_4$  consumption.
8. Organic matter. High levels of organic compounds will cause foaming problems and tend to reduce filtration rates by blinding the filter cake.

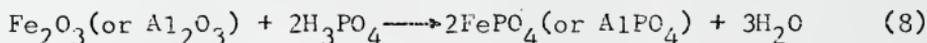
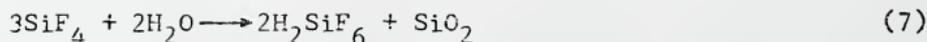
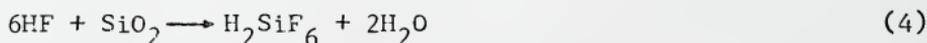
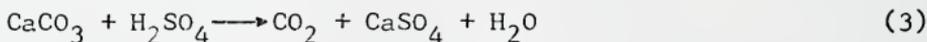
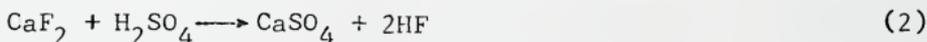
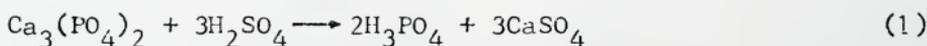
The rapidity of digestion is influenced by the particle size of the rock since the attack takes place primarily on the surface of the particle; therefore, the time required to dissolve a rock particle is pro-

portional to the diameter so long as other factors are held constant. Normally, the rock is ground to 60 to 70 percent minus 200 mesh; however, unground phosphate rock can also be used in the process.

The sulfuric acid used in the wet-process is 66° Be (93 to 98 percent). The strong acid is employed so that as much water as possible can be used in washing the gypsum filter cake. The amount of sulfuric acid used in the wet-process is approximately stoichiometrically equal to the CaO in the rock. The amount of free sulfuric acid in the digestion system is an important operating variable, since it affects the size and shape of the gypsum crystals formed.

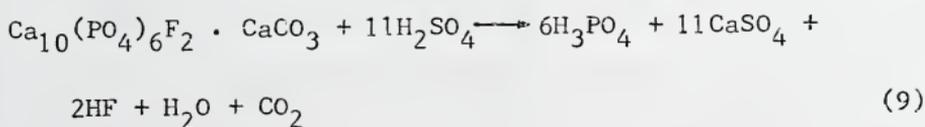
### Process Chemistry

Waggaman<sup>69</sup> and Slack<sup>70</sup> have reported the following reactions taking place throughout the process:



Phosphate rock is a very complex mineral; the principal mineral constituent, fluorapatite, contains

calcium, phosphate, fluoride, carbonate, and other elements or groups bound together. When the rock is treated with sulfuric acid, the apatite lattice is destroyed and the phosphate is solubilized as phosphoric acid. The principal reaction, Equation 1, is the reaction between tricalcium phosphate and sulfuric acid to give soluble phosphoric acid and insoluble calcium sulfate. The calcium fluoride reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate, Equation 2. The calcium carbonate is converted to carbon dioxide and calcium sulfate, Equation 3. The entire reaction between the major constituents and sulfuric acid has been described by Slack<sup>70</sup> as:



The hydrogen fluoride produced may react with the silica present to form silicon tetrafluoride, which then hydrolyzes to form fluo<sup>20</sup>silicic acid as shown in Equations 4 and 5.

The calcium sulfate formed in the reactions can be in three stages of hydration: anhydrite ( $\text{CaSO}_4$ ), semihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ), or dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), depending on the reaction temperature and the phosphoric acid concentration (see Figure 11). However, since the dihydrate occurs with low reactor temperatures and low  $\text{P}_2\text{O}_5$  concentrations in the acidulate slurry, it has

been and still is the favored method of producing wet-process phosphoric acid.

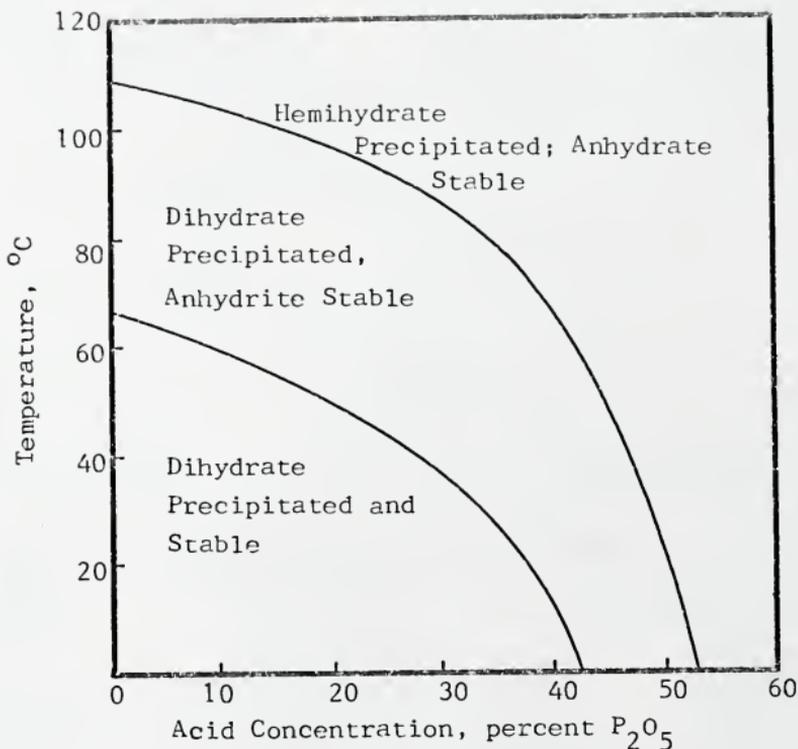


Figure 11: Precipitation and Stability of Calcium Sulfates in Phosphoric Acid

By increase in temperature or concentration, conditions can be reached under which dihydrate is precipitated but is converted in time to anhydrite ( $CaSO_4$ ).

In practice, however, the crystallization is affected by so many factors that prediction of the result is difficult. Free sulfuric acid changes the stability regions and impurities affect the rate of conversion of one crystal form to another. Since there are so many factors affecting crystallization, the dihydrate process is favored due to the lower temperatures and the lower concentrations. There are many variations in dihydrate processes, mainly in regard to type of filter and in design and arrangement of digestion (acidulation) equipment.

### Process Technology

There are many variations in dihydrate processes, mainly in regard to the type of filter and in the design and arrangement of the digestion (acidulation) equipment. The major areas in any phosphoric acid process are raw material feeding, reactor system, filtration, and effluent control.

Raw material in the form of phosphate rock and sulfuric acid is closely controlled. Gravimetric feeders or automatic batch scales are normally used for rock feeding. Sulfuric acid, recycled phosphoric acid, and washwater are normally controlled by flowmeters.

The reactor system varies from process to process. The most recent type is the single tank reactor with the necessary cooling, fume removal, and recycle facili-

ties. Older processes use a system of tanks. The single tank reactor is normally equipped with multiple agitators that promote the reaction. One process has a single tank with two compartments, an outer annulus in which the reaction takes place, and an inner core where the slurry formed in the reaction is held for crystal growth and stabilization. Average retention time in the reactor system is approximately eight hours. Foaming in the reactor often is a problem when the rock has a relatively high content of organic matter or carbonate. Various types of antifoaming agents are used to control foaming.

The heat produced by acidulation of rock and dilution of sulfuric acid is normally removed by one of the three following methods (1) blowing air into the slurry, (2) blowing air across the slurry, and (3) flash cooling under vacuum. Vacuum cooling is probably the most commonly used method at present since the effluent control system is smaller and less expensive.

Filtration of the acid-gypsum slurry requires that gypsum crystals of adequate size and shape be produced in the reactor. Satisfactory crystals depend upon:

1. Sulfate concentration. Insufficient sulfate produces thin, platelike crystals that are difficult to filter. Excessive sulfate produces crystals that are easy to filter

but are difficult to wash free of phosphate. The optimum sulfate concentration depends upon many factors, but normally is approximately 1.5 to 3.0 percent  $\text{H}_2\text{SO}_4$ . This level produces rhomboid crystals agglomerated together which filter and wash well.

2. Slurry recirculation. Recirculation of slurry is required in all systems in order to (1) reduce the effects on the process of surges, (2) reduce the effects of localized high concentrations of rock and acid, and (3) control the degree of supersaturation necessary for good crystal growth.
3. Phosphoric acid concentration. Crystals decrease rapidly in size as the acid concentration is increased above 32 percent  $\text{P}_2\text{O}_5$ . This is one of the major limiting factors on product acid concentration in the dihydrate process.
4. Rock impurities. Slack<sup>71</sup> reports that this area is not understood at present but is currently being studied.

Normally filtration occurs in three stages. The slurry, containing 30 to 45 percent solids, is filtered in the first stage to produce the product acid. Wash water is added to the last stage to wash traces of acid from the gypsum cake. Filtrate from

this stage is used as wash water for the second stage, where recycle acid of approximately 21 percent  $P_2O_5$  is produced. The filter cake formed may vary from 1 to 4 inches. The type of filter varies widely depending upon the process requirements. Early plants used plate-and-frame presses and rotary drum vacuum filters. At present, four types of horizontal vacuum filters are used:

1. Belt filter.
2. Horizontal rotary table filter.
3. In-line pan filter.
4. Horizontal rotary tilting-pan filter.

The horizontal rotary tilting-pan filter has become the standard in the new large-capacity plants since very large units are feasible.

Approximately two-thirds of the weight of phosphate rock and 98 percent of the sulfuric acid used in the process consist of unsalable by-products.<sup>72</sup> The result of these unusable by-products is the production of approximately 5 tons of by-product material per ton of  $P_2O_5$  produced. Effluent gases from the process contain fluoride compounds which must be removed. Normally, these compounds are removed in some type of liquid scrubbers such as spray chambers, impingement columns, packed towers, and venturi scrubbers. Fluorine recovery is practiced in some plants where the resulting fluosilicic acid liquor is recovered for sale. In other

plants, the liquor is pumped to the gypsum settling pond where it is recycled back to the process. Slack<sup>73</sup> reports that the fate of the fluoride in the pond is not well understood at present, and that it "presumably remains with the gypsum in the pond or is evolved from the pond surface as hydrogen fluoride." His statement is based upon operating data which show that the fluoride concentration in the recycled liquor builds up to a certain level, depending upon operating conditions, and stops there. Table 5 gives the fluoride balance for one plant using Florida phosphate rock.

TABLE 5

FLUORIDE BALANCE IN SWIFT & CO.  
WET-PROCESS PHOSPHORIC ACID PLANT<sup>73, a</sup>

Material	F content %	F/ton $P_2O_5$ , lb
Vapors from reactor	5.5	13
Gypsum cake	27.8	66
Vapors from vacuum evaporator	41.9	100
Concentrated Acid (54% $P_2O_5$ )	<u>24.8</u>	<u>60</u>
Total	100.0	239

a Phosphate rock used contained 32.57%  $P_2O_5$  and 3.89%F

The quantity of gypsum produced in a wet-process acid plant is normally 1.5 to 1.6 tons/ton of rock digested or about 4.6 to 5.2 tons of gypsum per ton of  $P_2O_5$  produced. Approximately 1 acre-foot of gypsum will be accumulated yearly as a result of the production of 1 ton of  $P_2O_5$  per day. In Florida, the gypsum

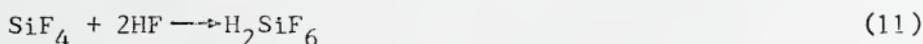
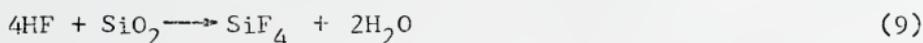
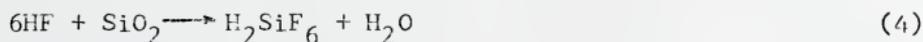
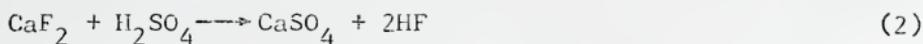
discharged from the filter is reslurried with water and pumped to the settling pond where the solids settle and the gypsum pond water is recovered for reuse. The settled solids are then used to build up the walls of the gypsum pond such that older plants have gypsum piles exceeding 90 feet above grade.

The effluent water from coolers, scrubbers, and the gypsum slurry passes through the pond, or ponds depending upon the plant design, and is recycled back into the process. Normally, little effluent water is dumped into water courses unless it is absolutely necessary due to high water conditions caused by heavy rain and/or plant imbalances. Before the water is dumped into fresh water sources, it is treated with lime to raise the pH.

### Fluoride Evolution

The quantity of fluoride evolved as gaseous silicon tetrafluoride during the acidulation of phosphate rock is usually only a fraction of the total fluorine in the rock, as shown in Table 5. However, this amount of fluoride can do considerable damage to animals and vegetation if allowed to escape from the confines of the plant.

The traditional view of fluoride evolution during the mixing of phosphate rock and sulfuric acid gave rise to the following reactions:



The formation of hydrofluoric acid by Equation 2 was generally considered to be an intermediate step since further reaction with silica would give gaseous silicon tetrafluoride ( $\text{SiF}_4$ ) and aqueous fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). Some of the silicon tetrafluoride produced in Equation 9 was released in the early stages of the process while Equations 10 and 11 were liquid-gas reactions that caused retention of the remaining volatile silicon tetrafluoride. The gases released in Equation 9 were normally carried to the scrubbing system where water or gypsum pond water was used as the scrubbing media to recover the fluoride as fluosilicate by Equation 10.

Recent studies<sup>74,75,76</sup> suggest that the traditional view wherein the formation of silicon tetrafluoride is a secondary reaction between hydrofluoric acid and silica in the rock, Equation 9, may not be entirely correct. These studies indicated that fluosilicic acid is formed directly in acidulation of phosphate rock and that the reaction between moderately strong hydrofluoric acid and either silica or silicates is too slow to account for the somewhat rapid evolution of silicon tetrafluoride that is experienced

under normal operating conditions. The studies suggest that fluoride behaves more as fluosilicic acid than hydrofluoric acid in acidulated rock.

In a study of factors affecting the evolution of silica tetrafluoride during the acidulation of phosphate rock, Fox and Hill<sup>74</sup> found that the amount of gas evolved on contact between the rock and acid increased with increasing concentration and temperature of the acid and with the degree of acidulation of the rock. Other minor factors affecting fluoride evolution included the order of mixing the rock, acid, and water and the amount of water taken up in the formation of the hydrates of the reaction products.

CHAPTER IV  
ABSORPTION THEORIES AND  
EMPIRICAL RELATIONSHIPS

Treybal<sup>77</sup> has defined gas absorption as "an operation in which a gas mixture is contacted with a liquid for the purposes of preferentially dissolving one or more components of the gas and to provide a solution of these in the liquid." A detailed discussion of the absorption process is beyond the scope of this dissertation which is concerned with the application of this method to gas purification and so it deals only briefly with the fundamental processes of absorption. A full treatment of gas absorption may be found in specialized texts by Treybal,<sup>77</sup> Kohl and Riesenfeld,<sup>78</sup> Sherwood and Pigford,<sup>79</sup> Morris and Jackson,<sup>80</sup> and Perry.<sup>81</sup> Those aspects which are of particular interest in the control of fluoride air pollution will be dealt with in detail.

Absorption Theories

The theoretical principles involved in the absorption process are quite complex and controversial. The newer theories attempt to resolve the apparent discrepancies involved in using the older theories.

## General Principles

Absorption deals with the transfer of material between two phases. In the case of gas absorption, when a soluble gas comes in contact with a liquid, molecules of the gas will enter the liquid to form a solution. Gas molecules also will tend to leave the solution to re-enter the gas phase at a rate which increases as the liquid phase concentration increases, until the gas pressure exerted by the solution is equal to the pressure on the system. When this point is reached, a dynamic equilibrium between the phases is established and the gas concentration in solution will no longer change. The concentration of the gas in solution at this point is termed the solubility of the gas in the liquid and varies with the temperature, pressure, and system components. At this equilibrium point, the partial pressure of the soluble gas in the main gas is related to the dissolved gas in the liquid. With this idea in mind, it can be stated that a very soluble gas will require a lower partial pressure than a slightly soluble gas in order to obtain a given concentration in the liquid. Figure 12 shows a typical equilibrium curve illustrating this idea. Equilibrium curves are normally determined by experimentation; however, if the solution and gas are considered ideal, certain gas laws may be applied.

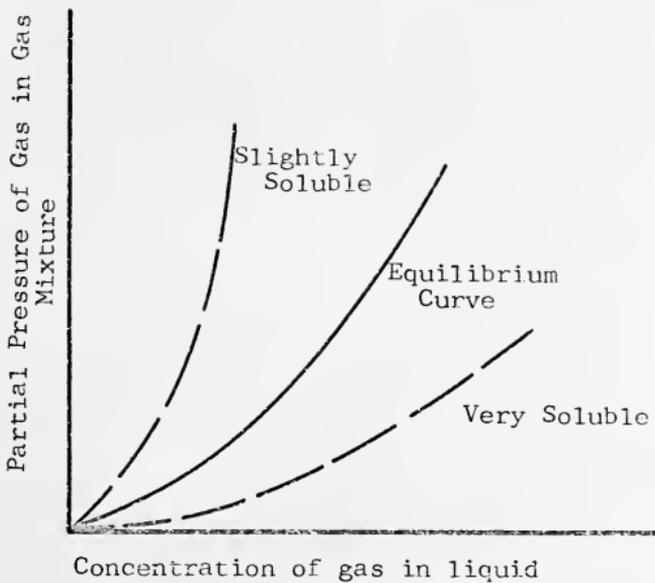


Figure 12: Equilibrium Diagram

Raouit's Law is normally applied to systems that approach equilibrium and states that

$$p = Px \quad (12a)$$

where:

$p$  = partial pressure of solute gas

$P$  = vapor pressure of solute gas at the same  
temperature

$x$  = mole fraction of solute gas in solution

When liquid solutions can not be considered ideal, Henry's Law is normally applied. Henry's Law related the solubility of gases to the partial pressure of the gas in the gaseous phase

$$S = Hp \quad (12b)$$

where:

S = concentration of gas in liquid

H = proportionality constant, sometimes called  
Henry's solubility coefficient

p = partial pressure of gas in gaseous phase

The constant may have any units required; for example, if S is in ppm, and p is in atmospheres, H will be in ppm/atm. The constant is normally determined experimentally for the particular system under study and is applicable to that system. The law holds for the solubility of nonreactive gases in water.

Since absorption of gases depends upon the transfer of molecules from the bulk of the gas to the bulk of the liquid, the case of a stagnant gas in contact with a liquid surface has been widely studied. When the liquid surface is brought into contact with the gas, the diffusion of the gas molecules is by molecular diffusion, and the rate of this depends on the pressure and temperature of the gas and the molecular species in the gas. The rate of molecular transfer is given by Fick's Law

$$N = -D \frac{dc}{dx} \quad (12c)$$

where:

N = rate of molecular transport, molar unit/  
unit area/unit time

$\frac{dc}{dx}$  = concentration gradient in the direction of  
diffusion,

D = molecular diffusivity, (length)<sup>2</sup>/time

Values for the diffusivity may be calculated using the Stokes-Einstein equation but normally they are determined experimentally and can be found in the International Critical Tables<sup>82</sup> when available. Normally gas diffusivity values are considerably higher, approximately  $10^5$  times as large, as liquid diffusivity values.

Equation 12c has been integrated for various cases and the two most used cases are:

Case 1.

Steady-state equimolar counter diffusion which frequently pertains to distillation operations and will not be described further.

Case 2.

Steady-state diffusion of A through non-diffusing B. This occurs, for example, when silicon tetrafluoride (A) is absorbed from air (B) into water. In the gas phase if the evaporation of water is neglected, only the silicon tetrafluoride diffuses, since air does not dissolve appreciably in water. Figure 13 illustrates this condition.

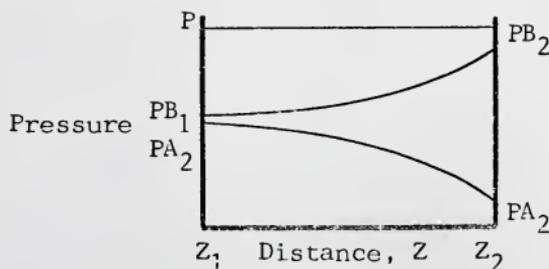


Figure 13: Diffusion of A Through Stagnant B

Treybal<sup>83</sup> reports the integrated form of Equation 12c for this case to be

$$N_a = \frac{DP}{RTZP_{1n}} (y - y_i) = k_g (y - y_i) \quad (13)$$

where:

$N_a$  = rate of transport, [moles/(time)(area)]

$D$  = diffusivity, (area/time)

$P$  = absolute pressure

$R$  = gas constant

$T$  = absolute temperature

$P_{1n}$  = log mean pressure of component B

$y$  = mole fraction

$y_i$  = mole fraction at interface

$k_g$  = mass transfer film coefficient,  
 [(moles)/(time)(area)(mole fraction)]

The use of the mass transfer coefficient in Case 2 is generally accepted since most practical situations involve turbulent flow in which it is generally not possible to describe the flow conditions mathematically. The mass transfer coefficient includes, in one quantity, effects which are the result of both molecular and turbulent diffusion and which differ from situation to situation. Mass transfer coefficients can, in a few limited situations, be deduced from theoretical principles, but in the great majority of the cases, direct measurement under known conditions is used for design purposes. Many theories have been postulated in order

to attempt to interpret or explain the behavior of the mass transfer coefficients. The most widely known are the two-film, penetration, and surface-renewal.

### Two-film Theory

The oldest and most widely used model for interpretation of mass transfer coefficients is the two-film theory<sup>84</sup> proposed by Lewis and Whitman. This model relies on a series of assumptions for its utilization:

1. Steady-state conditions exist in both phases.
2. Rate of transfer is proportional to the concentration gradient.
3. Equilibrium exists between liquid and vapor at the interface with no interfacial resistance to flow.
4. Hold-up at the interface is zero.

With these assumptions, when steady-state conditions of transfer have been reached, the rate of transfer  $N_a$  from gas stream to the interface, and from the interface to the liquid must be equal, and

$$N_a = k_g(p - p_i) = k_l(C_i - C) \quad (14)$$

where:

$p$  = partial pressure of the transferring component in the gas stream

$p_i$  = partial pressure at the interface

$C_i$  = concentration at the interface

$C$  = concentration in the liquid

$k_g$  = gas film mass transfer coefficient

$k_l$  = liquid film mass transfer coefficient

However, since the interface values  $p_i$  and  $C_i$  are very difficult to determine, the equation was redefined in two equations:

$$N_a = K_g(p - p^*) = K_l(C^* - C) \quad (15)$$

where:

$p^*$  = equilibrium partial pressure of gas over a solution having the same concentration  $C$  as the liquid

$C^*$  = concentration of a solution which would be in equilibrium with the gas partial pressure existing in the main gas stream

$K_g$  = over-all mass transfer coefficient for gas phase

$K_l$  = over-all mass transfer coefficient for liquid phase

$$\text{and } K_g = \frac{K_l}{m} = \frac{1}{\frac{1}{k_g} + \frac{m}{k_l}} \quad (16)$$

where:

$m$  = slope of solubility equilibrium line.

This model has been misapplied in highly soluble gas systems where the slope  $m$  approaches zero. Equation

$$16 \text{ would then become } K_g = k_g \quad (17)$$

indicating that the gas phase controls, and the liquid phase offers no resistance to mass transfer. Teller<sup>85</sup> has pointed out that in absorption with chemical reaction occurring a liquid is selected so that no equilibrium partial pressure exists for the gas when dissolved and  $m$  approaches zero. However, experimentation has shown that Equation 17 does not hold and that the liquid phase resistance can not be assumed to be negligible when chemical reaction occurs.

#### Penetration Theory

In 1935, Higbie<sup>86</sup> emphasized that in many situations the time of exposure of a fluid to mass transfer is short, so that the concentration gradient of the film theory, characteristic of steady-state, would not have time to develop. As an approximation to actual conditions, he applied Fick's second law equation for a one-dimensional case and with appropriate boundary conditions found that even with a constant concentration gradient, the rate of absorption decreases with time of exposure. However, he did not apply his results to absorption with chemical reaction which is the case in many applications at present.

#### Surface Renewal Theory

In 1951, Danckwerts<sup>87</sup> pointed out that the Higbie theory was a special case of a situation where the liquid eddy motion continuously brings fresh liquid

to the surface, increasing the rate of absorption. This motion would tend to increase mass transfer to a greater degree than that predicted by Higbie's penetration theory. While it expanded Higbie's theory, it still did not apply to absorption with chemical reaction and it could not be applied directly to highly turbulent flow conditions.

#### Film Penetration Theory

Toor and Marcello<sup>88</sup> proposed their film penetration model in 1958. They showed that the film and penetration models were not separate concepts, but only the limiting cases of their model. In doing this, their theory seemed to better explain some physical conditions than did previous theories.

#### Absorption with Chemical Reaction

When mass transfer occurs between phases across an interface, the resistance to mass transfer in each phase creates a concentration gradient in each phase. In the case of purely physical absorption, the rate of mass transfer is dependent upon concentration gradients and the diffusivities of the gas in both phases as was stated in the "film theory" and as is shown in Figure 14.

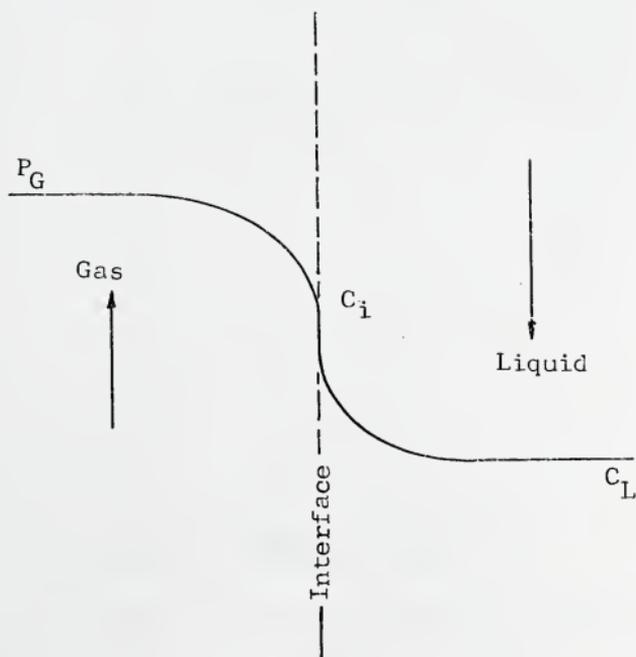


Figure 14: Interfacial Characteristics in Physical Absorption

With the addition of a rapid chemical reaction to the process, the distance through which the gas must diffuse in the liquid phase is generally decreased because upon meeting the liquid, reaction occurs. Therefore, the need for further diffusion no longer exists, increasing the over-all mass transfer rate. Figure 15 illustrates this concept.

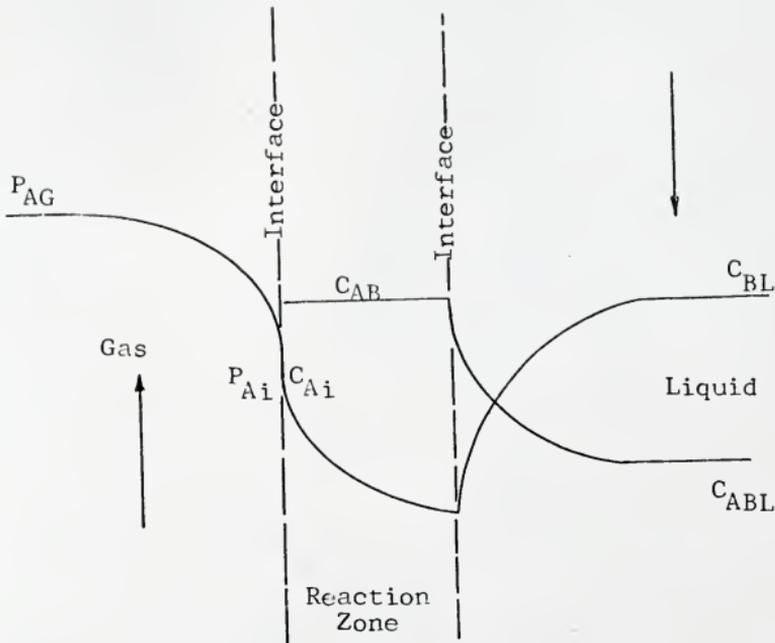


Figure 15: Interfacial Characteristics in Absorption with Chemical Reaction

When a slow chemical reaction occurs, the distance through which the gas must traverse is only slightly affected and the process approaches that of physical absorption.

Teller<sup>85</sup> indicates that as a result of the many complexities involved in the mechanism of absorption accompanied by chemical reaction, no rigorous analytical method of design has been developed; but for a first order reaction, the rate of absorption is proportional to the unreacted gas concentration at the interface. For a second order reaction, an increase in the concentration of unreacted gas at the interface

tends to remove unavailable unreacted liquid from the interfacial region and moves the reaction zone deeper into the liquid. With this in mind, an economical process dictates the selection of the proper liquid and the occurrence of a first order reaction or of a pseudo-first order reaction, an excess of liquid or low gas concentrations in the gas stream.

### Fluoride Absorption

Generally, the two-film theory is used for the design of fluoride absorption units and the interpretation of their performance.

### General Design Concepts

Simplified equations have been developed for design calculations where low gas and liquid concentrations are involved and where the equilibrium curve is linear or can be assumed linear over the range of concentrations used in the design. Equation 18 is the most widely used equation for design calculations and it is based upon the two-film theory

$$h = H_{og} N_{og} \quad (18)$$

where:

$h$  = height of tower

$H_{og}$  = height of transfer unit

$N_{og}$  = number of transfer units

This equation is arrived at using Equation 15 as the

starting point and a differential section of an absorption column  $dv$ , in which the rate of absorption is

$$N_a dv = K_g (p - p^*) dv = K_l (C^* - C) dv \quad (19)$$

If  $a$  is the interfacial area per unit volume of absorber, and  $S$  is the tower cross-section, then  $dv = aSdh$  (20)

However, the value of  $a$  is usually not known and difficult to determine, therefore, it is usual to combine the mass transfer coefficient with the interfacial area to form a composite coefficient  $K_g a$  and  $K_l a$ , the Equation 19 becomes:

$$N_a a S dh = K_g a (p - p^*) S dh = K_l a (C^* - C) S dh \quad (21)$$

For gas absorption, where the molar rates of flow of gas and liquid phases are not constant, due to the changes in composition which occur over the length of the absorber, it has been shown<sup>79</sup> that

$$d(Vy) = V_1 \frac{dy}{1-y} \quad (22)$$

where:

$V$  = molar rate of flow of gas phase

$y$  = mole fraction solute in gas stream.

Combining Equations 21 and 22 and utilizing simplifying assumptions yields the equation for the height of the absorption tower with gas film coefficients

$$h = \frac{G}{K_g a P} \int_{y_2}^{y_1} \frac{dy}{y-y_e} \quad (23)$$

where:

$G$  = molar mass velocity of gas, lb moles/(hr)  
(ft<sup>2</sup>) atm

$P$  = total pressure of system, atm

$y$  = mole fraction of solute in gas stream

$y_e$  = mole fraction of solute in gas in equilibrium with liquid

$y_1$  = solute concentration of gas entering the column, lb mole solute/lb moles inert gas

$y_2$  = solute concentration of gas leaving the column, lb moles solute/lb mole inert gas

This equation assumes that:

1. The equilibrium curve is linear over the range of concentrations encountered, therefore, over-all coefficients may be used.
2. The partial pressure of the inert gas is essentially constant over the length of the column.
3. The solute contents of gaseous and liquid phases are sufficiently low that the partial pressure and liquid concentration values may be assumed proportional to the corresponding values when expressed in terms of moles of solute per mole of inert gas.

Chilton and Colburn<sup>89</sup> introduced the concept that the calculation of column height invariably requires the integration of a relationship such as (from Equation 23)

$$\int_{y_2}^{y_1} \frac{dy}{y-y_e} \quad (24)$$

The dimensionless value obtained from the integration was called the number of transfer units based on an overall gas driving force,  $N_{og}$ , and is a measure of the difficulty of the gas absorption operation. By substitution Equation 23 becomes

$$h = \frac{G}{K_g a P} N_{og} \quad (25)$$

and the height of the transfer unit,  $H_{og}$ , can then be defined as

$$H_{og} = \frac{h}{N_{og}} = \frac{G}{K_g a P} \quad (26)$$

Values of  $N_{og}$  are particularly useful for expressing the performance of absorption equipment in which the volume is not of fundamental importance.

In fluoride absorption units, where a large excess of water is used, the concentration of the acid formed in the solution is low and  $Y_e$  may be neglected and Equation 24 is simplified to

$$N_{og} = \int_{y_2}^{y_1} \frac{dy}{y} = 1n \frac{y_1}{y_2} \quad (27)$$

Since the absorption efficiency,  $E$ , is directly related to  $y_1$  and  $y_2$  by

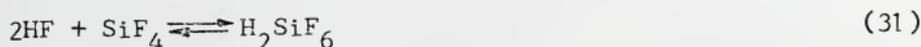
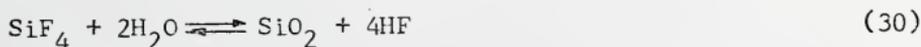
$$E = \left( \frac{y_1 - y_2}{y_1} \right) \times 100 \quad (28)$$

then Equation 27 can be rewritten as

$$N_{og} = 1n \left( \frac{1}{1 - E/100} \right) \quad (29)$$

The necessity for fluoride removal from effluent gases has been stated in previous chapters. Fortunately, both hydrogen fluoride and silicon tetrafluoride are very soluble in water and most commercial installations for control of fluoride emissions make use of this fact. The vapor pressure of hydrogen fluoride over aqueous solutions is shown in Figure 16, which is based on the data of Brosheer.<sup>90</sup> Whynes<sup>91</sup> has presented the data given in Figure 17 on the concentration of fluosilicic acid in equilibrium with silicon tetrafluoride vapors.

When silicon tetrafluoride is absorbed by water, it reacts to form fluosilicic acid. The mechanism of the absorption process has been studied by Whynes,<sup>91</sup> who suggested that the reaction probably occurs in steps, as represented by Equations 30 and 31.



The simple fluosilicic acid probably reacts with additional  $\text{SiF}_4$  or  $\text{SiO}_2$  to form a more complex form of this compound. The reaction given by Equation 31 is reversible to the point that solutions of fluosilicic acid exert a definite vapor pressure of HF and  $\text{SiF}_4$ .

As Figures 16 and 17 indicate, both hydrogen fluoride and silicon tetrafluoride are very soluble in

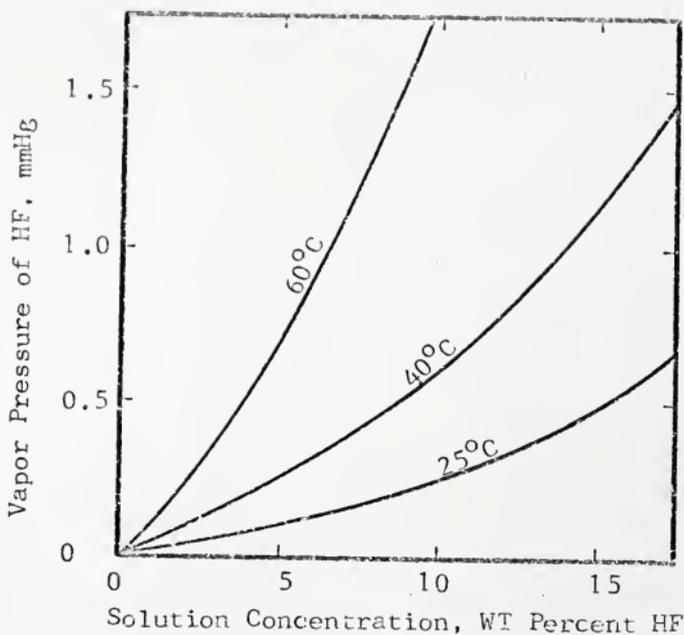


Figure 16: Vapor Pressure of Hydrofluoric Acid Over Dilute Aqueous Solutions.<sup>90</sup>

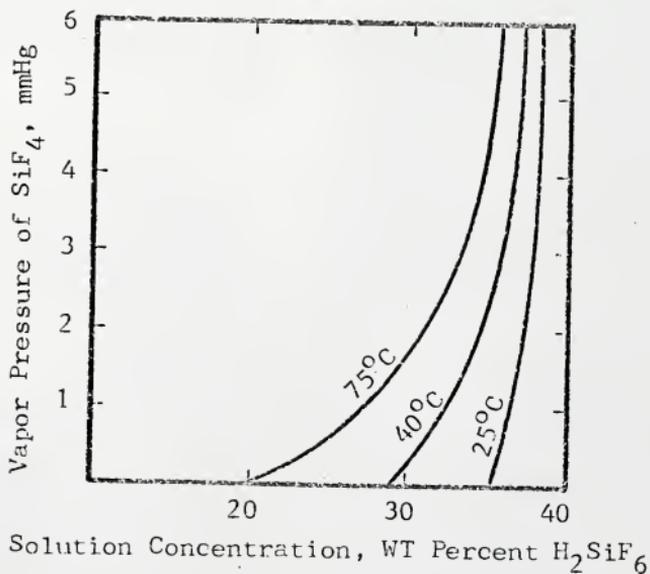


Figure 17: Vapor Pressure of Silicon Tetrafluoride Over Aqueous Solutions of Fluosilicic Acid.<sup>91</sup>

water and the gas film resistance would be expected to be the controlling factor in their absorption. This has generally been verified by experimental evidence although Whynes<sup>91</sup> found silicon tetrafluoride absorption to be complicated by a tendency to form mist droplets in the gas and the tendency of the silica, produced in Equation 30, to form a solid film on the outside of the water droplets, thus hindering absorption.

Whynes<sup>91</sup> reported that even though the absorption of silicon tetrafluoride in water is complex and involves a chemical reaction, the precipitation of silica, the results could be explained in terms of the two-film theory.

Types of absorption equipment which have been used or proposed for the removal of fluoride vapors from gas streams with water include the following general types:

1. Spray chambers (vertical and horizontal)
2. Packed towers (low-pressure grid packing)
3. Venturi scrubbers
4. Wet cells (beds of wetted fiber)
5. Plate columns
6. Ejectors

Since the scope of this research was limited to three types of absorption equipment; namely, spray chambers, venturi scrubbers, and plate columns, the discussion from this point on will be limited to the types studied.

### Absorption in the Cyclonic Spray Chamber

A spray chamber is the simplest type of absorption equipment. In general, it consists of a cylindrical tank in which spray nozzles are mounted in the upper section and the droplets generated fall downwards with some liquid flowing downward on the interior walls. Although the liquid and gas streams may be concurrent, the most common type is a countercurrent flow where the gas stream is introduced at the lower section of the tower tangentially so that a spiral motion is imparted to the gas and the liquid sprays are directed radially. True, countercurrent flow is difficult to maintain due to flow characteristics and spray entrainment, which tend to limit the mass transfer available. Some spray towers have been successful in the absorption of slightly soluble gases, but since the mixing of spray and gas is not as vigorous as in other equipment, the application of spray towers is best suited to operations involving easily absorbed gases.

In spray chambers, liquid dispersion is created by liquid phase mechanical power consumption. Due to scrubber design, gas phase power consumption is usually quite low, and Lunde<sup>92</sup> found that removal efficiency depends largely upon the power expended in the liquid phase. He stated that the number of transfer units would be related to power introduced in the liquid and gas phase by

$$N_{og} : : \frac{P_1^{0.1}}{P_g} \quad (32)$$

where:

$P_1$  = power introduced in liquid

$P_g$  = power introduced in the gas

Perry,<sup>81</sup> Sherwood and Pigford,<sup>79</sup> and Treybal<sup>77</sup>

have summarized various studies mainly pertaining to sulfur dioxide removal and have presented curves for the number of transfer units versus liquid and gas mass flow rates.

In any attempt to compare the performance of different types of absorption equipment, fixed operating conditions for each installation present a problem, and an uncertainty exists as to the controlling factors in the performance of the equipment, unless these factors have been explored over a wide range on a pilot plant scale. Unfortunately, laboratory or pilot plant data on the absorption of fluorides are practically non-existent. Sherwin<sup>93</sup> reported on 14 full-size widely differing installations ranging from continuous spray towers to continuous ejection systems. Efficiencies up to 99.3 percent were obtained and values for  $K_g a$  were reported. However, the volume coefficient  $K_g a$  has little value as a means of correlating spray equipment because the area for mass transfer varies with liquid rate, nozzle design, liquid pressure, distance from nozzle, and other factors. Performance of different fluoride

vapor absorbers may be compared on the basis of the number of transfer units in a given piece of equipment, or, more simply, on the basis of percentage removal efficiency.

### Absorption in the Venturi

In the venturi scrubber, the velocity of the gases causes the atomization of the scrubbing liquid. A typical venturi scrubber has the gas stream pass at a high velocity through the venturi with the scrubbing liquid being introduced at relatively low pressure at the venturi throat where shearing of the liquid and droplet formation take place. Large areas of liquid are made available to contact the gas as a result of a high degree of dispersion which takes place at the throat, due to an increase in the throat velocity. The energy required for forming droplets and intimate mixing with the gas is furnished by the gas stream. The resulting spray of liquid mixes with the gas and absorption takes place. It is necessary that an entrainment separator be provided at the discharge of the venturi to remove the entrained liquid from the gas. The entrainment separator is usually of cyclonic design and normally the venturi-cyclonic spray chamber is installed as a single unit.

Venturi scrubbers were designed originally for dust and mist removal, and considerable research<sup>94,95</sup> has been done in this area. Lunde<sup>92</sup> has reported on

venturi installations for sulfur dioxide removal and has suggested that their performance on fluoride vapors would be controlled by the same factors as  $\text{SO}_2$ . The literature contains isolated cases reporting on the performance of various venturi scrubber installations in removing gaseous fluoride from process gases.<sup>91,92,93</sup> Lunde<sup>92</sup> reported on venturi units using water as the scrubbing liquid with removal efficiencies generally in the 95 to 98 percent range when employed for hydrogen fluoride absorption.

In general, the average pressure drop across a venturi varies from 10 to 50 inches of water depending upon scrubber design. The liquid requirement has been found to be between 3 to 15 gpm per 1000 cfm with power requirements in the range from 1 to 10 horsepower per 1000 cfm. Lunde<sup>92</sup> also reports on attempts to correlate the number of transfer units with power requirements and he proposed that

$$N_{og} \propto (P_1^{0.3})(P_g^{0.8}) \quad (33)$$

This indicates the dependence of the efficiency of the venturi on the energy introduced to the gas phase.

#### Absorption in the Baffle Plate Impingement Column

In plate towers, the gas-liquid contacting takes place on a series of plates installed in a cylindrical column. The plates are perforated by small holes through which the gas passes while the liquid flows across the

plate to a downcomer to the next plate in the column. The gas stream passes up through the perforated holes in the form of irregular bubbles and through the liquid layer on top of the plate and mixes with the liquid. Rapid absorption occurs by virtue of the large interphase surface produced by the small bubbles generated.

The literature abounds with studies on this type of scrubber and the American Institute of Chemical Engineers has published a design manual<sup>96</sup> relating many of the variables of these studies. Studies have related mass transfer efficiency to plate characteristics such as weir height, to gas flow rates and velocities, and to liquid flow rates. However, as Perry<sup>81</sup> indicates, studies must be performed under similar conditions and this has generally not been the case. Since this type of scrubber is not generally employed in fluoride removal processes, no information was available in the literature regarding fluoride scrubbing. However, if a parallel may be drawn with sulfur dioxide scrubbing, efficiencies above 90 percent have been reported with high liquid to gas ratios (50 to 100 gpm per 1000 cfm).

#### Correlation of Scrubber Efficiencies

Absorption data are usually presented in terms of the effect of liquid or gas mass flow rates on the mass transfer coefficient, or on the height of transfer unit. The economic evaluation of equipment requires

translating these data into over-all performance as measured by efficiency or number of transfer units. Perry<sup>81</sup> and Lunde<sup>92</sup> have indicated that it is difficult to compare two basically different types of equipment in terms of mass transfer coefficients, mass flow rates, or height of transfer unit.

Semrau,<sup>97</sup> Lunde,<sup>92</sup> and others have correlated the efficiency of a scrubber expressed in number of transfer units, with total power consumption, the pressure loss of the gas passing through the scrubber and the pressure loss required for atomization of the scrubbing liquid. To date this seems to be the most accepted method of making comparisons between different types of equipment. Semrau<sup>97</sup> has plotted the number of transfer units against total power consumption on a log-log plot and expressed the results in the form

$$N_t = \alpha P_T^\beta \quad (34)$$

where  $\alpha$  and  $\beta$  are characteristic parameters of the material being removed. He applied this equation to dusts and mists and determined that the efficiency of collection could be expressed in terms of total power used and the characteristics for the dust being collected, and independently of the actual type of scrubber being used.

For this study, since the prediction of exact mass transfer characteristics would be very difficult due to the unavailability of data, the procedure described by

Lunde<sup>92</sup> was used. No specific models nor correlations were used to predict the results of this experiment. Only references to general tendencies of variables and comparisons with previous correlations were made.

CHAPTER V  
THE EXPERIMENT

The purpose of this research project was to study the effects of certain scrubber operating variables upon the removal efficiency of gaseous fluoride emitted from a wet-process phosphoric acid plant. In order to accomplish this purpose, a portable pilot plant was constructed and taken to the Occidental Chemical Company facility located near White Springs, Florida. The pilot plant contained four types of air cleaning devices, liquid and gas handling equipment, and laboratory facilities. The description and use of the equipment, the experimental procedures followed, and the analytical techniques used for fluoride determinations will be discussed in this chapter.

The previous discussion on the mechanism of absorption, especially fluoride absorption, formed the basis for the selection of the variables studied in this experiment. The description of the experimental pilot plant will help clarify many of the decisions regarding the variables studied and the experimental procedure.

## Experiment Design

### Operating Variables

From the previous discussion of absorption, it can be seen that the absorption phenomenon is exceedingly complex and is normally studied under laboratory conditions. Pilot plant operation requires the selection of operating variables that can be measured accurately with relative ease. Also, the variables measured should give information that can be used for improvement of existing equipment and for the design of new equipment. The variables considered for this project were:

1. Fluoride concentration in acid plant effluent gas
2. Effluent gas flow rate
3. Effluent gas temperature
4. Scrubbing liquid
5. Liquid flow rate
6. Liquid temperature
7. Energy requirements

Since the White Springs phosphoric acid plant was an integral part of a fertilizer manufacturing complex, the plant's production requirements were closely controlled. Since the pilot plant operation was secondary to the operation of the phosphoric acid plant, the pilot plant used whatever effluent gas was available from the reactor. For this reason, the gas from the reactor varied in fluoride concentration depending upon

operating conditions. The effluent gas temperature also depended upon the reactor conditions which were under the control of the plant operating personnel. Temperatures recorded in the pilot plant operations were between 145° and 165°F.

The gas flow rate was limited by the capacity of the pilot plant equipment and by the pressure drop in the connecting ductwork between the pilot plant and the acid plant reaction tank. The gas flow rate was controlled as required but was also influenced by liquid flow rates in certain equipment.

The types of scrubbing liquid used were limited to the liquids readily available at a wet-process phosphoric acid plant, well water and gypsum pond water. The liquid temperature was limited to that associated with the liquids available for this study. Well water temperature is fairly constant year-round, but gypsum pond water varies depending upon the season of the year.

The liquid flow rate was limited by the capacities of the equipment studied. Most manufactures of absorption equipment specify the liquid flow rate for their equipment based upon liquid/gas ratios that have been established for each type of equipment. The liquid flow rate was controlled over a wide range of flow rates, which included the manufacturer's suggested flow rate.

The energy requirements of each type of scrub-

ber were dependent upon the operating conditions of the scrubber and were, therefore, only indirectly controlled. However, the energy requirements are an important means of determining the most economical type of equipment for a given application and the parameters affecting energy loss were measured.

After consideration of the variables mentioned, the scrubbing liquid and the liquid-to-gas flow rate ratio were selected for study in this experiment.

### Preliminary Investigations

Due to the design of the pilot plant, it was found that the capacity of the cyclonic spray chamber and the venturi-cyclonic scrubber was limited to approximately 75 percent of the rated capacity of the unit. This limit in capacity was due in part to the pressure drop caused by the extended run of ductwork from the reaction tank to the pilot plant. Since this level was below the rated capacity, it was felt that there was nothing to be gained by running at a level lower than the 75 percent level; therefore, the gas flow rate was held essentially constant throughout this study. This limitation led to a change in the design of the experiment, and required that the liquid/gas ratio be varied by holding the gas flow rate constant and varying the liquid flow rate.

### Response

The response selected to measure the results of the experimentation was the percentage removal of fluoride, which gives a measure of the efficiency of each type of equipment under various operating conditions. Other characteristics of the absorption process, such as number of transfer units, can be readily obtained from the response selected.

### Replication of Experiments

In a statistical analysis, replication is necessary in order to estimate the experimental error. Since the process would vary from day-to-day, and at times from hour-to-hour, it was necessary to run the replications back-to-back. While this did not completely randomize the data, it was felt that this would be the only procedure that would provide an estimate of the experimental error involved.

### Equipment Description

The equipment used in this research was installed on two twelve-ton trailers, moved to the Occidental Chemical Corporation plant at White Springs, Florida, and connected into the wet-process phosphoric acid process reaction tank. The completed installation at White Springs is shown in Figure 18. Figure 19 shows the installation from another vantage point.

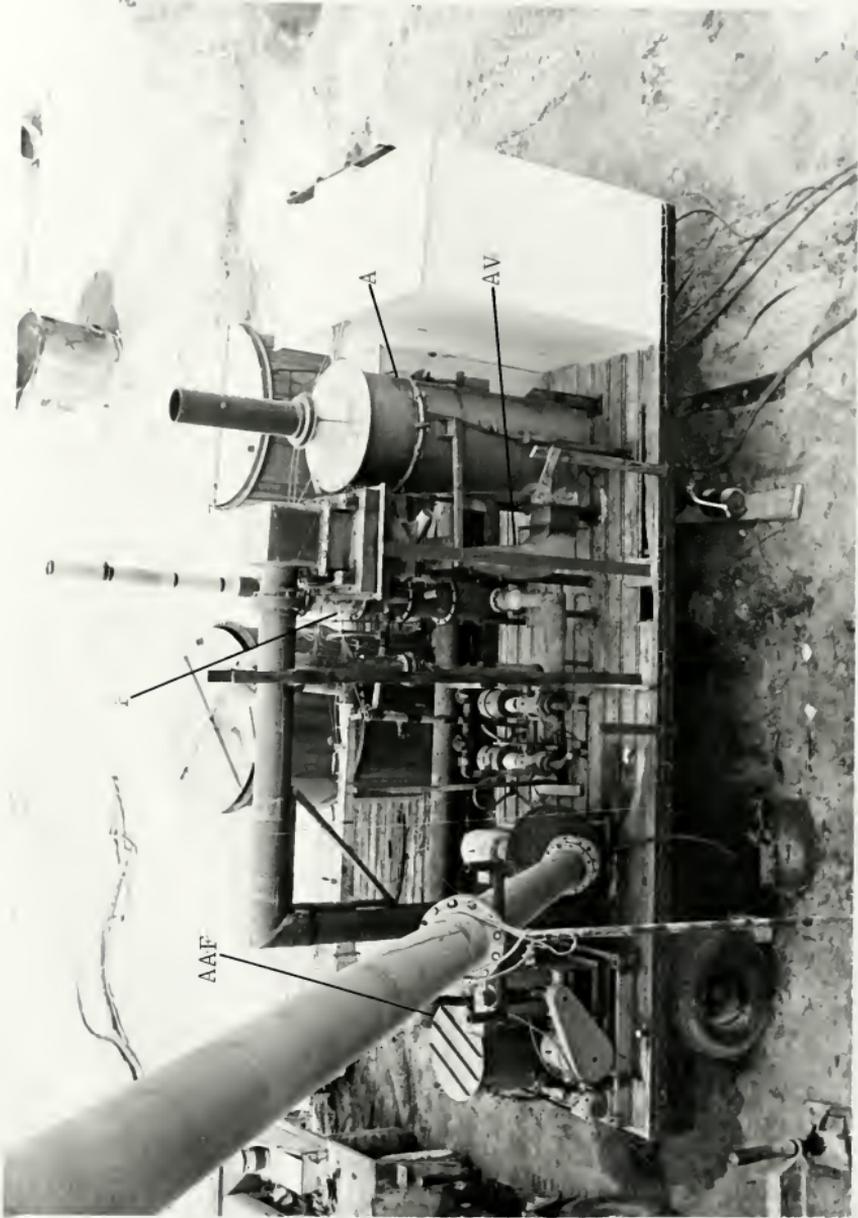


Figure 18: Equipment Trailer from Roof of Acid Plant Reactor Tank



Figure 19: Side View of Equipment Trailer

The four scrubbing units studied are shown in Figure 18. In this figure, "A" is the Airetron cyclonic spray chamber, "AV" is the Airetron venturi, "P" is the Peabody impingement baffle plate column, and "AAF" is the American Air Filter variable throat venturi scrubber.

#### Wet-Process Phosphoric Acid Plant

The Occidental Chemical Company plant at White Springs was built by Dorr-Oliver Company in 1965 and at that time was the most modern phosphoric acid plant in the world. It had a single-tank reactor, vacuum cooling of the reactor slurry, and a Bird-Prayon rotary filter. Slack<sup>55</sup> reports, as of 1966, this plant was the largest single-tank phosphoric acid plant in the world, with a capacity of 650 tons of  $P_2O_5$  per day. Slack lists a total of 19 installations using this process, ranging in capacity from less than 50 tons of  $P_2O_5$  per day to over 650 tons of  $P_2O_5$  per day. Figure 20 is a flow diagram for the plant located at White Springs, Florida.

Since the acidulation process releases large amounts of fluoride in the reaction tank some form of air pollution control equipment is required for the process. Normally, the single-tank reactor is vented to a cyclonic-type of wet scrubber using contaminated, cooled, gypsum pond water as the scrubbing liquid.

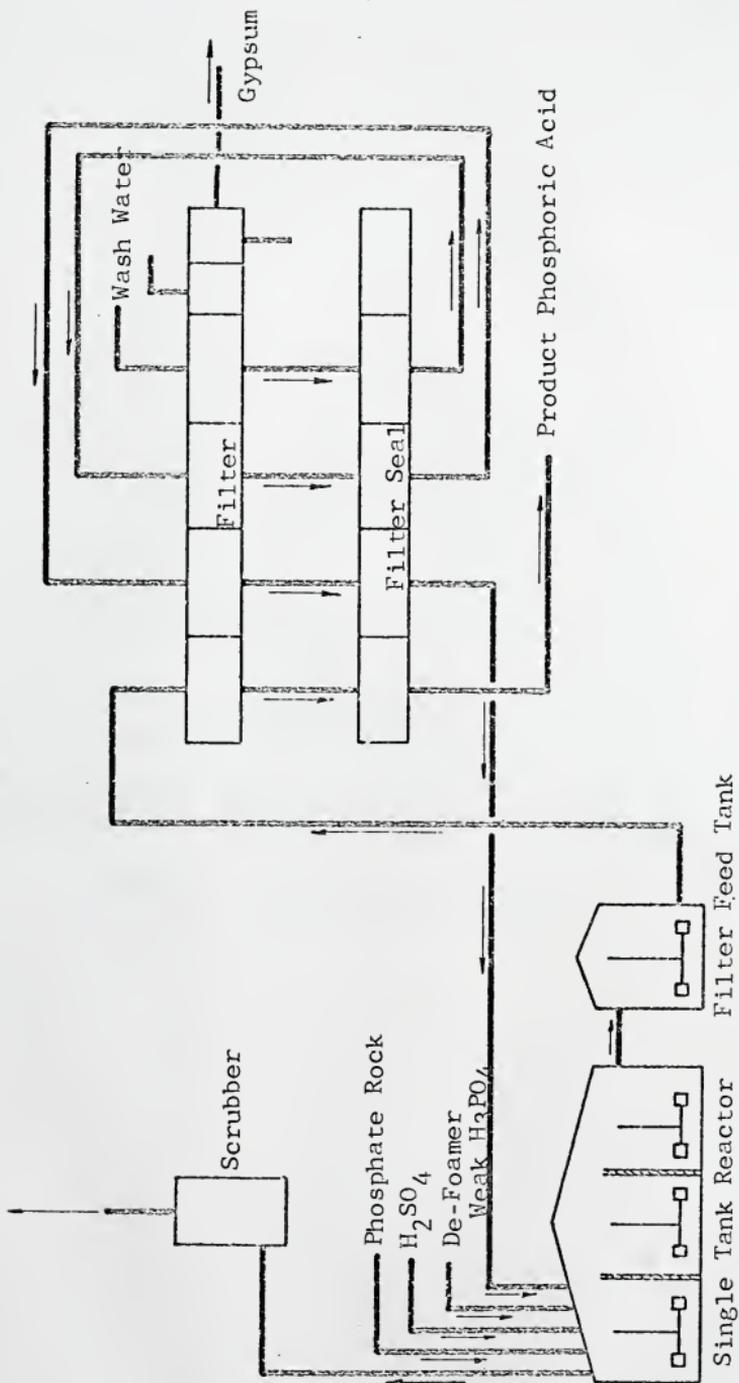


Figure 20: Flow Diagram Occidental Wet-Process Phosphoric Acid Plant

Occidental Chemical Corporation employs two Airetron cyclonic spray chamber scrubbers in series to remove the fluorides evolved in and around the wet-process phosphoric acid plant. The scrubbers were designed for an inlet loading of 282 mg per cu ft at a temperature of 135°F. Figure 21 shows the Occidental installation.

### Liquid Handling System

Figure 22 is a schematic diagram of the liquid handling system. Pictorial views of this system are given in Figures 18 and 19.

The storage tanks were 6-feet in diameter and 6-foot 10-inches high. Liquid in the form of gypsum pond water and well water was supplied to the tanks from outlets located in and around the wet-process phosphoric acid plant. The tanks were fabricated from Type 316 stainless steel. Figure 23 shows the tanks located on the tank trailer.

An open impeller end suction pump, Type 1½ CORV manufactured by Ingersoll-Rand Corporation, was used for liquid pumping. A second pump serves as a standby unit in case of emergency. Both pumps had 5 horsepower, 440 volt, 3 phase, 3600 rpm, TEFC, 60 cycle General Electric motors and were designed for 90 gpm at 97 foot total head.



Figure 21: Occidental Wet-Process Phosphoric Acid Plant  
Effluent Control System

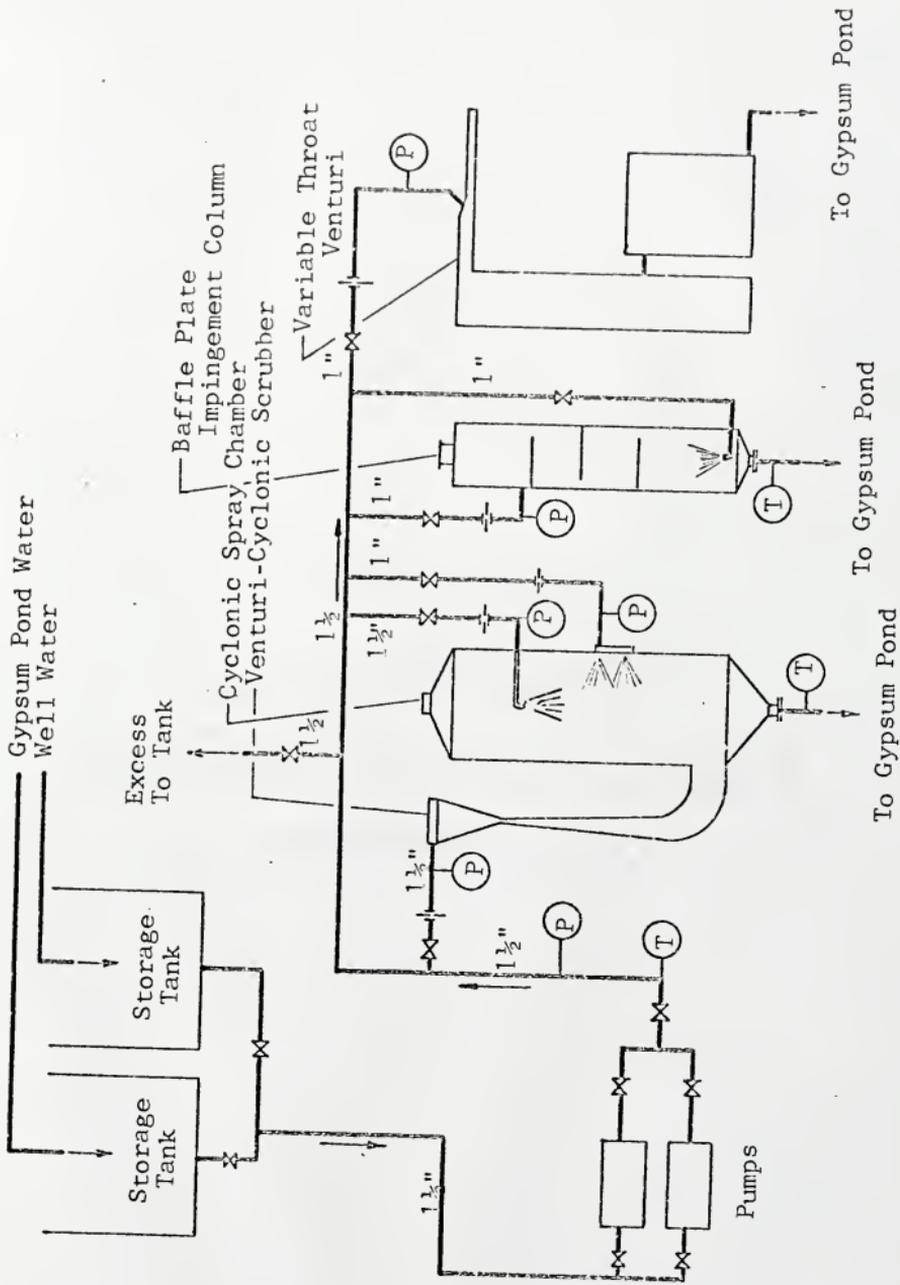


Figure 22: Schematic Diagram of Liquid System



Figure 23: Liquid Storage Tank Trailer

The piping was sized for the purposes desired and was constructed from Type 1 PVC (polyvinyl chloride) due to the acidic conditions that were experienced. All required valves and fittings were also of PVC construction. A piping schematic is shown in Figure 22 and pipe line sizes are noted thereon.

Liquid flow was measured by sharp-edge orifices, which were calibrated at the plant site. The orifices were made to the specifications contained in the ASME Power Test Code Manual and were manufactured by Daniel Industries, Incorporated. The diameters of the orifices are given in Table 6 and the locations of the orifices are shown schematically in Figure 22. The orifices were calibrated by weighing the volume of liquid passing through the orifice for a period of time and noting the pressure drop associated with this flow rate. Pressure gauge locations are shown schematically in Figure 22.

TABLE 6

## LIQUID HANDLING SYSTEM ORIFICES

Location	<u>Diameter (inches)</u>
Airetron spray chamber	0.750
Airetron spray nozzles	0.750
Airetron venturi	0.750
Peabody tray feed	0.625
<u>American air filter</u>	<u>0.500</u>

Temperature was measured using copper-constantan thermocouples placed in Type 316 stainless steel thermocouple wells. Thermocouple locations are shown schematically in Figure 22.

### Gas Handling System

The gas handling system included a blower, ductwork, scrubbers, and exhaust stacks. The system is shown schematically in Figure 24 and pictorially in Figures 18 and 19.

The blower was manufactured by the New York Blower Company. The original "Type P" unit was modified for the previous studies conducted by Crowley<sup>98</sup> and Galeano.<sup>99</sup> The impeller and fan housing were rubber coated for this study due to the corrosive nature of the gas which was handled. The blower had a 25 horsepower, 440 volt, 3 phase, 3600 rpm, TEFC, 60 cycle electric motor, and was designed for 2500 cfm at 0.7516 pounds per cubic foot air density at a static pressure of 41 inches of water. The blower is shown in Figures 18, 19 and 23.

The ductwork was of Type 1 PVC and filament wound glass construction. The diameter varied according to location. Flanged connections were used whenever possible. A system of blind flanges were used to direct the gas flow into the equipment under study. Figure 24 schematically shows the blind flange locations.

Gas flow was measured by square-edge orifices of

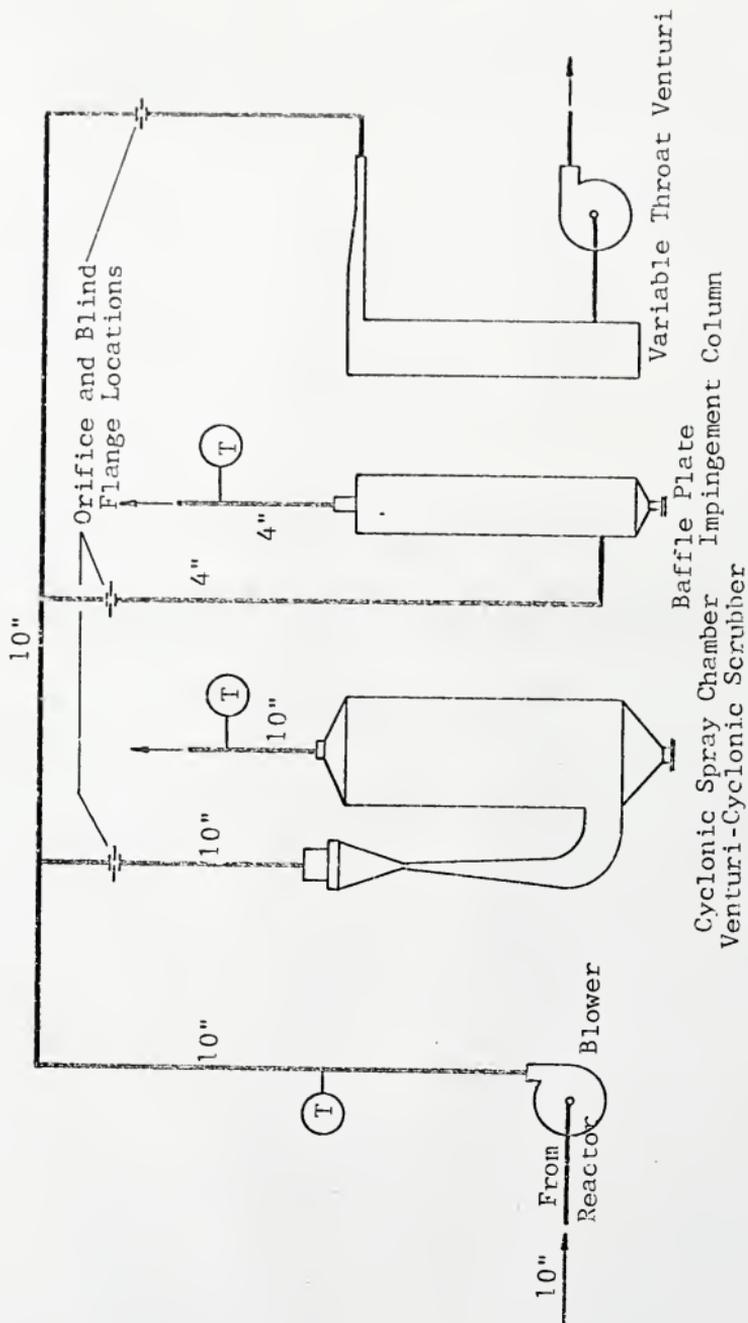


Figure 24: Schematic Diagram of Gas Handling System

Type 316 stainless steel construction. Orifice locations are shown schematically in Figure 24. The orifices were made to the specifications contained in the ASME Power Test Code Manual<sup>100</sup> and were manufactured by Daniel Industries, Incorporated. The orifices were calibrated using a pitot tube traverse across a section of known duct diameter and noting the pressure drop across the orifice associated with this flow rate. The pressure drop across each orifice was measured by a water-filled manometer. Table 7 indicates the orifice locations and diameters. Figure 24 schematically locates the orifices. Since the orifices could not be installed with proper distances (upstream and downstream) between the orifices and elbows in the ductwork, it was necessary to calibrate each orifice in place.

TABLE 7

## GAS HANDLING SYSTEM ORIFICES

<u>Location</u>	<u>Diameter (inches)</u>
Airetron duct	5.000
Peabody duct	3.000
<u>American air filter duct</u>	<u>3.000</u>

Gas temperature was measured using copper-constantan thermocouples placed in Type 316 stainless steel thermocouple wells. Thermocouple locations are shown schematically in Figure 24.

### Cyclonic Spray Chamber Scrubber

The 2600 cfm rated capacity cyclonic spray chamber scrubber was designed and manufactured by Airetron Engineering Company. Figure 25 diagrammatically describes this unit. Crowley<sup>98</sup> and Galeano<sup>99</sup> described this unit in some detail. In general, the unit was constructed of Type 316 stainless steel and consisted of a circular chamber 3 feet in diameter and 7 feet high, and had a lower cone 15 inches high with a 3 inch diameter bottom liquid drain. A 6 inch Yorkmesh Demister was initially located at the top of the circular chamber; however, due to silica gel formation the demister was removed. The amount of silica gel formed was sufficient to cause the pressure drop in the spray chamber to rise from 1 inch of water to approximately 12 inches of water in a 2-to-3 hour period.

The scrubbing liquid was fed to this scrubber from a 1½ inch pipe to an outer circular ring on the top of the chamber which fed 4 spray boxes located at 90° intervals about the chamber. Each spray box contained 4 Type 316, Model No. 47 flat spray jet nozzles with a 0.093 inch diameter orifice. The spray boxes were individually valved in order to provide approximately the same liquid flow to each spray box.

A 1½ diameter Type 1 PVC header was located under the demisting section and was used to supplement the liquid flow from the sprays when necessary. This header

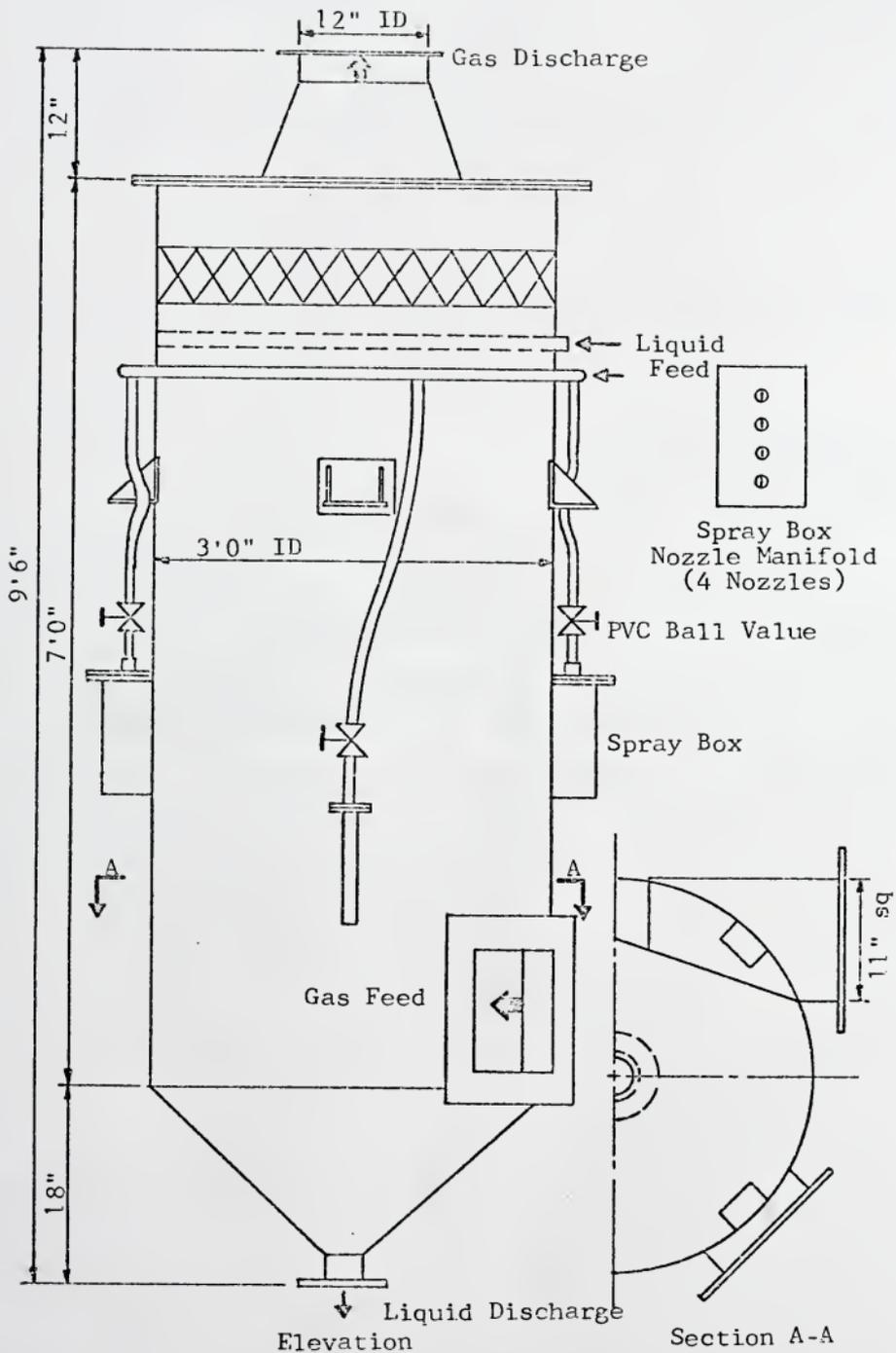


Figure 25: Diagrammatic View of Cyclonic Spray Chamber

was equipped with 4 Airetron full cone, 90° spray nozzles having a recommended operating pressure of 50 psig. The scrubber was operated in the cyclonic spray chamber configuration with the venturi section in place but without feedwater to the venturi.

#### Venturi - Cyclonic Scrubber

The 2600 cfm rated capacity venturi - cyclonic scrubber was designed and manufactured by Airetron Engineering Corporation. Figure 26 diagrammatically describes this unit. Crowley<sup>98</sup> and Galeano<sup>99</sup> described this unit in detail. It was the same unit as described previously with a Type 316 stainless steel venturi section installed on a tangential inlet. The venturi had a 2 x 11 inch throat and was 8 inches high. The scrubbing liquid was introduced into the top of the venturi by two weir boxes. The liquid flowed over each weir into the venturi, down two sides of the converging section to the throat under gravity.

Gas entered the venturi through a 90° fiberglass box located on the top of the venturi as shown in Figure 19. No design changes were made to this piece of equipment for the purpose of this study.

#### Impingement Baffle Plate Column

The 350 cfm rated capacity impingement baffle plate column was designed and manufactured by Peabody Engineering Corporation. Figure 27 diagrammatically

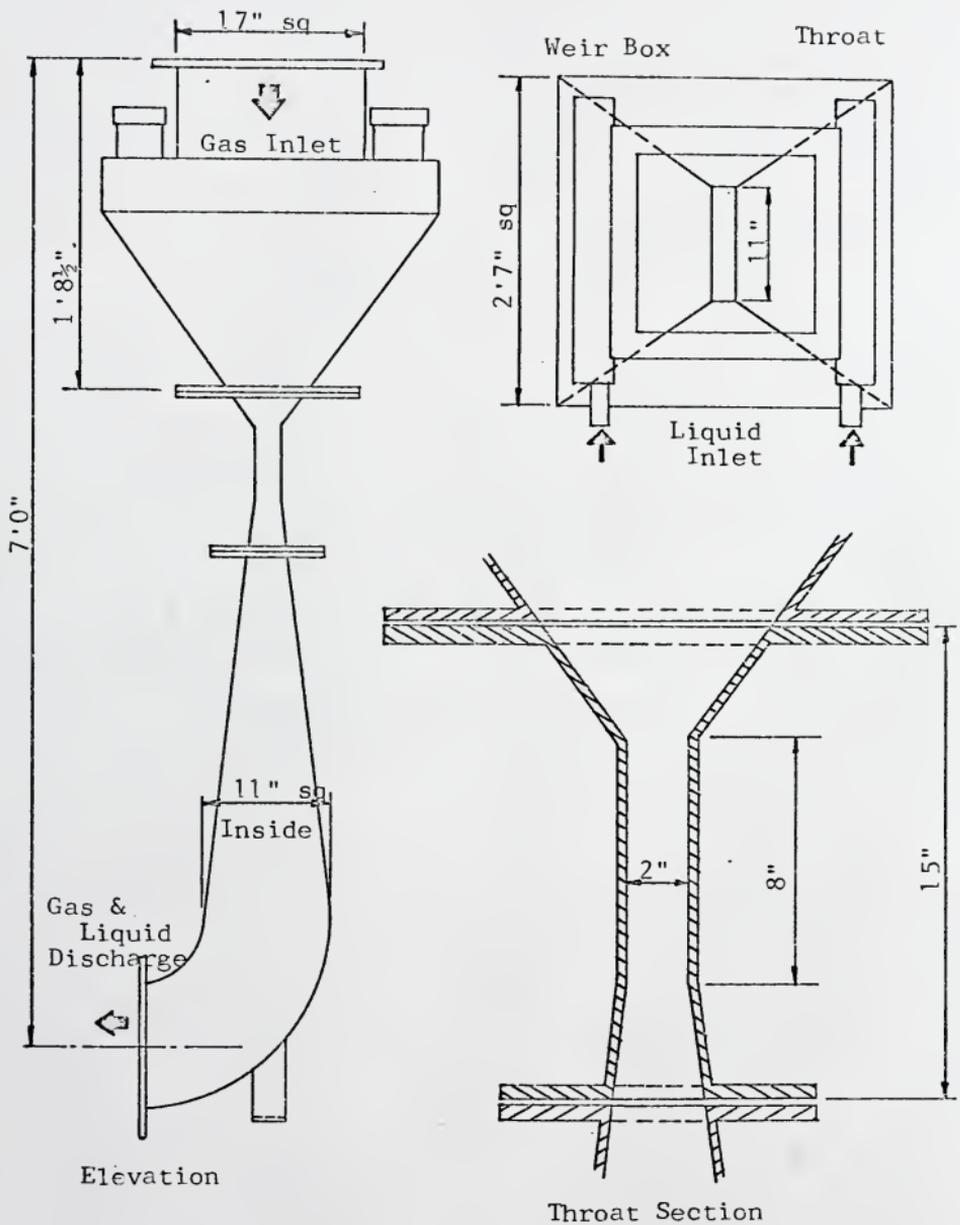
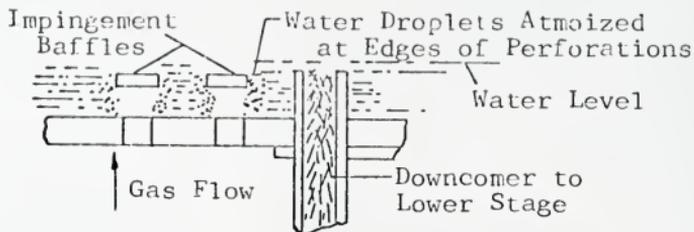
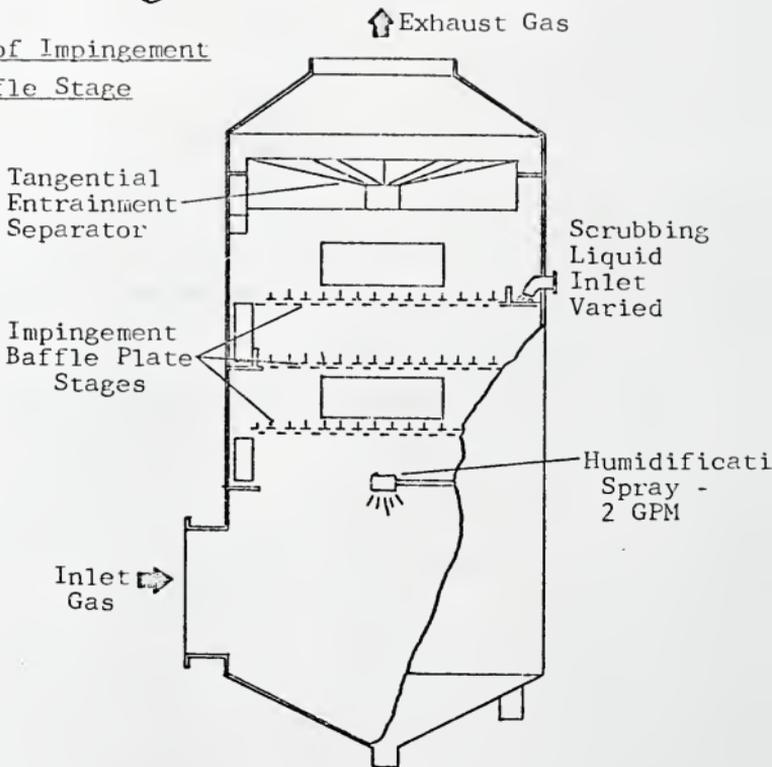


Figure 26: Diagrammatic View of Venturi



Details of Impingement  
Baffle Stage



Column Internals

Figure 27: Diagrammatic View of Impingement Baffle Plate Column

describes this unit. Crowley<sup>98</sup> also described this unit in some detail. In general, it was 14 inches in diameter, 8 feet high, and had a 6 inch radial inlet and a 6 inch center outlet. There were three impingement baffle plate stages and a tangential entrainment separation stage at the top. Each plate had a downcomer pipe that lead to the next lower plate. The downcomer liquid flowed onto the plate, over an influent weir, across the plate, and to the next downcomer. The liquid discharge level from the top and center plates was controlled by an adjustable effluent weir set at a height of one inch. The discharge level from the bottom plate was not controlled. Each plate was perforated with approximately 600 3/16 inch diameter holes providing approximately 22 percent open area. A baffle was installed over each hole to cause the bubbling action necessary for adequate mass transfer to take place.

Scrubbing liquid was fed into the scrubber at two points. A flow of 2 gpm was maintained at the gas inlet for use as a humidifying spray while the remaining liquid was fed to the top plate to complete the flow cycle previously mentioned.

#### Variable Throat Venturi

The 1000 cfm rated capacity variable throat venturi was designed and manufactured by the American Air Filter Company. Crowley<sup>98</sup> described this unit in

some detail. In general, the unit contained a variable throat venturi, a "Rotoclone" type demisting section, blower, liquid recirculation tank, and pump. The scrubbing liquid was sprayed into the gas stream through a nozzle located in the throat. The throat dimensions were 3 inches by 2.75 inches giving a full open throat area of 8.25 square inches and an one-half open area of 4.125 square inches.

The demisting section consisted of a 14 inch diameter column with an inverted cone inside, which was an American Air Filter Company "Roto-Clone," a type of centrifugal demister. The recirculation tank and pump were not used in this study.

### Instrumentation

Gas flow rates were measured with water-filled manometers installed in the instrument room. Liquid flow rates were measured with mercury-filled manometers installed in the instrument room.

Temperatures were measured by means of copper-constantan thermocouples installed in Type 316 stainless steel wells as stated previously. The leads of the thermocouples were connected to a 16-point recording potentiometer for continuous monitoring and recording. The recorder was a Minneapolis - Honeywell Electronic, Model 153x60 - F16-II-III-31-F1, calibrated for copper-constantan thermocouples and used recorder chart number 5270 with a full scale range of 0 to 500°F.

Flue gas moisture was measured by means of wet-bulb mercury thermometers placed in the gas ductwork at locations shown in Figure 24. All gas flows were corrected to 68°F, 29.92 inches of mercury, and dry conditions. Relative humidity was found by using the psychrometric chart published by the American Society of Heating, Ventilating, and Air Conditioning Engineers.<sup>101</sup>

Static pressure was measured by water-filled manometers. Type 316 stainless steel tubing was used to connect all pressure taps with the manometer board located in the instrument room.

### Experimental and Analytical Procedures

#### Preparation for the Study

Since the operation of the scrubbing equipment was dependent upon the operation of the wet-process phosphoric acid plant, it was necessary to check the operating schedule for the plant prior to beginning data collection on any given day. Initially, the process operator was questioned to see if the plant would be running all day and if he was experiencing any operating difficulties. Then, the covers on the reaction tank, launder to filter feed tank, and filter feed tank were checked to insure that they were in place and were providing an adequate seal.

Once it had been established that the plant was operating and would continue to operate throughout the

day, the scrubbing liquid was then fed into the correct storage tank. One tank was reserved for well water and the other tank was reserved for gypsum pond water. Both the well water and gypsum pond water were supplied from outlets inside the phosphoric acid plant. Normally, the flow rate to the tanks exceeded the flow rate to the scrubbers, therefore, it was occasionally necessary to observe the fluid level in the tanks to avoid overflow.

#### Typical Experimental Run

A typical experimental run was as follows:

1. All pressure taps for measuring gas flow and gas pressure were cleaned. This was necessary since at times the silica gel build-up at these points was sufficient, over a period of 1-2 hours, to cause erroneous readings.
2. The gas blower was started.
3. The valves in the liquid lines were opened to allow flow from the storage tank, to the pump, and back to the storage tank.
4. The liquid pump was started and the valves controlling the flow rate to the unit under study were adjusted to the required level. This operation necessitated balancing the flow rate to the storage tank and to the unit.

5. The temperature recorder was started.
6. The unit was allowed to reach equilibrium conditions before any data collection began. A 30-minute period was allowed for equilibrium to occur, because it had been observed that equilibrium would occur after 15 to 20 minutes.
7. During the time allotted to attain equilibrium, the sampling trains were set-up and tested for operation. The gas flow rate through each train was adjusted and the initial dry gas meter readings were recorded at this time.
8. Once equilibrium was assumed to have been reached, the outlet sampling probe was placed into the duct, and the outlet sampling train was started. Normally, 15 to 18 minutes at approximately 0.9 cfm were required to obtain a sample in the concentration range desired for fluoride measurement.
9. The inlet sampling probe was placed into the duct and the sampling train was started. Normally, 5 to 8 minutes at approximately 0.85 cfm were required to obtain a sample in the concentration range desired for fluoride measurement. The inlet sampling train was placed in operation approximately 5 minutes

after the outlet sampling train was placed in operation.

10. When required, samples of the inlet and outlet scrubbing liquid were obtained.
11. During the experimental run, the following values were recorded:
  - a. Pressure drop across the gas flow orifice
  - b. Pressure drop across the scrubber
  - c. Pressure drop across the liquid flow orifice
  - d. Liquid pressure at the scrubber
  - e. Wet-bulb temperature of inlet and outlet gas
  - f. Temperatures and pressures at the dry gas meters.
12. After both gas samples were taken, the final dry gas meter readings were recorded.
13. The inlet and outlet sample tubing was removed from the probes and placed with the impingers for cleaning and analysis.
14. The replication for the experiment was run following the same procedure as outlined above. The liquid flow rate was reset as closely as possible to the initial flow rate.
15. The scrubber was then made ready for the next experimental run. It was not possible, nor was it considered necessary, to wash the

unit down after each experiment. Due to equipment difficulties, the blower was not shut down between runs and, therefore, the only change necessary to begin a new experimental run was to set a new liquid flow rate. This procedure may have affected the assumed independence of experiments and introduced statistical bias; however, it was the only method possible under the operating conditions.

16. The impinger samples were analyzed while awaiting equilibrium conditions to be reached for the next experimental run.

### Fluoride Sampling and Analysis

Considerable interest has been directed toward the determination of gaseous and particulate fluoride in ambient air and stack effluents. However, sampling of effluents that contain fluorides is often hampered by the reactivity of fluoride. The techniques that have been developed for sampling ambient air are not applicable to stack sampling where the effluent contains much higher concentrations of fluoride. Analytical methods for the determination of fluoride in ambient air such as volumetric,<sup>102</sup> conductimetric,<sup>103</sup> potentiometric,<sup>104</sup> gravimetric,<sup>102</sup> and colorimetric<sup>105</sup> have been reported. The most widely accepted ambient air sampling analytical methods are colorimetric and have

evolved from the concepts presented by Willard and Winter.<sup>106</sup> The most widely accepted stack sampling methods are also based upon colorimetric methods and are the Spadns - Zirconium Lake Method<sup>105</sup> and the Lanthanon III - Alizarin Method.<sup>107</sup>

The colorimetric procedures normally require distillation of the fluoride from perchloric or sulfuric acid to remove interferences prior to the analysis. These methods involve a number of steps and elaborate test equipment, are time-consuming, and rely upon distillation techniques and colorimetric determinations which, if not closely controlled, reduce the accuracy of the measurement. For these reasons, the existing methods for fluoride determinations are at times questionable and newer methods are continually being proposed.

In recent years, the development of specific ion electrodes has stimulated interest in the possibility of determining fluoride with this method. In 1966, Frant and Ross<sup>108</sup> reported on the development of a fluoride specific ion electrode for use in determining fluoride ion activities in aqueous solutions. The electrode gave a Nernstian response over a wide range of fluoride ion activity and was highly selective for fluoride in the presence of many ions commonly associated with fluoride. Since 1966, the electrode has been used for many purposes including the determination of fluoride concentrations in chromium plating baths,<sup>109</sup> in

bone,<sup>110</sup> in toothpaste,<sup>111</sup> and in water supplies.<sup>112</sup>

Elfers and Decker<sup>113</sup> reported on using the electrode for determination of water-soluble fluoride in ambient air and stack gas samples. They reported that the electrode could be used to measure as little as 0.25 ppb fluoride in the ambient air. Results obtained with the electrode and the Spadns - Zirconium Lake Method for fluoride determination in stack gas were compared and at the 0.05 significance level no difference existed between the two methods.

An Orion<sup>26</sup> Model 96-09 Combination Fluoride Electrode was used in this research since it had been proven for use in determination of fluoride in aqueous solutions, and since it had been shown<sup>112,113,114</sup> to be more rapid, reliable, reproducible, convenient, and appeared to be less susceptible to interferences than other methods presently available. This electrode was identical with previous models except for the addition of the reference electrode into the body of the fluoride electrode, thereby eliminating the need for a separate reference electrode. The electrode consisted of a fluoride-sensitive crystal of lanthanum-fluoride ( $\text{LaF}_3$ ), doped with a rare earth, europium (II), installed in a plastic tube containing a reference filling solution. When the electrode was immersed in a solution of fluoride, a potential difference was established; the magnitude of which depended upon the ratio of the fluoride ion activities

between the sample and the internal reference solution. The potential of the electrode was then measured against that of the reference electrode, which matched a conventional saturated KCl-calomel electrode, on an expanded-scale pH meter. The potential difference could then be used as an indication of the fluoride ion activity in the solution. This method permits the determination of high (1M fluoride, or 19,000 ppm) and low ( $10^{-6}$ M fluoride or 19 ppb) fluoride concentrations with accuracies comparable to the generally accepted colorimetric methods.<sup>105,107</sup>

The only common interfering ions are the hydroxide ions when in excess of the fluoride concentration,<sup>115</sup> and cations such as  $Al^{+3}$  and  $Fe^{+3}$ , which could complex with the fluoride and reduce its activity. The extent to which complexing takes place depends upon the solution pH and the relative levels of the fluoride and complexing species. In acid solutions, hydrogen ion forms complexes with the fluoride ion, such as the undissociated acid HF and the ion  $HF^{-2}$ . Figure 28 shows the proportion of free fluoride ion in acid solutions. Above pH 5, hydrogen complexing is negligible. Figure 29 shows the effect of pH on electrode response in acid solutions.

Hydroxide ion interferes<sup>108</sup> with the electrode response to the fluoride ion when the level of hydroxide present is greater than one-tenth the level of

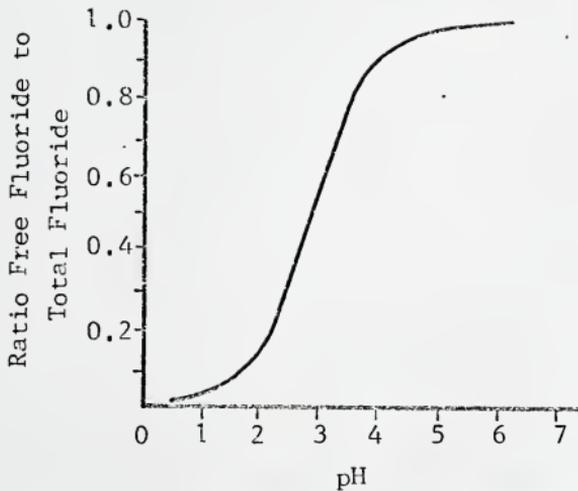


Figure 28: Fraction of Free Fluoride as a Function of Solution pH, where hydrogen ion is the only complexing species.<sup>115</sup>

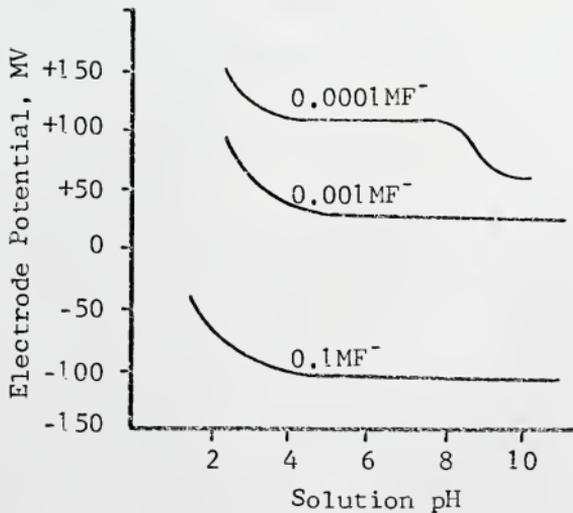


Figure 29: Effect of pH on Electrode Response (Sodium Fluoride Standard).

fluoride ion present. When the amount of hydroxide is less than one-tenth the amount of fluoride, no significant error occurs. Figure 29 shows the electrode response in alkaline solutions.

Orion<sup>115</sup> reports that the electrode does not respond to other anions commonly found with fluoride, such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{-3}$ , even when present in excess of a thousandfold or more. The carbonate and phosphate anions do not directly interfere with the electrode response; however, they do make a solution more basic, increasing the hydroxide ion concentration. Whenever high levels of these anions are present, the pH must be controlled before making dilute fluoride determinations.

Although the electrode responds to fluoride activity, it was possible to calibrate the potentials in terms of concentration. The activity and concentration in any given solution are related by

$$A_F = \gamma_F C_F \quad (35)$$

where:

$A_F$  = fluoride ion activity

$\gamma_F$  = fluoride ion activity coefficient

$C_F$  = free fluoride ion concentration

The fluoride activity coefficient depends upon the total ionic strength of the solution and on the formation of complexes. In order to keep the activity to

concentration ratio constant, the total ionic strength must be held constant. In order to approximate this condition, an ionic strength adjustor was added to both samples and standardizing solutions so that the standards and samples were made to have approximately the same total ionic strength. After laboratory investigations of various ionic strength adjustors, a 2 percent by weight sodium acetate solution (0.147 M) was selected as the ionic strength adjustor to be used in this research. Any changes in the sample ionic strength were assumed to be negligible when compared to the total ionic strength of the acetate and sample mixture. The use of the sodium acetate also buffered the standard and sample solutions to a pH between 5 and 8.

Since the literature<sup>1,15</sup> indicated that silicon tetrafluoride would be the predominant effluent gas, standard solutions of  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ , and  $10^{-1} \text{MF}^{-}$  concentrations were prepared using hydrofluosilicic acid as the source of the fluoride ion. The electrode response to one part of the standard solution and 9 parts of 2 percent sodium acetate solution was then determined, and a calibration curve similar to Figure 30 was drawn. The same procedure was followed using standard solutions where the fluoride was supplied from hydrofluoric acid. Since at the 0.01 significance level no difference existed between the two methods, and since it had been determined that very little hydrogen fluoride gas could be expected, all standards were prepared using hydrofluoro-

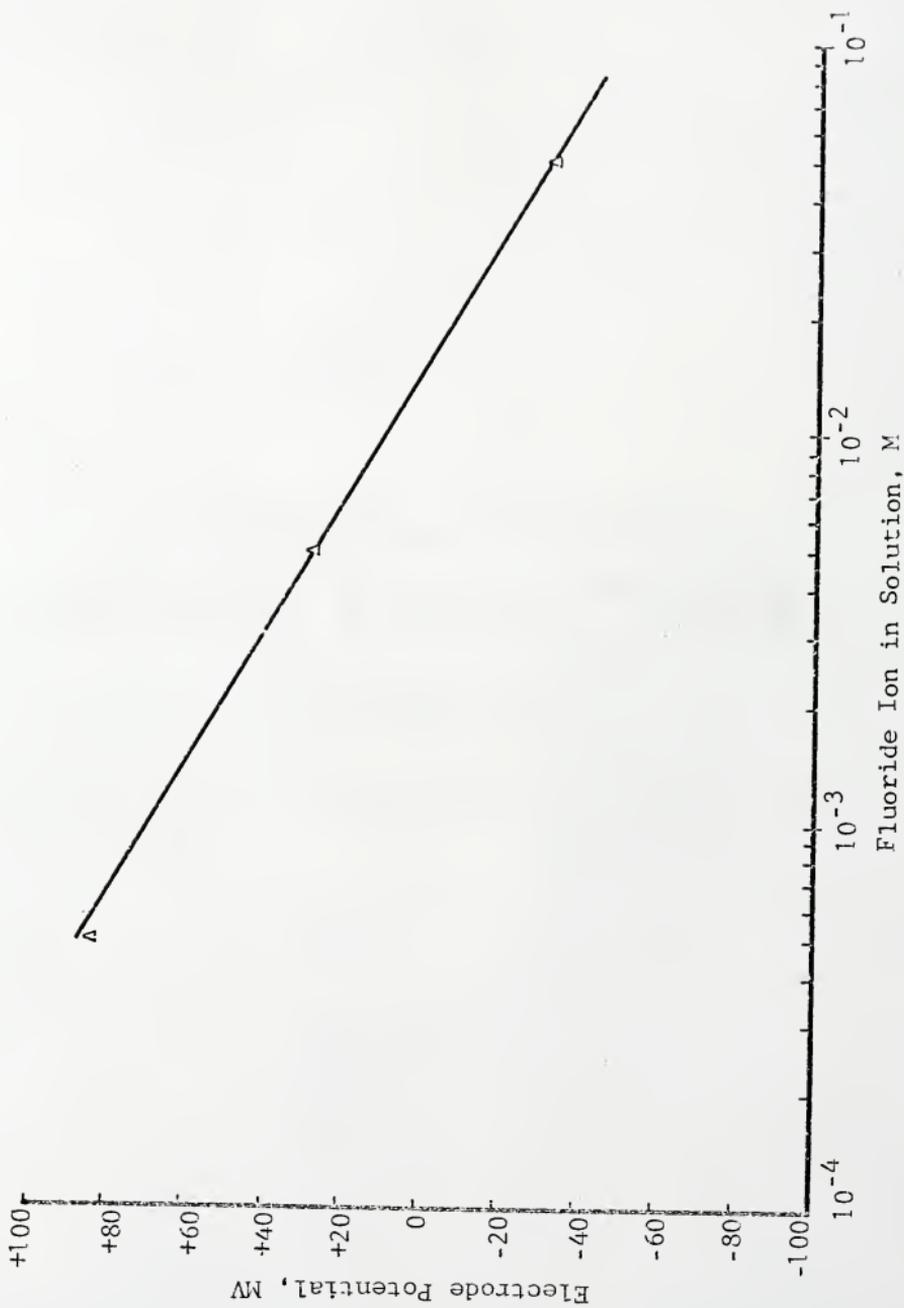


Figure 30: Calibration Curve Using 2 Percent Sodium Acetate Solution

silicic acid as the source of the fluoride ion.

The Orion specific ion electrode was quite suitable for use in the field. Since the potential difference measured by the electrode is temperature dependent as shown by the Nernst equation

$$E = E^0 - 2.3 RT/nF \log A_{F^-} \quad (36)$$

where:

$E$  = measured potential of the system

$E^0$  = constant, characteristic of the particular measuring and reference electrodes employed

$R$  = gas constant

$T$  = absolute temperature

$n$  = valence of the ion

$F$  = Faraday's constant

$A_{F^-}$  = Fluoride activity in the sample

it would have been preferred to maintain a constant 25°C in the laboratory on the trailer. The Nernst factor,  $2.3 RT/nF$  in Equation 36, is equal to 59.16 mv at 25°C when  $n = 1$  and the other terms are as previously described. Due to the unavailability of power for the air conditioner on the trailer, it was not possible to control the temperature in the laboratory. The maximum temperature recorded in this room was 30°C (86°F). This would only cause approximately a 1.7 per cent error in the electrode response at the highest

temperature noted. Since it was felt that this error was tolerable, it was decided not to attempt to provide additional power to air-condition the laboratory. Babcock and Johnson<sup>112</sup> reported on the effects of temperature upon the electrode response and stated "wide variations in temperature affect fluoride measurement only slightly, and temperature effects can usually be neglected."

As was previously mentioned, pH of the solution could have an effect upon the electrode response. At pH values of less than 4, hydrogen ions complex with free fluoride to form hydrogen fluoride, which is not detected by the electrode. Since the sodium acetate solution, when used in the procedure described, always provided a solution with a pH greater than 5, hydrogen fluoride complexing was not considered a problem. At a high pH, a significant interference is introduced by the hydroxide ion, as the fluoride ion and hydroxide ion have similar charges and ionic radii.<sup>108</sup> When the hydroxide ion concentration is greater than one-tenth that of the fluoride ion concentration, the electrode will respond to both ions. The 2 percent sodium acetate solution was selected for use in this experiment since for the fluoride concentrations expected and found, the hydroxide ion concentrations were considerably less than one-tenth of the fluoride ion concentrations. The maximum pH recorded during any of the

sample analyses was 6.65, or a hydroxide concentration of approximately  $4.5 \times 10^{-8}$ , which requires a fluoride ion concentration of  $4.5 \times 10^{-5}$  or greater for the desired accuracy. All fluoride ion concentrations were greater than  $10^{-4}M$  and could be controlled by varying the length of time taken to obtain the sample. Normally the pH of the inlet sample was between 5.0 and 6.0 and the pH of the outlet sample was between 5.5 to 6.5.

Aluminum and iron are also known to complex with fluoride ions at pH values of 7 or less, however, an experiment involving the addition of a 1 percent sodium citrate solution indicated that there was little or no complexing in the gas samples studied. Since both aluminum and iron are found in the rock and are expected to be found in the acid product, they could possibly be entrained in the effluent reactor gas. Since the gas had no noticeable particulate loading, no aluminum or iron was detected in the complexing experiment.

Oliver<sup>116</sup> reported that it is not necessary to distill samples when using the fluoride specific ion electrode. In order to test this concept and to check on the accuracy of the analytical technique employed in the field, Occidental agreed to analyze a few of the impinger samples. Occidental had an earlier model of the Orion electrode which they used for fluoride determinations in their gypsum pond water and in other process studies. Impinger samples from 3 experimental runs and

one known sample were split, with Occidental performing one analysis of the samples, and the author performing another. Table 8 reports the results obtained from this study.

TABLE 8  
OCCIDENTAL LABORATORY ANALYSIS

<u>Sample</u>	<u>Author</u> <u>MF<sup>-</sup></u>	<u>Occidental</u>	
		<u>Direct</u> <u>MF<sup>-</sup></u>	<u>Distilled</u> <u>MF<sup>-</sup></u>
1	0.0500	0.0515	0.0443
2 (known 0.0500MF <sup>-</sup> )	0.0510	0.0511	0.0539
3	0.2785	0.3000	0.2945
4	0.2813	0.2475	0.2410

Occidental employed a 5 percent sodium acetate solution for their analyses. Due to dilution of the samples and use of 5 percent sodium acetate by Occidental, the above data appeared to be quite acceptable.

One of the criteria of any sampling method to be satisfied is that of reproducibility. Since the laboratory procedure involved the establishment of a calibration curve on each day, it was decided to determine the deviation for any given day. Realizing that the sodium acetate solution concentration was not constant, a statistical analysis of the calibration data was run. Table 9 reports the results of this statistical study.

TABLE 9

## STATISTICAL ANALYSIS OF CALIBRATION CURVE DATA

Standard Solution $\text{MF}^-$	Electrode Response (mv)	
	Mean	Standard Deviation
$5 \times 10^{-4}$	+74.09	$\pm 4.510$
$5 \times 10^{-3}$	+26.32	$\pm 1.675$
$5 \times 10^{-2}$	-33.00	$\pm 1.613$

Most of the samples taken in the impinger train were in the  $10^{-3}$  to  $5 \times 10^{-1} \text{MF}^-$  range where the standard deviation was quite low. In this range on the calibration curve, a change of 1 mv would cause a 2.06 percent error in the result. However, the accuracy of reading the expanded scale pH meter was  $\pm 0.5$  mv. This accuracy, along with changes in the sodium acetate solutions and in the standardizing solutions, would explain the high standard deviation found in this analysis. The high standard deviation at  $5 \times 10^{-4}$  solution was due, in part, to the fact that the  $5 \times 10^{-4}$  solution when added to the sodium acetate solution, was in actuality a  $5 \times 10^{-5} \text{MF}^-$  solution. The accuracy of the electrode becomes very questionable in this range. The slope of the calibration curve in the area of most use was approximately 59.32 mv which compares quite favorably with the theoretical slope calculated using Nernst's equation at  $25^\circ\text{C}$  of 59.16 mv.

Figure 3! schematically illustrates the fluoride sampling trains. Each train consisted of the following:

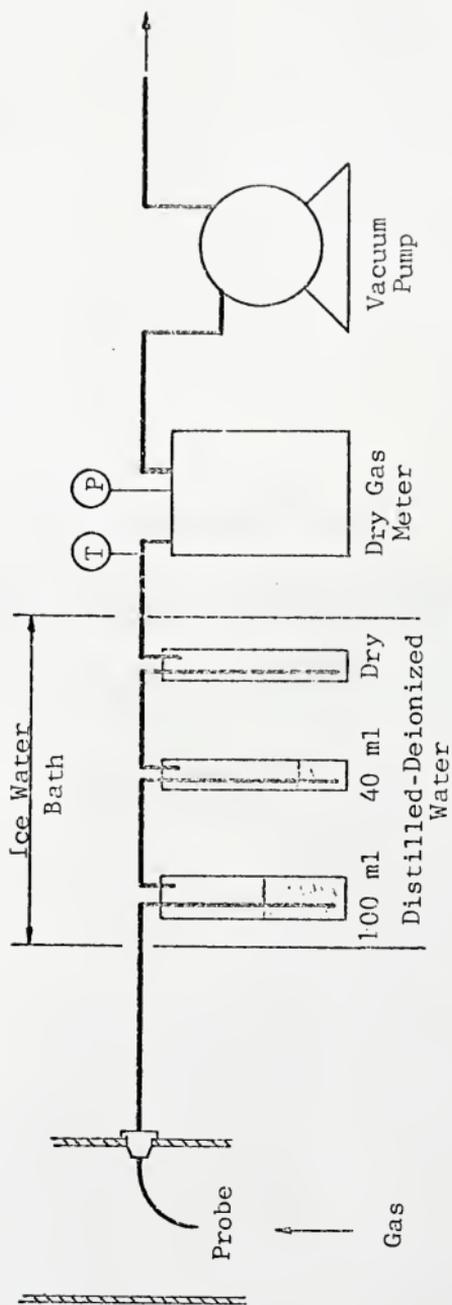


Figure 31: Fluoride Sampling Train

1. A Type 316 probe which was screwed into the gas duct. Since gaseous fluoride was the only concern, an isokinetic sample was not taken.
2. Natural rubber tubing connecting the probe with the first impinger. Polyethylene quick-disconnect couplings were used wherever possible.
3. A "modified" 250 ml Greenburg-Smith impinger containing approximately 100 ml of distilled-deionized water. The impinger was modified by removing the orifice. This was necessary due to the formation of silica gel in the sampling train. A similar situation was encountered by Dorsey and Kemnitz<sup>117</sup> who reported an efficiency of 96 percent for this type of impinger.
4. A standard 100 ml impinger containing approximately 40 ml of distilled-deionized water.
5. A trap to catch any liquid before it reached the dry gas meter.
6. A calibrated dry gas meter with temperature and pressure measuring gauges.
7. A vacuum pump.

8. The impingers, dry gas meter, and vacuum pump were connected with either tygon or natural rubber tubing.
9. The impingers and traps were placed in ice water baths to insure saturated conditions at the dry gas meter.

All work in the laboratory indicated that the sampling train selected would be satisfactory in the field. The gases used in the laboratory calibration period were hydrogen fluoride and silicon tetrafluoride. No silica gel formation occurred in either study.

When the sampling train was used in the field, it proved to be satisfactory for this type of stack sampling. However, the formation of silica gel as described in Equation 7 proved to be quite a problem. The silica gel formed in the condensate that occurred in the tubing between the probe and the sampling train impingers. It was not known during the laboratory studies that the reactor gases would be at or very near to saturation; therefore, this condition was not expected. In the preliminary data runs, as the silica gel formed, the pressure drop across the sampling train became unsatisfactory and cross-contamination between samples occurred. It was necessary to clean the inlet and outlet sampling probes after each run in order to avoid contamination of samples and to maintain a reasonable pressure drop across the sampling train.

Previous sampling trains<sup>116,117</sup> had employed a heated probe to avoid condensation before the impingers. It was felt that this probe would help avoid the silica gel formation and one was tried in the field. The probe did accomplish this goal, however, it was quite cumbersome to handle due to its size, surface temperature and its fragility. Unless the connecting tubing between the probe and the impingers was also heated, condensation would occur and silica gel again became a problem. For these reasons, the heated probe concept was discarded in favor of the unheated probe method described. Although this method required additional time for cleaning the probes, it proved to be considerably easier to use in the field.

An over-all efficiency of approximately 99.2 percent had been reported<sup>117</sup> for this type of sampling train and laboratory investigations showed this value to be reasonable. The second impinger always showed no more than trace amounts of fluoride when it was analyzed separately from the first impinger. Field determinations also indicated that, due to condensation of water and formation of silica gel in the tubing between the probe and the initial impinger, the tubing had to be washed with distilled-deionized water or erroneous values would be measured. Depending upon the length of this tubing and the amount of silica gel formed, this section would at times serve as an initial absorber.

Reagents which were used for the analysis were:

1. Distilled-deionized water, obtained in Gainesville and transported to White Springs as needed.
2. ACS-reagent grade 30 percent hydrofluosilicic acid, used to prepare the fluoride standard solutions.
3. ACS-grade sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ), used to prepare the 2 percent ionic strength adjustor. It was found that this reagent had a shelf life of approximately one week; therefore, new solutions were prepared as required.
4. Orion Ionalyzer filling solution 90-00-01, purchased from Orion Research and used as the reference filling solution for the specific ion electrode.

Laboratory equipment used in the analysis included:

1. Corning Model 10 expanded scale pH meter (0-300 mv).
2. Beckman Zeromatic II expanded scale pH meter ( $\pm$ 0-700 mv).
3. Sargent magnetic stirrer with Teflon coated magnets.
4. Plastic containers ranging in capacity from 50 ml to 200 ml. Since fluoride is absorbed by glass, plastic containers were required

for storage of standardizing solutions. For dilute solutions ( $10^{-4}$  M or below in fluoride ion) plastic beakers for holding solutions during measurement were also required.

5. Pipettes and other glassware as required.

Prior to performing the laboratory analysis on any given day, the pH meter was standardized with a  $7.00 \pm 0.01$  pH buffer and a calibration curve was run for the specific ion electrode. The procedure for determining the calibration curve for the specific ion electrode at White Springs was the same as that used in the laboratory in Gainesville. The laboratory procedure followed in performing the fluoride analysis was:

1. The tubing from the probe to the first impinger was washed out with distilled-deionized water. The washings went into the first impinger.
2. The contents of the two impingers and the trap were placed into a 250 ml volumetric flask.
3. The impingers were washed with distilled-deionized water. All washings were added to the 250 ml volumetric flask.
4. The 250 ml volumetric flask was then filled to the 250 ml mark with distilled-deionized water, stoppered, and shaken.

5. Two 5 ml aliquot samples were pipetted from the 250 ml flask into each of two 50 ml plastic beakers.
6. Two 45 ml aliquots were taken from the 2 percent sodium acetate solution and placed in the 50 ml beakers.
7. Each beaker was placed on the magnetic stirrer, and stirred while the pH and specific ion electrode response were noted and recorded.
8. The values from the two samples were averaged, if there was any deviation between the two, and this final value was used in reporting the result of the experimental run.
9. A blank was run by the same method.

## CHAPTER VI

### RESULTS OF THE EXPERIMENT

This chapter will cover both a presentation and a discussion of the results obtained in the experimentation performed in this research effort.

In general, all the results in this section appeared to be in keeping with the generally accepted theory describing the absorption process. In all cases, scrubbing with gypsum pond water, which had 8500 to 9500 ppm free fluoride, produced lower removal efficiencies than scrubbing with well water at the same liquid/gas ratio. The slope of the curves varied with the type of equipment and the number of transfer units was dependent upon the total contacting power to each type of equipment.

The analyses for this section required the plotting of the graphs shown in Figures 32 to 48. The fitting of the curves in these figures was by eye, and the limited number of observations affects the absolute values of the calculated slopes. It should be noted that all of the data were used for these graphs, and that the variation of the independent variables ( $F^-$  concentration, gas temperature, liquid temperature, and gas flow rate) could affect the plotted results. Therefore, these graphs show general relationships and trends and were used

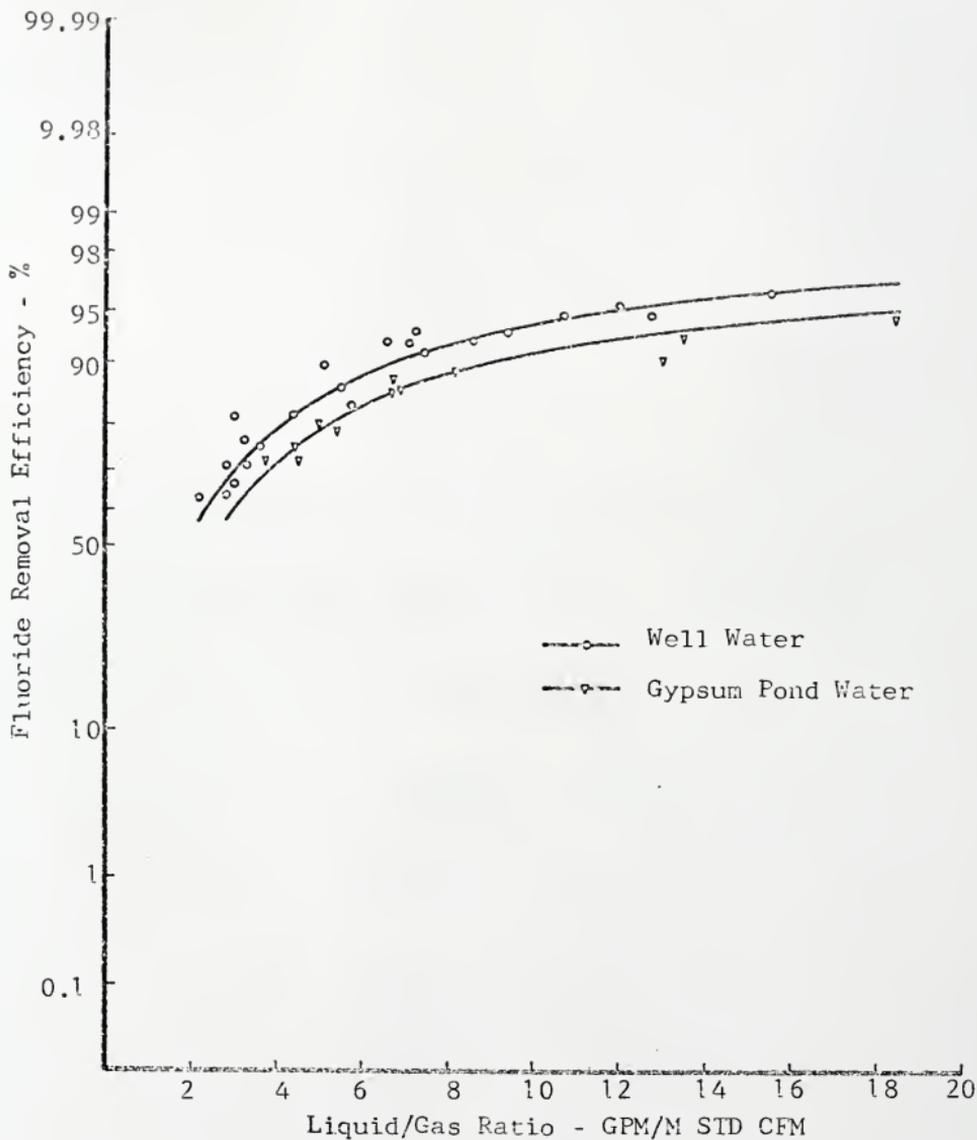


Figure 32: Effect of Liquid/Gas Ratio on Fluoride Removal Efficiency in Spray Chamber

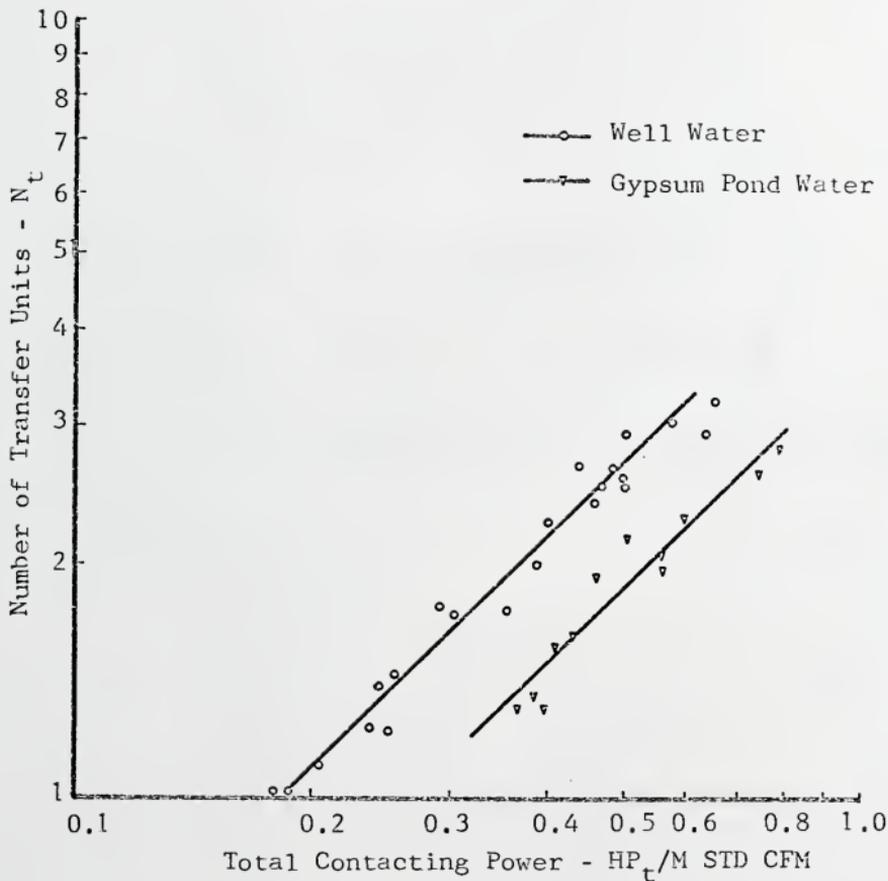


Figure 33: Effect of Total Contacting Power on Number of Transfer Units in Spray Chamber

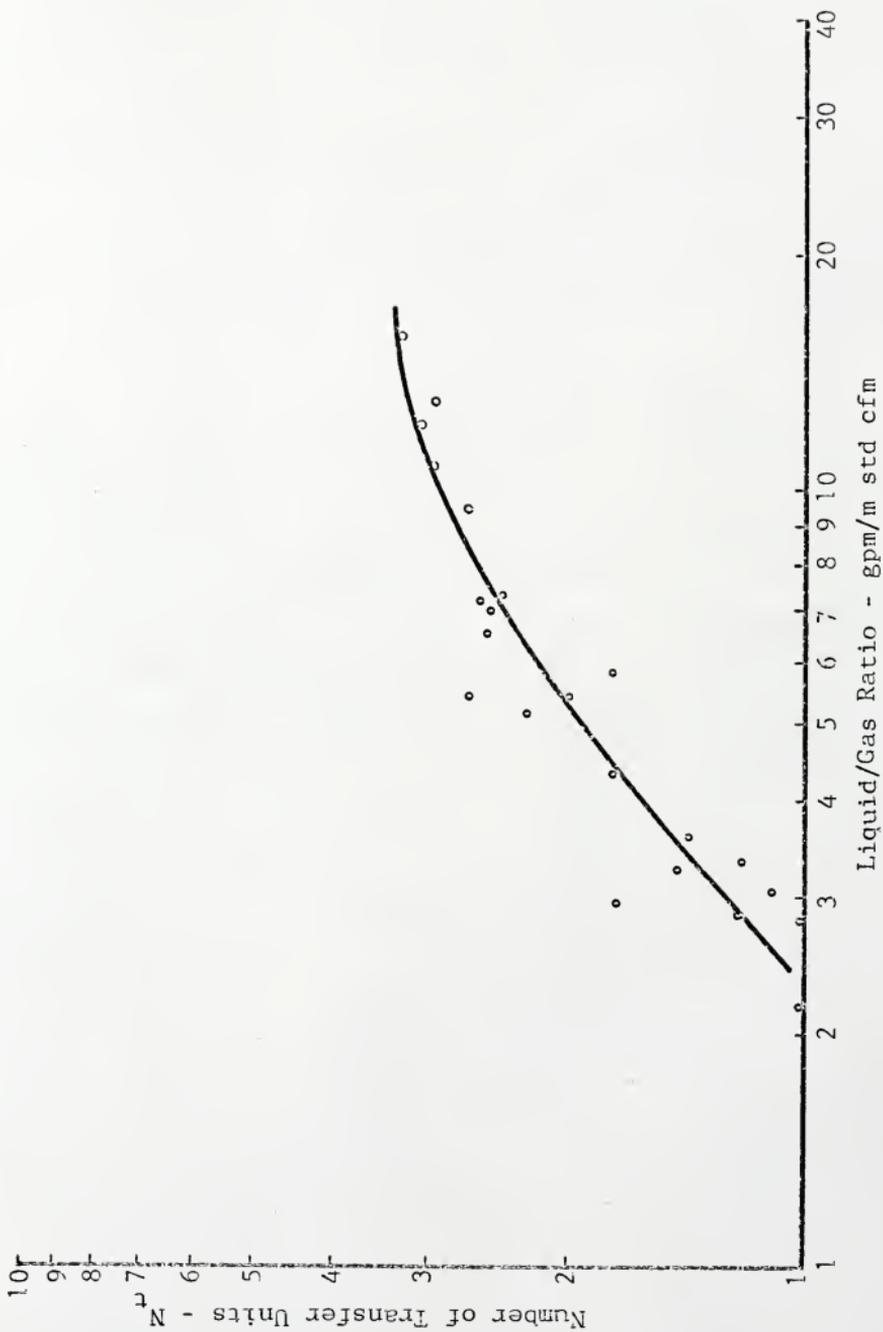


Figure 34: Effect of Liquid/Gas Ratio on Number of Transfer Units for Spray Chamber Using Well Water

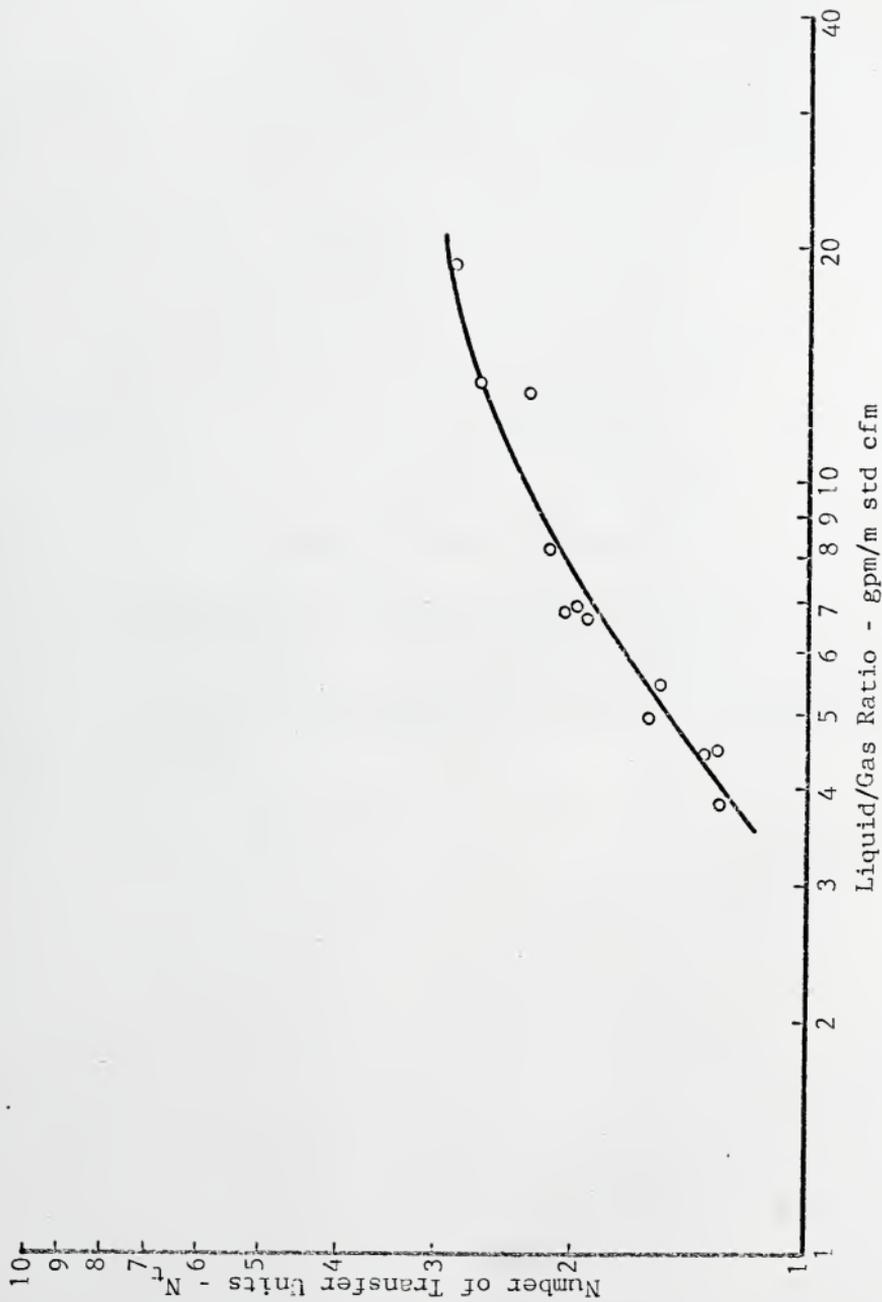


Figure 35: Effect of Liquid/Gas Ratio on Number of Transfer Units for Spray Chamber Using Gypsum Pond Water.

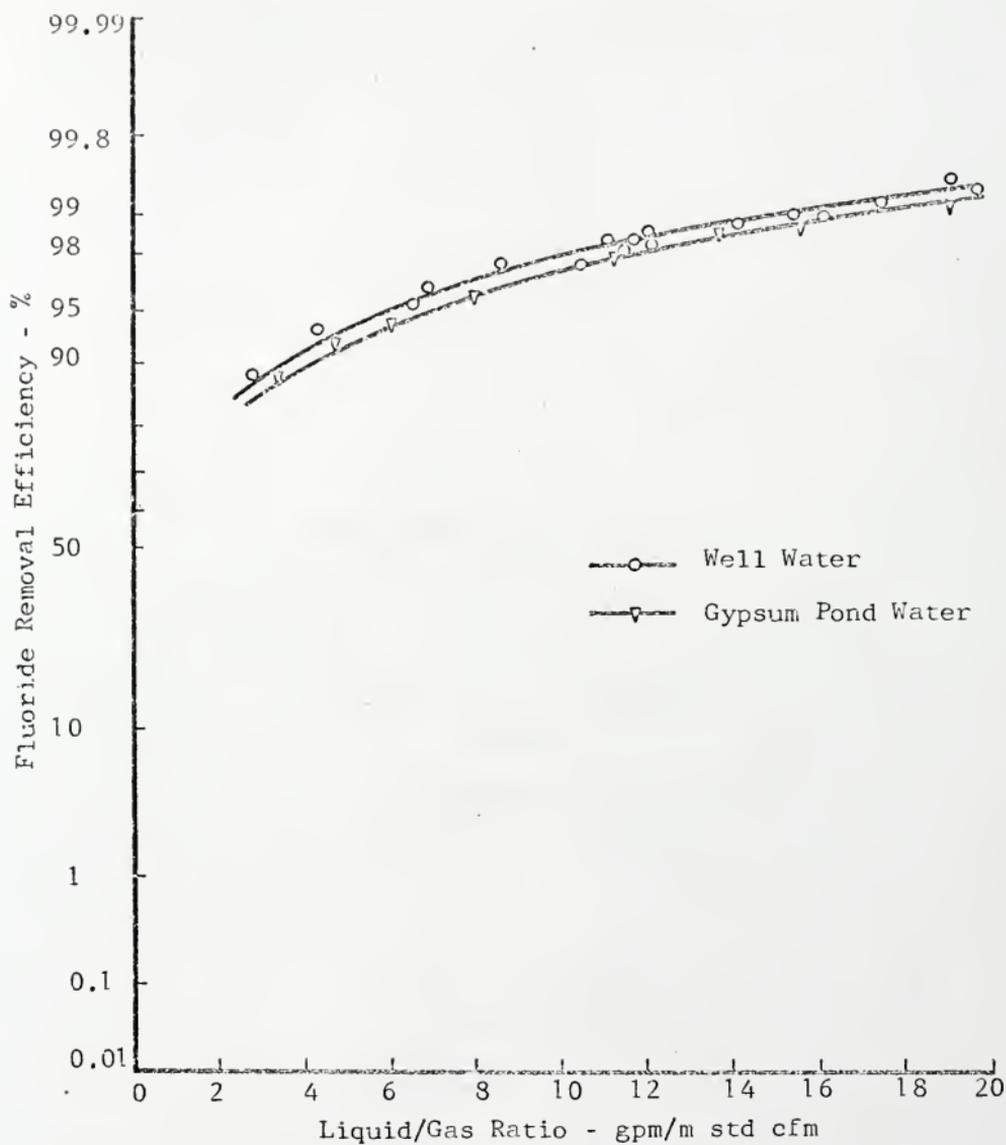


Figure 36: Effect of Liquid/Gas Ratio on Fluoride Removal Efficiency in Venturi

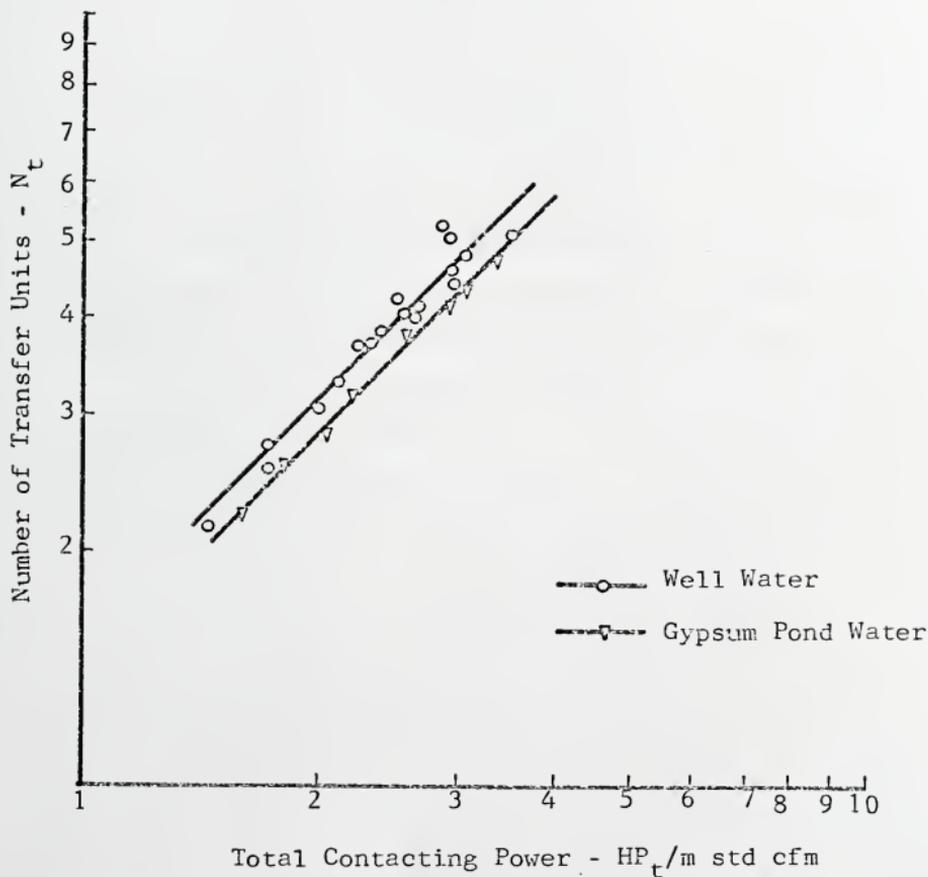


Figure 37: Effect of Total Contacting Power on Number of Transfer Units in Venturi

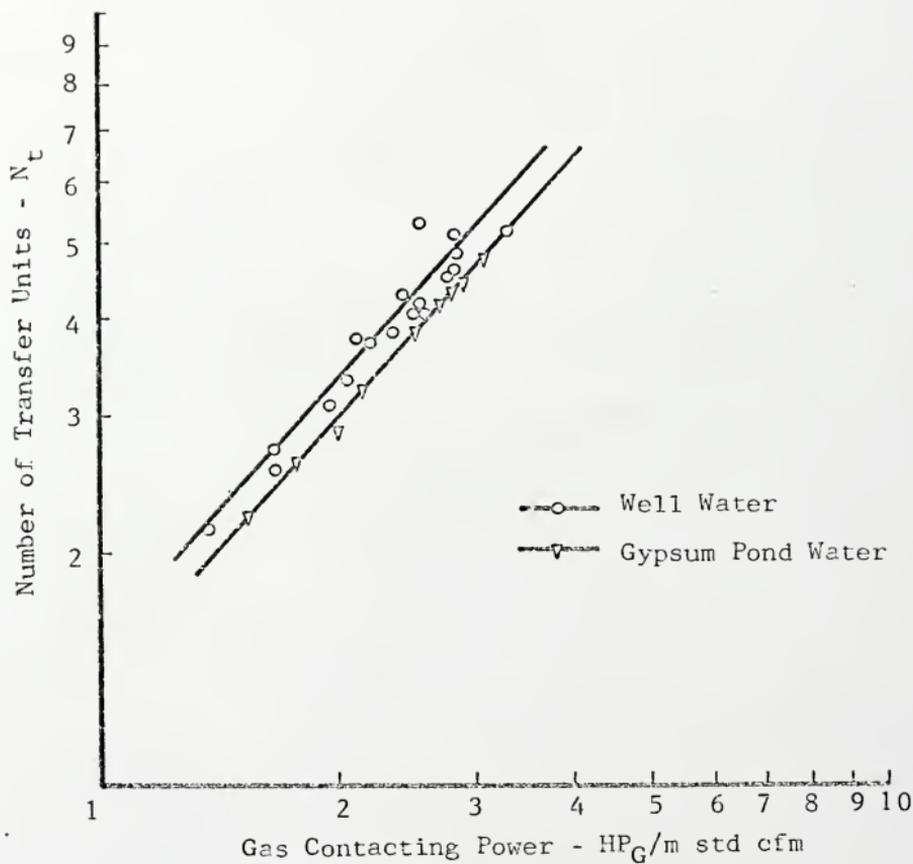


Figure 38: Effect of Gas Contacting Power on Number of Transfer Units in Venturi

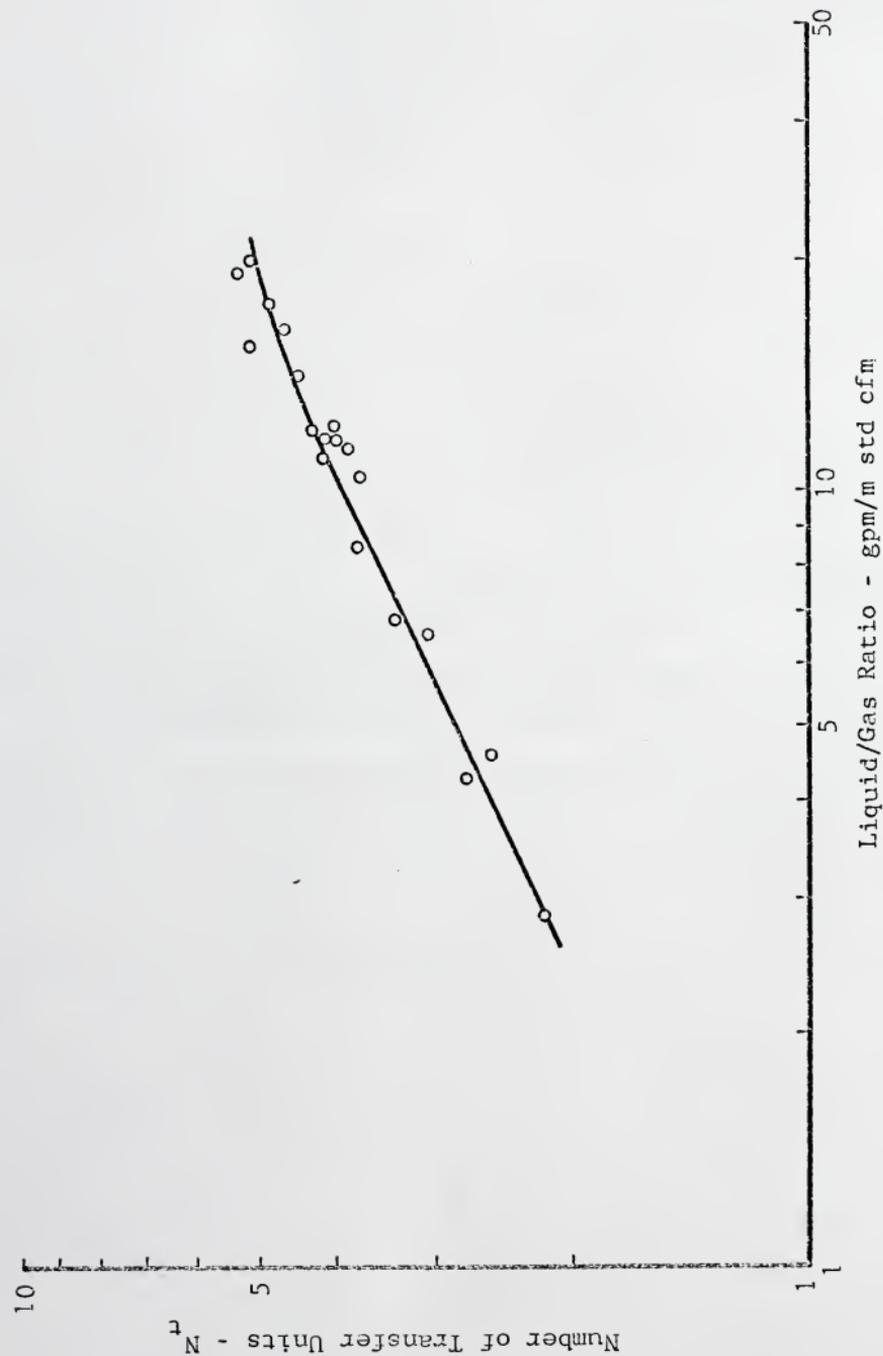


Figure 39: Effect of Liquid/Gas Ratio on Number of Transfer Units for Venturi Using Well Water

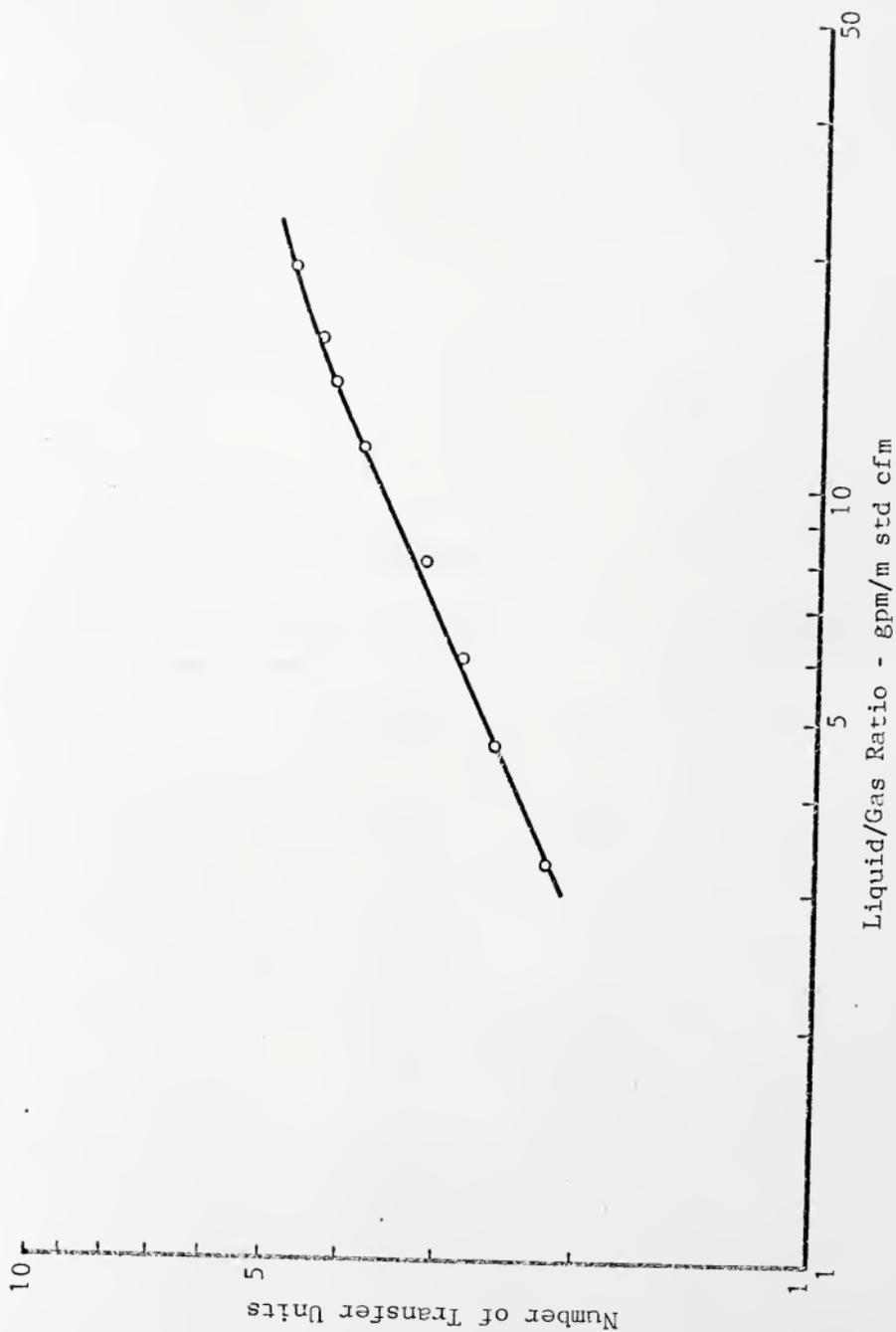


Figure 40: Effect of Liquid/Gas Ratio on Number of Transfer Units for Venturi Using Gypsum Pond Water

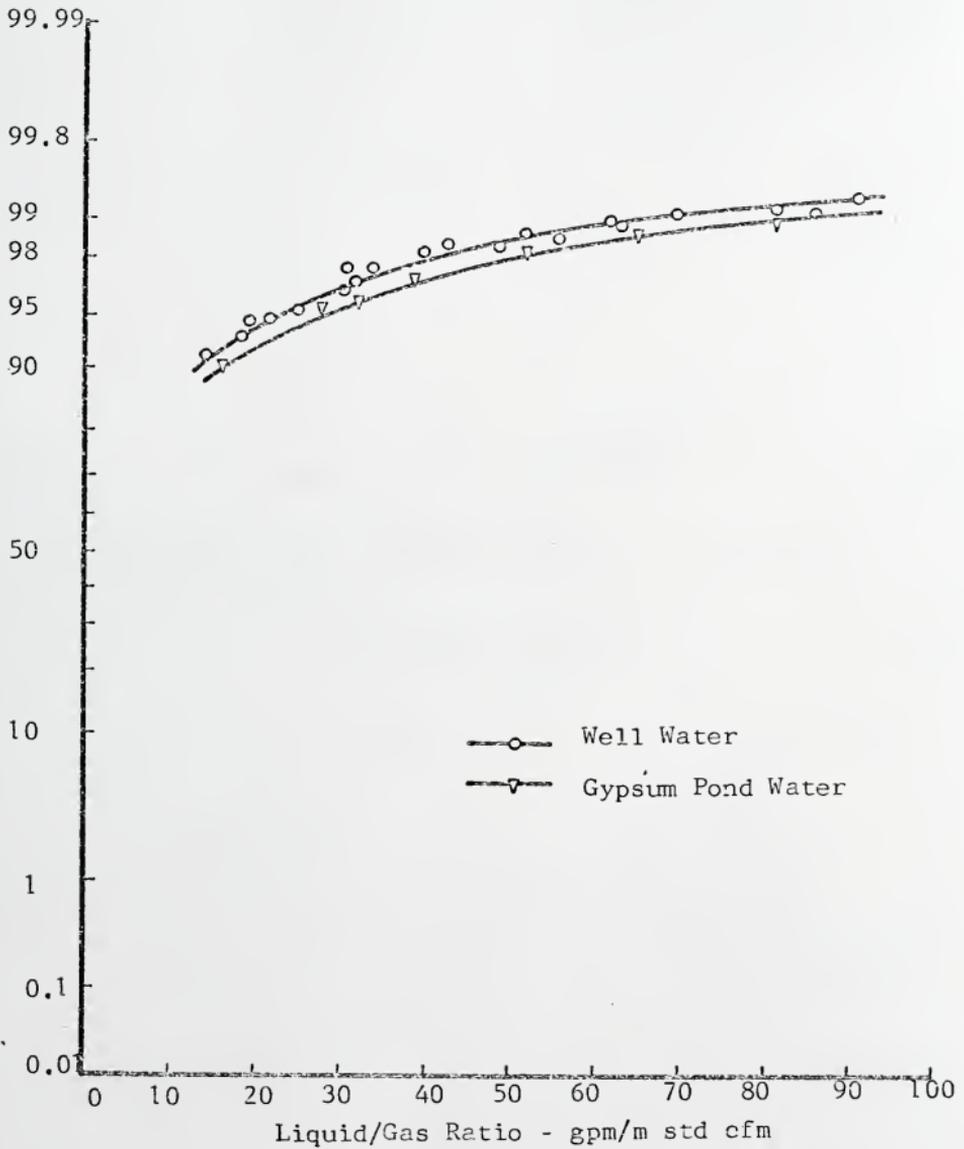


Figure 41: Effect of Liquid/Gas Ratio on Fluoride Removal Efficiency in Baffle Plate Impingement Column.

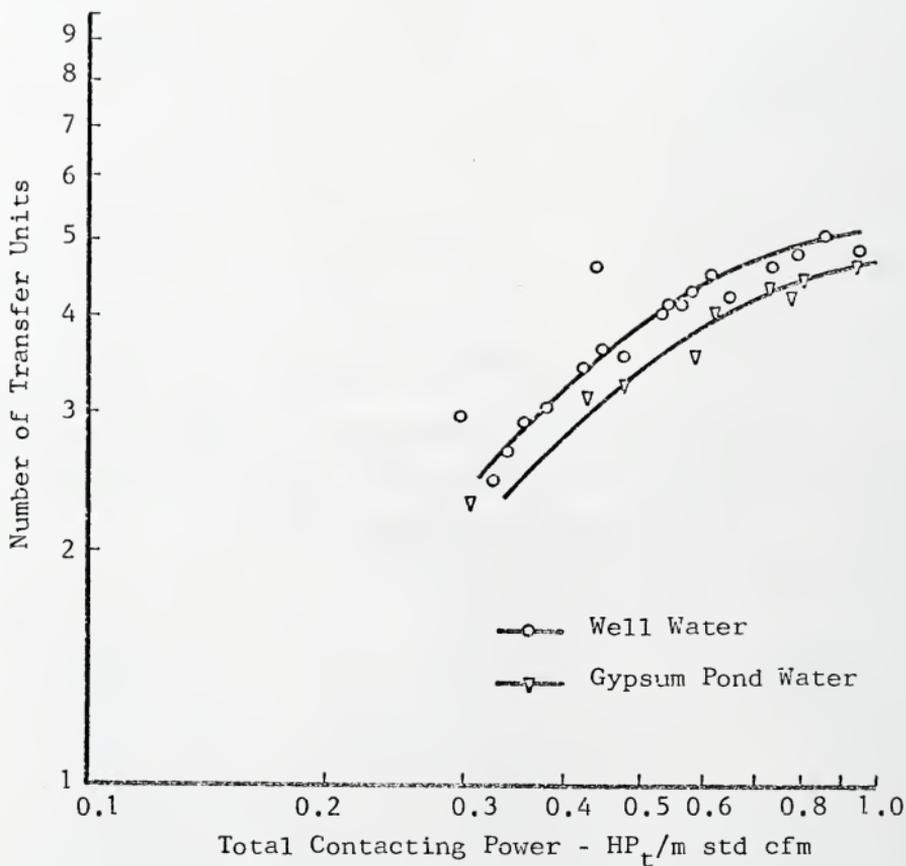


Figure 42: Effect of Total Contacting Power on Number of Transfer Units in Baffle Plate Impingement Column.

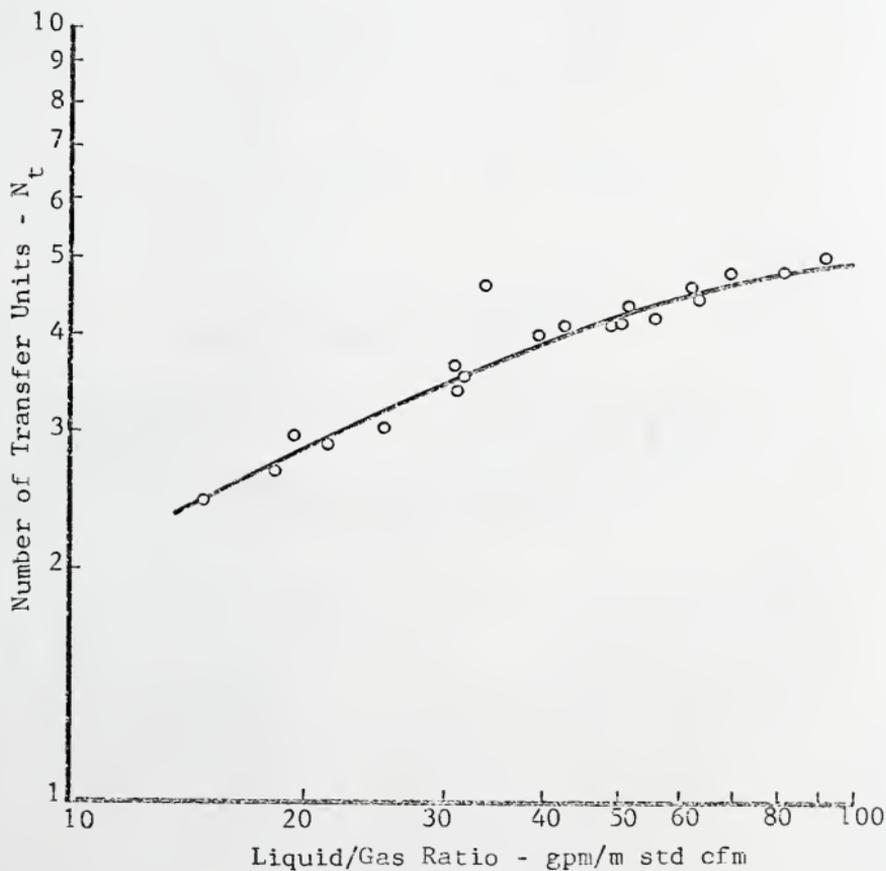


Figure 43: Effect of Liquid/Gas Ratio on Number of Transfer Units for Baffle Plate Impingement Column Using Well Water.

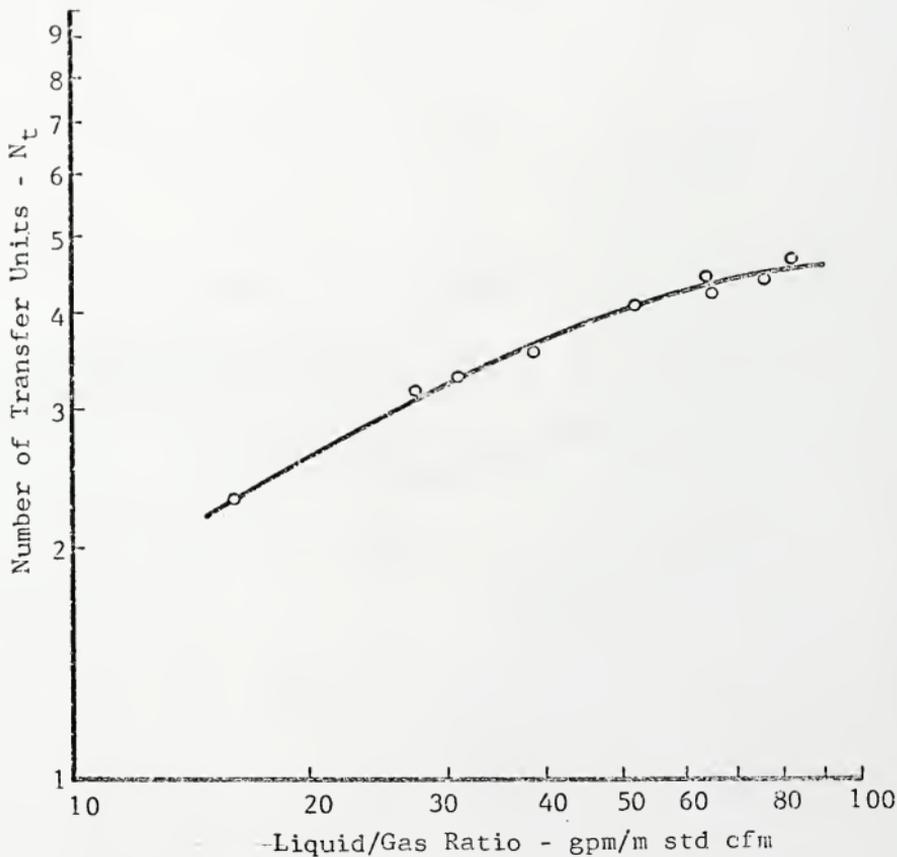


Figure 44: Effect of Liquid/Gas Ratio on Number of Transfer Units for Baffle Plate Impingement Column Using Gypsum Pond Water.

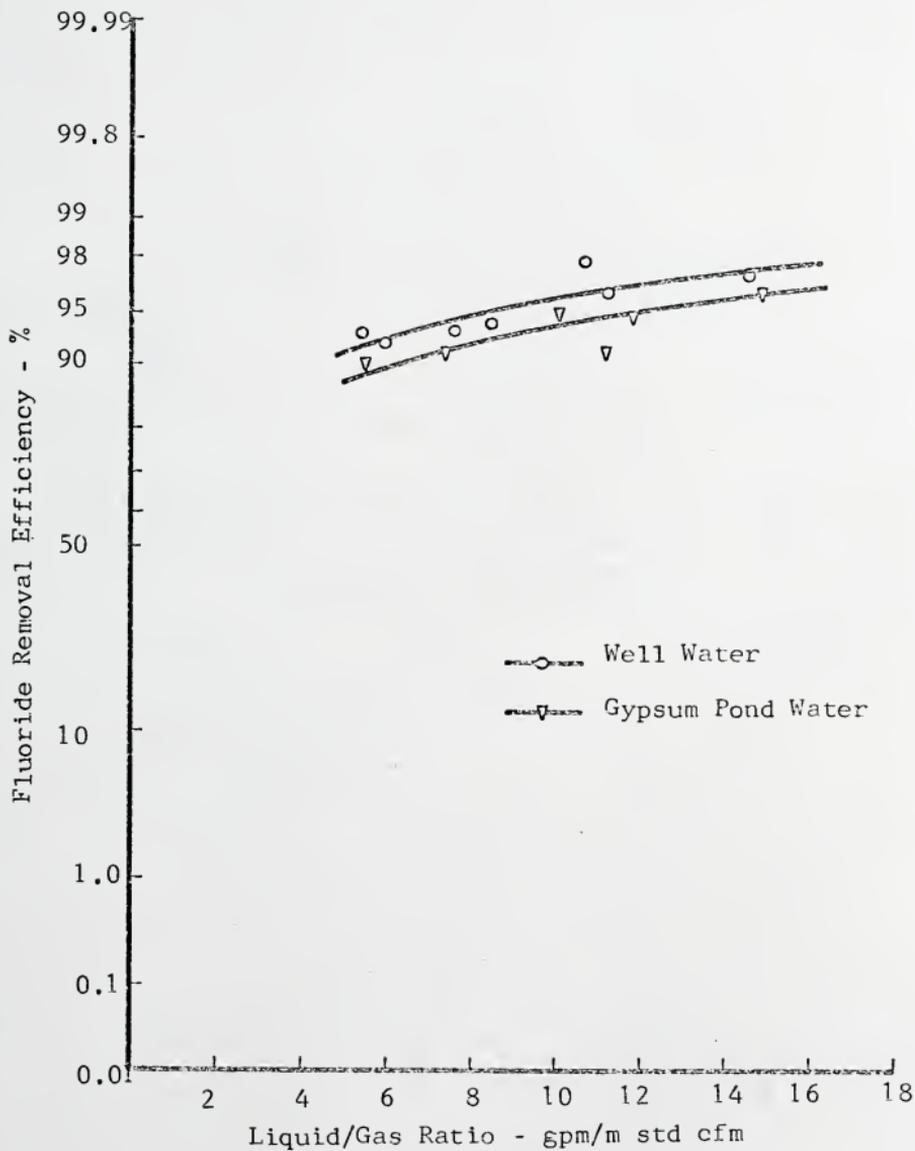


Figure 45: Effect of Liquid/Gas Ratio on Fluoride Removal Efficiency in Variable Throat Venturi.

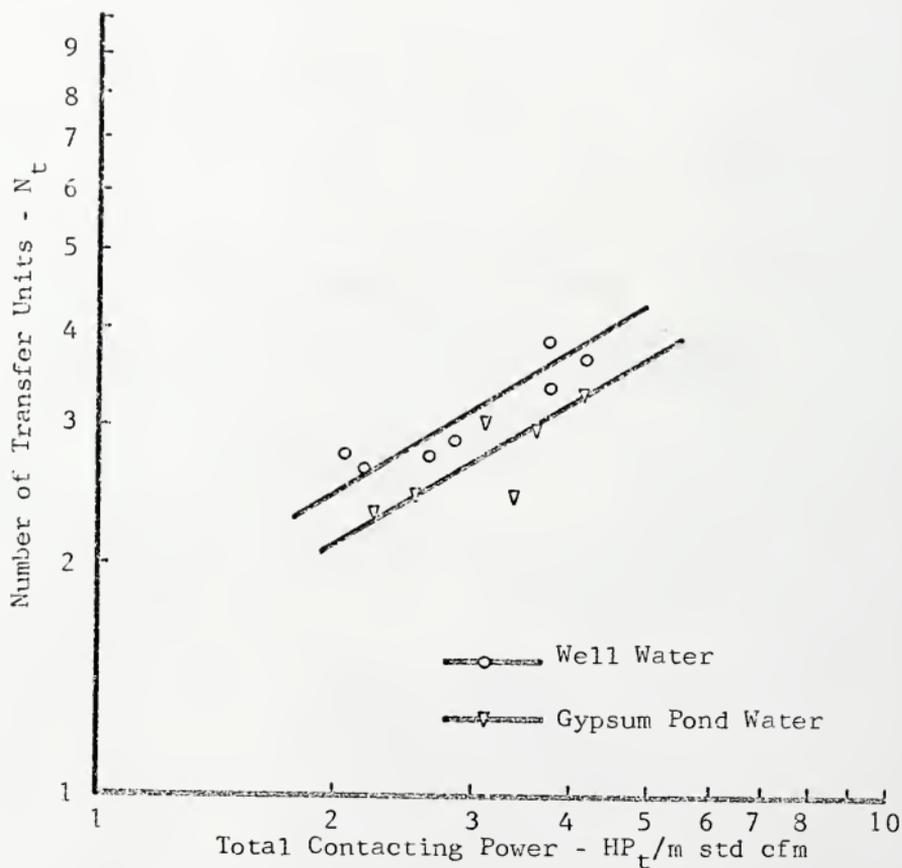


Figure 46: Effect of Total Contacting Power on Number of Transfer Units in Variable Throat Venturi.

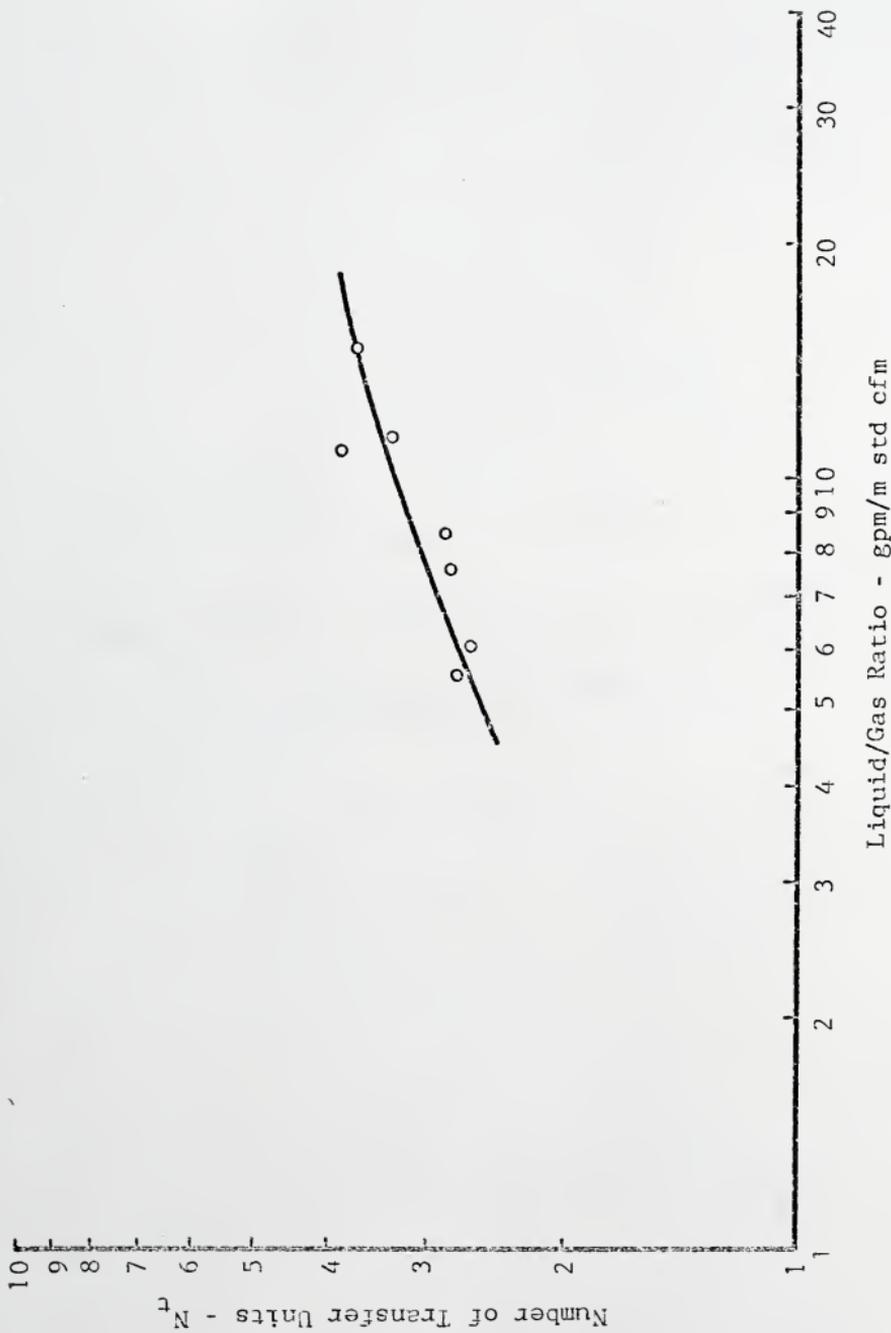


Figure 47: Effect of Liquid/Gas Ratio on Number of Transfer Units for Variable Throat Venturi Using Well Water.

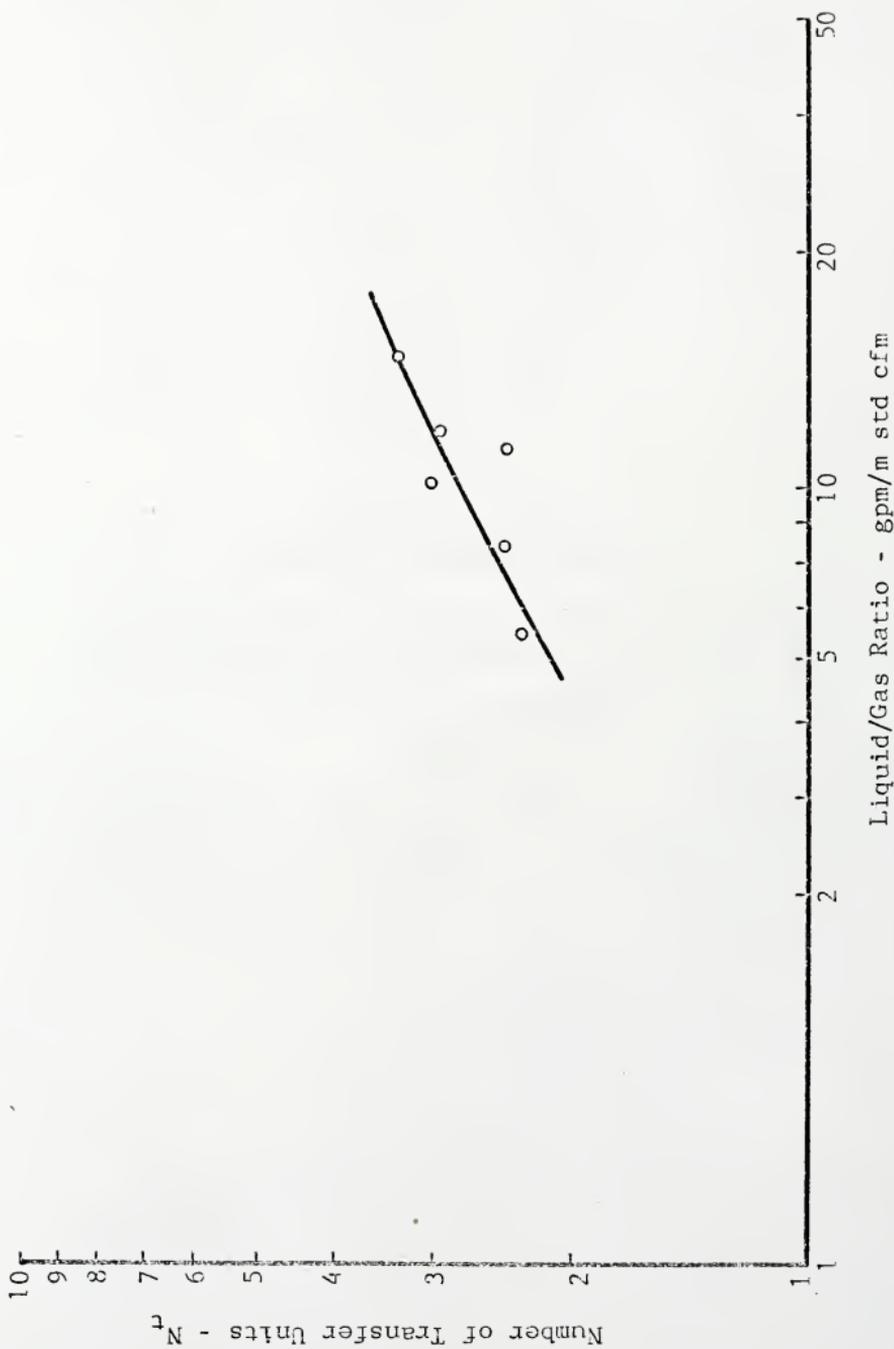


Figure 48: Effect of Liquid/Gas Ratio on Number of Transfer Units for Variable Throat Venturi Using Gypsum Pond Water.

for general correlations. Most data found in the literature are normally plotted for conditions where all other variables are held constant; therefore, comparison of the experimental data with the literature can only be general, since slopes and absolute values would probably vary due to the different conditions.

### Cyclonic Spray Chamber

The experimental data for the spray chamber are given in Appendix I, Tables 10 and 11. Gaseous fluoride removal efficiencies of 63.2 to 96.1 percent were obtained for liquid/gas ratios of approximately 2.2 to 15.5 gpm/m std cfm using well water as the scrubbing liquid. For these same ratios and with well water, the total contacting power ranged from approximately 0.2 to 0.7 HP<sub>t</sub>/m std cfm. When gypsum pond water was used as the scrubbing liquid, removal efficiencies of 72.8 to 94.2 percent were obtained for liquid/gas ratios of approximately 3.8 to 18.3 gpm/m std cfm. For these ratios, the energy requirements were approximately 0.4 to 0.8 HP<sub>t</sub>/m std cfm.

Calvert<sup>118</sup> defined a "flooding" condition as that gas flow at which the amount of liquid carried over (entrained) by the gas becomes excessive. This "flooding" or entrained liquid may have caused the spread in the data that can be seen in Figures 32 to 35.

Galeano<sup>99</sup> reported on the difficulty, which was typical

with the spray chamber, of obtaining meaningful results from replications at the same conditions. At the higher liquid flow rates, the unit seemed to be considerably more predictable and more balanced in operation, while at the lower liquid flow rates, the scrubber operation appeared to be considerably more erratic. Since, in general, most spray chamber scrubbers operate in the 5 to 15 gpm/m<sup>3</sup> std cfm range, it appears that, in the upper part of this range, the unit becomes balanced and more predictable.

The performance of this scrubber with both well water and gypsum pond water was as could be expected. The removal efficiency with gypsum pond water was lower than that with well water at every liquid/gas ratio. This is to be expected since the gypsum pond water was recirculated plant process water which was already contaminated with fluorides. The normal fluoride loading in this liquid was between 8500 to 9500 ppm. This lowered the concentration gradient between the gas and the liquid, reducing the mass transfer slightly between gas and liquid. The water balance in the wet-process phosphoric acid plant is watched closely, and every effort is made to keep fresh water out of the gypsum pond in order to avoid dilution of the pond water. For this reason, and because of economic conditions, gypsum pond water is normally used in process plant scrubbing systems and the slight reduction in mass transfer is tolerated.

Figure 32 illustrates the effect of the liquid/gas ratio upon the removal efficiency in this unit. It can be seen that well water provides better mass transfer for this system.

Figure 33 illustrates the effect of total contacting power on the number of transfer units, which in reality is a measure of the efficiency of the unit. For a given number of transfer units (or a set removal efficiency) the total power required when scrubbing with well water would be less than that required when scrubbing with gypsum pond water. Correlations show that the number of transfer units are proportional to the total power introduced to approximately the 1.0 power.

Figures 34 and 35 illustrate the effect that the equipment studied was limited in the maximum number of transfer units available. At the higher liquid/gas ratios, the addition of more liquid produces less of an effect upon the number of transfer units than the addition of more liquid at lower liquid/gas ratios. Since this type of scrubber is limited in the maximum number of transfer units available most commercial installations in the phosphate industry have a two-stage removal system. Figure 21 illustrates the two-stage scrubbing system employed by Occidental to control their effluent gases off the acid reactor.

When well water, with an entering pH of 7.2 to 7.4, was used as the scrubbing liquid, the pH of the effluent liquid was normally 3.3 to 4.4. When gypsum pond water, with an entering pH of 2.0 to 2.5, was used as the scrubbing liquid, the pH of the effluent liquid was normally 0.5 to 0.8. The effluent liquid was returned to the gypsum pond for recirculation and reuse in the plant. Since the liquid flow rates were quite low no dilution problems were experienced in the pond. This was satisfactory for pilot plant purposes but would not be so for a large commercial installation which might require 250 gpm of scrubbing water.

The limitation on the maximum pressure available to the spray nozzles may have had some effect upon the efficiencies obtainable with this scrubber. The maximum pressure developed by the pump was approximately 40 psig. This is on the low side of stated requirements for this type of unit, which normally range from 40 to 100 psig. If a higher spray pressure could have been developed, better atomization at each spray nozzle would have occurred, thus promoting more surface area available for mass transfer. Due to the piping arrangement, it was not possible to run the spare pump in series with the active pump and it was not possible to achieve pressures greater than 35 psig at the spray nozzles.

Venturi - Cyclonic Scrubber

The data for experimentation in the venturi-cyclonic scrubber are given in Appendix I, Tables 12 and 13. Gaseous fluoride removal efficiencies of 88.3 to 99.5 percent were obtained for liquid/gas ratios of approximately 4.4 to 26.5 gpm/m std cfm when well water was used as the scrubbing liquid. For the same liquid/gas ratios and with well water, the total energy requirements were 1.45 to 2.86 HP<sub>t</sub>/m std cfm. When gypsum pond water was used, removal efficiencies of approximately 89.0 to 99.2 percent were obtained with liquid/gas ratios of approximately 3.2 to 19.0 gpm/m std cfm. The total energy requirements for these ratios when gypsum pond water was used as the scrubbing liquid were approximately 1.6 to 3.4 gpm/m std cfm.

"Flooding" in the effluent gas did not appear to be a problem. The spread in the data was low and reproducibility did not appear to be a problem. The cyclonic section of this scrubber served as a demisting section and it appeared to be quite satisfactory in operation.

Figure 36 illustrates the effect of the liquid/gas ratio on fluoride removal efficiency. It can be seen that well water provides a better medium for fluoride absorption than gypsum pond water, however, the difference between the two scrubbing solutions was not very great. The difference was due to the fluoride

loading in the gypsum pond reducing the concentration gradient, thereby lowering the driving force. The difference between the two liquids would not be great enough to change the water balance in the plant, and it would appear that well water and gypsum pond water could be used interchangeably without a serious effect on the the removal efficiency of the unit. The fluoride concentration in the gypsum pond water was in the same range as for studies with the cyclonic spray chamber, 8500 to 9500 ppm.

Figure 37 illustrates the effect of total contacting power on the number of transfer units. The results again appear to be quite satisfactory due to very little, if any, flooding in the effluent gas. Scrubbing with gypsum pond water required more contacting power than with well water for a given number of transfer units. Figure 38 illustrates the relationship between gas contacting power and number of transfer units. Since the gas pressure drop affects the number of transfer units in this type of scrubber, this relationship was to be expected. Gas phase power consumption controls mass transfer efficiency in venturi operations as illustrated in Figure 38. Correlations show that the number of transfer units is proportional to the total power introduced to approximately the 1.0 power, and is proportional to the power introduced in the gas phase to approximately the 1.1 power.

Figures 39 and 40 illustrate that the high liquid/gas ratios used in this study began to approach the maximum removal efficiency for this type of unit. The upper level of liquid/gas ratio achieved with this scrubber produced a higher number of transfer units (and, therefore, a greater removal efficiency) than that achieved with the spray chamber scrubber but with a higher energy requirement.

The pH change in both well water and gypsum pond water was approximately the same as those observed with the spray chamber scrubber. No limitations were encountered with available liquid pressure since the pump capacity was more than adequate for this unit. No operating problems were experienced and this unit seemed to function properly throughout the entire experimental period with the only exception occurring when the demisting section was installed. Plugging of the demisting section occurred, thereby increasing the pressure drop across the unit, and decreasing the gas flow rate.

#### Baffle Plate Impingement Column

The data for the experimental runs for the baffle plate impingement column are given in the Appendix I, Tables 14 and 15. Fluoride removal efficiencies of 91.5 to 99.4 percent were obtained for liquid/gas ratios of approximately 14.8 to 90.9 gpm/m std cfm, using well water as the scrubbing liquid. When gypsum

pond water was used, removal efficiencies of 91.5 to 99.4 percent were obtained with liquid/gas ratios of approximately 16.0 to 81.0. Energy requirements for these liquid/gas ratios for well water were approximately 0.33 to 0.86  $\text{HP}_t/\text{m}$  std cfm and for gypsum pond water 0.31 to 0.94  $\text{HP}_t/\text{m}$  std cfm. The liquid/gas ratio is not normally used to describe the performance of this type of scrubber, since it does not completely describe the operating conditions. This is due to the necessity for specific liquid depths on the plates. The depths require high liquid flow rates and consequently high liquid/gas ratios.

Figure 41 illustrates the effect of liquid/gas ratio on removal efficiency in this unit. As can be seen, the gypsum pond water produced a lower efficiency at a given liquid/gas ratio than well water at the same ratio. The reason for this was covered in the discussions of the results of the spray chamber and venturi-cyclonic scrubber. The spread in the data was quite low and the reproducibility was quite good. The reproducibility and low spread in the data were due in part to a satisfactory liquid entrainment removal system which eliminated "flooding."

Figure 42 illustrates the effect of total contacting power on the number of transfer units (and on the removal efficiency). For this unit, it appears that above a total contacting power of 0.5 to 0.6  $\text{HP}_t/\text{m}$  std

cfm, the effect on the number of transfer units becomes less and less; and contacting power added above this level would be inefficient.

Again, in order to obtain a given number of transfer units (or a desired efficiency) it would be necessary to introduce a greater contacting power when scrubbing with gypsum pond water than when scrubbing with well water. Economic considerations along with water balance considerations must be studied before deciding upon the type of liquid used in the scrubber.

Figures 43 and 44 illustrate the effect of liquid/gas ratio on the number of transfer units. Again, it can be seen that at the higher ratios, the maximum capacity of the unit was approached.

The pH of the effluent liquid was within the range of that encountered with the other types of scrubbers studied. No limitations on pressure were encountered since the pump capacity was more than adequate to meet the requirements of this unit. No operating problems were experienced during the experimental period which amounted to approximately 5 days.

#### Variable Throat Venturi

The experimental data for the variable throat are given in Appendix I, Tables 16 and 17. The throat was in the open position throughout the experimental runs. Gaseous fluoride removal efficiencies of 92.9

to 97.8 percent were obtained with liquid/gas ratios of approximately 6.0 to 10.6 gpm/m std cfm. When gypsum pond water was used in the scrubber the efficiencies obtained were 90.1 to 96.3 with liquid/gas ratios of approximately 5.5 to 14.7 gpm/m std cfm.

Energy requirements for the stated maximum and minimum conditions were approximately 2.2 to 3.8  $HP_t/m$  std cfm with well water, and approximately 2.2 to 4.2  $HP_t/m$  std cfm with gypsum pond water.

Figure 45 illustrates the effect of the liquid/gas ratio on the removal efficiency. The spread in the data can be attributed to "flooding" which was a serious problem in this scrubber. When this unit was operated at or near its rated capacity, excessive flooding occurred, rendering the experimental run invalid. For this reason, the variable throat venturi was operated at a reduced capacity throughout the experimental period. Even at reduced capacity, there was some liquid entrainment. If "flooding" had not been present, it can be assumed that the spread between the curve for well water and that for gypsum pond water would be considerably less, and probably approach that found with the venturi-cyclonic scrubber.

Figure 46 illustrates the effect of total contacting power upon the number of transfer units. The spread in the data can be attributed to "flooding" as was previously mentioned. Scrubbing with gypsum pond

water required a higher contacting power for a given level of number of transfer units than scrubbing with well water. The reason for this has been covered in the discussion of the results for the other equipment studied.

A correlation shows that the number of transfer units is proportional to the total power introduced to approximately the 0.61 power. The limited number of data points, and the spread in these points can indicate only a trend and should not be considered completely accurate. The small amount of data makes it nearly impossible to accurately correlate these data, therefore, the stated correlation is very general.

Figures 47 and 48 illustrate the effect of liquid/gas ratio on number of transfer units. Here again, the limited data, and the spread in these data only allow a general trend to be identified. It can be seen that the maximum number of transfer units in this unit would be less than 4.5.

The pH of the effluent liquid was within the range of that encountered with the other types of scrubbers studied. There was a limitation on the gas flow due to the "flooding" conditions that have been previously discussed. Even at reduced gas flow rates, the liquid flow rate could not exceed 10 gpm or "flooding" would occur.

## CHAPTER VII

### CONCLUSIONS AND RECOMMENDATIONS

Figure 49 summarizes the results of this study. It can be seen that the selection of a scrubber for use in effluent control of wet-process phosphoric acid reactor gases would depend upon the desired removal efficiency (or number of transfer units) and upon the energy requirements of the unit selected. Using governmentally set regulations and overall plant design capacity, the required efficiency could be determined. Figure 49 could then be used along with economic considerations, such as capital cost and operating expense, to determine which type of scrubber would be most satisfactory for installation. Since economic factors vary with time and with process requirements, it was decided not to include an economic analysis with this work.

The liquid/gas ratios employed in this research were typical of those to be expected in actual operating conditions. They were

- Cyclonic spray chamber - 2.2 to 18.3 gpm/m std cfm
- Venturi-Cyclonic scrubber - 3.2 to 26.5 gpm/m std cfm
- Baffle plate impingement column - 14.8 to 90.9 gpm/m std cfm
- Variable throat venturi - 6.0 to 10.6 gpm/m std cfm

Typical commercial installations on this type of process

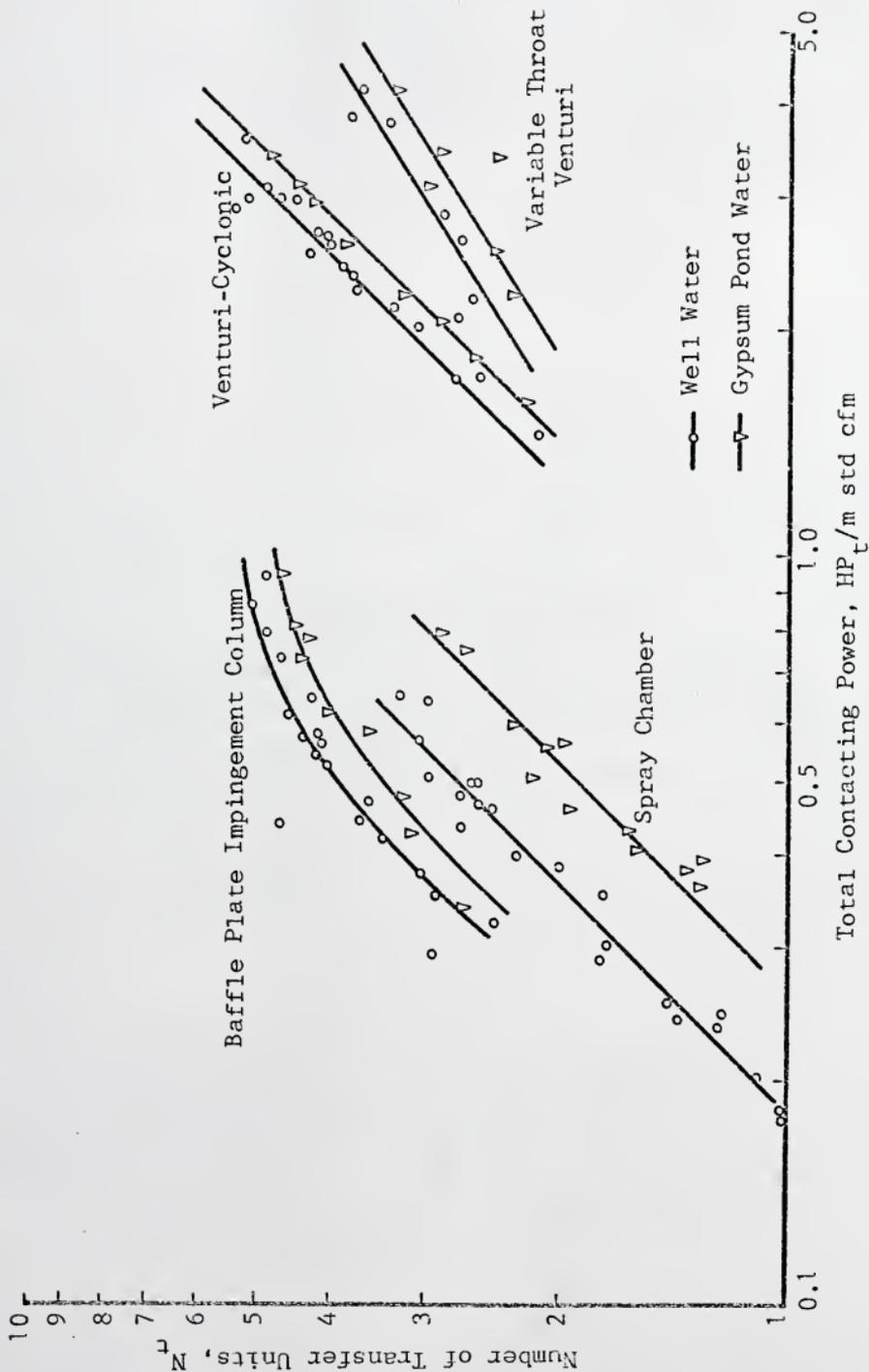


Figure 49: Comparison of the Effect of Total Contacting Power on Number of Transfer Units in Equipment Studied.

are

Occidental Chemical Company (two-stage cyclonic spray chamber with a 23,000 cfm capacity)

Wetting Section - 2.2 gpm/m acfm

1st Stage - 10.9 gpm/m acfm

2nd Stage - 7.6 gpm/m acfm

Agrico Chemical Company

Two-stage cyclonic spray chamber (55,000 cfm capacity) - 5 to 8 gpm/m acfm/stage

Teller, horizontal packed chamber (80,000 cfm) - 10 gpm/m acfm.

None of the units studied provided a sufficient number of transfer units to be acceptable for use in a commercial installation on a wet-process phosphoric acid plant. It would appear that two-stage installations are necessary in order to meet the required removal efficiencies of greater than 99.75 percent.

The following conclusions and recommendations can be drawn from this experimentation:

1. The sampling train and method of analysis were entirely satisfactory and should be used in any future fluoride analyses. The silica gel was a problem but if specific care is taken an accurate sample can be obtained.
2. A mesh type demister would not be satisfactory in this type of installation. The silica

build-up on the mesh surfaces rapidly increased the pressure drop across the demister. This could not be tolerated in a commercial installation because the energy requirements would increase and the capacity of the scrubbing unit would decrease.

3. Generally, the slopes calculated and consequent correlations for these scrubber configurations agree with those found by Lunde<sup>92</sup> in his studies. It appears that the maximum number of transfer units obtainable with the spray chamber scrubber is less than 3.5, with the venturi-cyclonic scrubber less than 5.5, with the baffle plate impingement column less than 5.5, and with the variable throat venturi less than 4.5. None of the scrubbers alone would produce the 6 transfer units which are commonly recommended for this type of operation. A two-stage installation would be required in order to attain the desired number of transfer units (or required removal efficiency).
4. The data for the four scrubbing systems studied show the important relationship of removal efficiency to the liquid/gas ratio, and the fact that the efficiency

obtainable in each type of scrubber decreases when gypsum pond water is used in place of well water.

5. It would appear that well water and gypsum pond water could be used interchangeably for scrubbing purposes in this equipment. However, since the water balance in the wet-process phosphoric acid plant must be maintained, gypsum pond water would appear to be the most satisfactory scrubbing liquid. It would not reduce the efficiency enough to affect the performance of a two-stage scrubbing operation and would maintain the water balance in the plant.
6. The venturi-cyclonic scrubber proved to be the most satisfactory as far as operating performance was concerned. It would be the recommended unit if the higher energy requirements could be tolerated in the process economic considerations.
7. While the baffle plate impingement column performed well in these experiments, there is an unresolved question with respect to the accumulation of silica gel. Mass transfer in this equipment is developed by small interstices which could become plugged by the silica formation, reducing the efficiency

of the unit and adding operating expense.

8. A chemical reaction took place in the scrubbing system with silica gel as the by-product of the reaction. This by-product caused considerable difficulty throughout the experimental period, but is a common occurrence in the phosphate fertilizer industry. Additional work should be undertaken to study this problem and determine some means of bringing it under control. Until this is accomplished, it will be necessary to shut commercial scrubbing installations down periodically, in order to remove the silica gel build-up.
9. The portable scrubbing pilot plant concept proved to be a highly valuable tool for actual field measurement and control of a process effluent gas. When utilized on other processes, it should provide additional information that can be used in the design of effluent control systems for these processes.

## APPENDICES

APPENDIX I  
RESULTS OF EXPERIMENTATION

TABLE 10  
 SPRAY CHAMBER EXPERIMENTAL DATA  
 SCRUBBING LIQUID - WELL WATER

Run No	Plant Production Tons/Day H <sub>3</sub> PO <sub>4</sub>	Liquid			Gas			
		Flow Rate GPM	Pressure Psig	Temperature of In Out	Flow Rate ACFM	Pressure Drop Across Unit in H <sub>2</sub> O	Temperature of In Out	
1	650	3.8	14	84	2060	0.6	157	140
2	650	5.0	18	83	2060	0.8	161	152
3	650	5.2	18	81	2060	1.0	160	147
4	500	9.4	22	82	1890	1.1	160	141
5	500	11.8	28	82	1975	1.4	158	132
6	500	11.4	28	84	1830	1.4	163	139
7	500	8.4	22	84	1725	1.3	162	141
8	500	11.3	30	84	1840	1.5	155	137
9	500	6.7	20	85	1810	1.0	156	143
10	400	9.2	22	79	1975	1.2	157	141
11	400	6.0	16	78	1955	0.8	155	142
12	400	21.2	32	79	1960	1.5	156	125
13	400	11.0	35	80	1950	1.3	154	131
17	650	9.1	21	80	1950	1.4	154	135
18	650	5.5	15	81	1910	0.8	150	140
19a	650	4.6	16	81	1900	0.6	150	140
19b	650	5.0	15	82	1890	0.7	159	147
20	585	19.6	30	79	1920	1.4	158	129
21	585	17.3	30	79	1905	1.3	160	133
22	585	5.1	18	80	1845	0.9	162	151
24	585	21.4	32	85	1910	1.4	160	128
26	585	13.9	28	82	1875	1.3	157	130

TABLE 10 CONTINUED

Run No	Mean Fluoride Concentration MG/SID CU FT		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio		Number of Transfer Units	Contacting Power HP/M STD CFM	
	In	Out		GPM/M STD CFM	STD CFM		Gas	Liquid
1	65.4	24.1	63.2	2.15	1.00	0.17	0.02	0.19
2	59.5	17.6	70.5	2.86	1.22	0.22	0.03	0.25
3	87.6	15.6	82.2	2.96	1.73	0.28	0.03	0.31
4	67.9	11.8	82.6	5.84	1.75	0.28	0.8	0.36
5	59.5	4.7	92.1	7.00	2.54	0.39	0.12	0.51
6	80.1	7.1	91.2	7.36	2.43	0.34	0.12	0.46
7	85.7	9.0	89.6	5.15	2.26	0.33	0.07	0.40
8	72.3	5.6	92.3	7.16	2.56	0.37	0.13	0.50
9	69.4	12.0	82.7	4.32	1.75	0.24	0.05	0.29
11	85.4	11.7	86.4	5.45	2.00	0.32	0.07	0.39
12	94.8	23.3	75.4	3.58	1.40	0.21	0.03	0.24
13	85.6	4.4	94.8	12.64	2.96	0.40	0.24	0.64
17	82.5	6.5	92.1	6.55	2.54	0.34	0.13	0.47
18	81.4	5.6	93.2	5.44	2.69	0.37	0.07	0.44
19a	72.5	21.5	70.3	3.33	1.22	0.21	0.03	0.24
19b	83.7	30.3	63.7	2.80	1.01	0.15	0.03	0.18
20	75.4	37.0	65.5	3.05	1.10	0.18	0.03	0.21
21	51.4	2.4	95.3	11.96	3.06	0.36	0.21	0.57
22	65.5	3.4	94.8	10.65	2.96	0.32	0.19	0.51
24	113.6	26.7	76.5	3.26	1.45	0.22	0.03	0.25
26	110.3	4.2	96.1	15.46	3.25	0.36	0.29	0.65
27	107.6	7.5	93.1	9.35	2.68	0.33	0.15	0.48

TABLE 11  
 SPRAY CHAMBER EXPERIMENTAL DATA  
 SCRUBBING LIQUID - GYPSUM POND WATER

Run No	Plant Production Tons/Day $H_3PO_4$	Liquid			Gas			
		Flow Rate GPM	Pressure PSIG	Temperature of In Out	Flow Rate ACFM	Pressure Drop Across Unit in $H_2O$	Temperature of In Out	
10	400	7.7	18	80	141	1.2	156	142
14	400	11.3	35	77	143	1.6	158	140
16	400	9.2	20	80	132	1.3	151	133
23	585	13.1	26	80	138	1.5	160	138
25	585	18.5	28	80	130	1.7	160	130
28	585	11.3	40	72	140	1.5	155	136
29	585	7.2	20	78	146	1.3	163	148
30	585	6.2	18	80	150	1.4	166	154
31	585	10.8	20	79	147	1.5	167	147
32	585	8.0	18	80	146	1.5	167	151
34	585	29.7	40	83	127	1.4	167	132
35	585	21.8	36	84	131	1.8	168	134

TABLE 11 CONTINUED

Run No	Mean Fluoride Concentration		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio		Number of Transfer Units	Contacting Power	
	MG/STD In	CU FT Out		GPM/STD	CFM		HP/M Gas	STD Liquid Total
10	84.5	22.7	73.2	4.54	1.32	0.32	0.05	0.37
14	78.2	10.7	86.3	6.84	1.99	0.42	0.14	0.56
16	93.0	19.4	79.2	5.44	1.57	0.35	0.06	0.41
23	83.5	9.7	88.4	8.13	2.16	0.38	0.13	0.51
25	88.5	8.9	90.0	12.93	2.30	0.38	0.21	0.59
28	79.4	10.1	87.3	6.68	2.06	0.40	0.16	0.56
29	81.6	21.0	74.3	4.41	1.36	0.34	0.05	0.39
30	92.4	25.1	72.8	3.82	1.30	0.36	0.04	0.40
31	90.6	13.1	85.6	6.65	1.94	0.38	0.08	0.46
32	87.3	17.4	80.1	4.94	1.61	0.38	0.05	0.43
34	78.5	4.6	94.2	18.28	2.85	0.36	0.43	0.79
35	79.9	5.7	92.9	13.37	2.65	0.46	0.28	0.74

TABLE 12  
 VENTURI EXPERIMENTAL DATA  
 SCRUBBING LIQUID - WELL WATER

Run No	Plant Production Tons/Day $H_3PO_4$	Liquid			Gas				
		Flow Rate GPM	Pressure PSIG	Temperature Of In Out	Flow Rate ACFM	Pressure Drop Unit in $H_2O$	Temperature Of In Out		
1	525	16.3	15	84	121	1720	11.0	155	125
2	525	17.8	14	84	119	1750	10.3	157	119
3	400	27.0	20	76	95	1600	14.8	154	122
4	400	16.8	10	77	99	1700	11.3	158	135
5	400	20.2	11	76	97	1690	12.6	158	132
6	400	22.2	13	78	113	1660	12.7	160	123
7	400	17.4	9	78	119	1710	11.0	162	127
8	400	9.6	9	77	133	1750	8.4	161	141
9	750	7.0	8	77	148	1800	7.1	161	151
10	750	4.4	5	80	139	1830	5.6	161	153
11	400	26.5	28	78	114	1640	14.0	160	121
12	400	24.0	23	82	117	1620	13.0	156	125
13	750	21.5	12	75	119	1640	12.8	155	126
14	750	16.9	9	80	127	1700	11.1	156	130
15	750	12.6	15	80	133	1740	9.6	156	138
16	845	10.2	10	80	137	1750	8.8	157	141
17	845	16.6	5	82	133	1710	10.3	160	137
18	845	15.0	4	82	136	1700	9.8	161	140
19	585	6.5	18	84	139	1780	7.0	157	144

TABLE 12 CONTINUED

Run No	Mean Fluoride Concentration		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio GPM/N STD CFM	Number of Transfer Units	Contacting Power		
	MG/STD CU FT In	MG/STD CU FT Out				HP/M STD CFM Gas	HP/M STD CFM Liquid Total	
1	64.3	1.03	98.4	11.03	4.14	2.55	0.10	2.65
2	55.2	0.77	98.6	11.90	4.27	2.42	0.10	2.52
3	60.8	0.37	99.4	19.60	5.12	3.31	0.22	3.53
4	55.7	1.01	98.2	11.58	4.02	2.58	0.07	3.65
5	58.4	0.70	98.8	13.98	4.42	2.87	0.09	2.96
6	47.9	0.48	99.0	16.00	4.61	2.83	0.12	2.95
7	52.5	0.95	98.2	12.00	4.02	2.51	0.06	2.57
8	51.0	2.35	95.4	6.46	3.08	1.96	0.04	2.00
11	45.6	3.56	92.2	4.57	2.55	1.70	0.02	1.72
12	57.4	6.72	88.3	2.82	2.15	1.37	0.08	1.45
14	65.1	0.40	99.5	18.96	5.30	2.55	0.31	2.86
15	63.6	0.64	99.2	17.30	4.83	2.83	0.24	3.07
16	58.0	0.58	98.9	15.27	5.11	2.83	0.11	2.94
17	54.6	0.97	98.3	11.61	4.08	2.54	0.06	2.60
18	48.2	1.23	97.6	8.46	3.73	2.24	0.08	2.32
19	48.0	4.75	96.4	6.82	3.32	2.07	0.04	2.11
20	55.6	1.09	97.9	11.40	3.86	2.36	0.03	2.39
21	52.5	1.30	97.6	10.38	3.73	2.22	0.03	2.25
23	50.6	3.29	93.5	4.26	2.74	1.67	0.05	1.72

TABLE 13  
 VENTURI EXPERIMENTAL DATA  
 SCRUBBING LIQUID - GYPSUM POND WATER

Run No	Plant Production Tons/Day $H_3PO_4$	Liquid		Temperature of		Flow Rate		Pressure		Temperature of	
		Flow Rate GPM	Pressure PSIG	In	Out	Rate ACFM	Drop Unit in $H_2O$	Across Unit in $H_2O$	In	Out	
13	820	19.4	25	78	139	1690	12.0		161	141	
24	520	16.3	8	83	133	1710	11.0		158	137	
25	520	11.8	6	88	139	1750	9.3		161	144	
26	585	7.1	6	89	148	1810	7.4		161	149	
27	585	5.0	6	90	148	1830	6.5		164	154	
28	585	9.0	8	91	135	1760	8.5		155	140	
29	585	26.5	28	78	100	1645	14.0		162	124	
30	585	21.5	27	79	120	1640	12.8		160	127	

TABLE 13 CONTINUED

Run No	Mean Fluoride Concentration MG/STD CU FT		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio GPM/M STD CFM		Number of Transfer Units	Contacting Power HP/M STD CFM		
	In	Out		GPM/M STD CFM	Ratio		Gas	Liquid	Total
13	85.7	1.35	98.5	13.51		4.20	2.72	0.20	2.92
24	75.2	1.58	97.9	11.17		3.86	2.52	0.05	2.57
25	97.8	4.06	95.9	7.94		3.20	2.17	0.03	2.20
26	101.1	7.00	92.5	4.62		2.59	1.79	0.2	1.81
27	99.2	10.82	89.0	3.23		2.21	1.58	0.01	1.59
28	80.2	7.92	94.2	5.96		2.85	2.02	0.03	2.05
29	87.6	0.70	99.2	19.00		4.75	3.07	0.31	3.38
30	93.5	1.12	98.8	15.40		4.38	2.80	0.24	3.04

TABLE 14  
 BAFFLE PLATE IMPINGEMENT COLUMN  
 SCRUBBING LIQUID - WELL WATER

Run No	Plant Production Tons/Day H <sub>3</sub> PO <sub>4</sub>	Liquid			Gas		
		Flow Rate GPM	Pressure PSIG	Temperature OF In Out	Flow Rate ACFM	Pressure Drop Across Unit in H <sub>2</sub> O	Temperature OF In Out
3	525	13.5	8	74 132	326	7.8	161 89
4	525	9.3	6	76 134	326	7.5	162 93
5	525	6.5	6	78 134	306	7.2	162 101
6	525	22.9	10	78 129	297	8.2	163 88
8	525	11.9	10	80 130	284	7.6	166 93
9	525	4.6	5	80 131	284	6.5	166 107
10	525	8.8	5	76 148	337	8.0	165 100
11	715	5.2	5	76 150	337	6.4	166 112
12	715	4.2	5	78 152	337	6.3	168 128
13	715	14.6	7	78 150	337	8.3	170 96
14	715	8.6	5	77 152	336	7.6	177 104
15	550	19.1	9	67 143	375	8.4	176 80
17	550	20.2	10	72 146	352	8.4	176 85
18	550	18.5	6	69 143	358	8.4	176 81
19	450	25.4	11	58 137	375	8.4	170 75
20	450	11.8	7	75 120	346	7.9	149 94
21	450	5.6	4	74 147	310	7.4	165 98
22	450	9.0	7	79 153	338	7.8	166 103
23	450	12.4	7	80 126	345	8.0	164 92
24	450	16.5	8	81 136	350	8.1	165 89

TABLE 14 CONTINUED

Run No	Mean Fluoride Concentration		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio		Number of Transfer Units	Contacting Power	
	MG/STD In	CU FT Out		GPM/STD	CFM		HP/M STD	Gas Liquid Total
3	150.8	2.49	98.4	48.7	4.12	0.34	0.23	0.57
4	189.2	3.88	97.5	33.7	4.69	0.33	0.11	0.44
5	173.4	8.34	95.2	25.0	3.04	0.29	0.09	0.38
6	156.5	3.69	99.4	90.9	5.04	0.33	0.53	0.86
8	134.5	2.16	98.4	49.8	5.14	0.29	0.29	0.58
9	119.5	6.07	94.9	19.3	2.98	0.24	0.06	0.30
10	147.3	3.69	97.5	30.9	3.69	0.36	0.09	0.45
11	159.0	10.97	93.1	18.3	2.68	0.29	0.05	0.34
12	161.7	13.73	91.5	14.8	2.47	0.29	0.04	0.33
13	136.5	1.78	98.7	51.7	4.34	0.37	0.21	0.58
14	147.2	4.86	96.7	30.9	3.41	0.33	0.09	0.42
15	125.4	1.25	99.0	61.4	4.61	0.41	0.32	0.73
17	137.3	1.1	99.2	69.2	4.83	0.39	0.40	0.79
18	152.5	1.68	98.9	62.4	4.51	0.39	0.22	0.61
19	141.1	0.99	99.3	80.9	4.89	0.42	0.52	0.94
20	139.6	2.61	98.2	39.4	4.02	0.37	0.16	0.53
21	172.8	9.18	94.7	21.4	2.94	0.30	0.05	0.35
22	165.3	4.80	97.1	31.6	3.54	0.35	0.13	0.48
23	152.7	2.44	98.4	42.5	4.14	0.37	0.17	0.54
24	169.4	2.38	98.6	55.6	4.27	0.38	0.26	0.64

TABLE 15  
 BAFFLE PLATE IMPINGEMENT COLUMN  
 SCRUBBING LIQUID - GYPSUM POND WATER

Run No	Plant Production Ton/Day H <sub>3</sub> PO <sub>4</sub>	Liquid			Gas			
		Flow Rate GPM	Pressure PSIG	Temperature OF In Out	Flow Rate ACFM	Pressure Drop Across Unit in H <sub>2</sub> O	Temperature OF In Out	
1	525	26.0	11	69	114	8.3	143	79
2	525	19.5	11	72	130	8.3	160	84
7	525	18.1	10	78	128	7.8	164	88
16	550	12.0	8	74	122	8.3	152	90
25	525	4.2	5	70	153	6.2	165	125
26	525	7.6	6	71	152	7.6	166	115
27	525	9.0	7	72	154	7.8	168	105
28	525	15.0	8	74	152	8.3	167	94
29	525	19.5	10	75	133	8.3	164	84

TABLE 15 CONTINUED

Run No	Mean Fluoride Concentration		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio		Number of Transfer Units	Contacting Power	
	MG/STD In	CU FT Out		GPM/M STD CFM	HP/M STD CFM		Gas Liquid Total	
1	144.5	1.45	99.0	81.0	4.61	0.42	0.52	0.94
2	128.5	1.54	98.8	63.4	4.42	0.40	0.41	0.81
7	169.0	9.10	98.7	74.8	4.34	0.29	0.44	0.73
16	181.5	5.26	97.1	38.5	3.54	0.40	0.18	0.58
25	153.2	15.18	90.1	16.0	2.30	0.26	0.05	0.31
26	165.4	7.11	95.7	27.4	3.15	0.33	0.10	0.43
27	137.8	5.36	96.1	31.6	3.24	0.35	0.13	0.48
28	151.3	2.58	98.3	51.7	4.08	0.38	0.24	0.62
29	131.6	1.71	98.7	64.8	4.27	0.39	0.38	0.77

TABLE 16  
 VARIABLE THROAT VENTURI EXPERIMENTAL DATA  
 SCRUBBING LIQUID - WELL WATER

Run No	Plant Production Tons/Day $H_3PO_4$	Liquid		Gas			
		Flow Rate GPM	Pressure PSIG	Temperature In of	Flow Rate ACFM	Pressure Drop Across Unit in $H_2O$	Temperature In of
1	525	5.7	8	67	790	26.2	155
2	525	5.2	5	68	810	24.1	160
3	525	4.2	3	69	830	19.7	162
4	525	3.9	2	70	845	18.2	164
5	525	7.2	11	70	775	34.3	162
6	525	7.3	12	72	740	35.6	159
7	525	9.0	27	75	705	39.8	160

TABLE 16 CONTINUED

Run No	Mean Fluoride Concentration		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio		Number of Transfer Units	Contacting Power	
	MG/STD In	CU FT Out		GPM/M STD CFM	HP/M STD CFM		Gas Liquid Total	
1	121.5	7.20	94.2	8.41	2.85	2.79	0.04	2.83
2	120.8	7.65	93.8	7.54	2.78	2.62	0.02	2.64
3	127.5	9.05	92.9	5.96	2.65	2.18	0.01	2.19
4	132.6	8.49	93.6	5.45	2.75	2.05	0.01	2.06
5	191.8	4.02	97.8	10.57	3.82	3.69	0.07	3.76
6	155.6	5.68	96.4	11.13	3.32	3.68	0.08	3.76
7	115.3	3.07	97.4	14.45	3.65	3.91	0.23	4.14

TABLE 17  
 VARIABLE THROAT VENTURI EXPERIMENTAL DATA  
 SCRUBBING LIQUID - GYPSUM POND WATER

Run No	Plant Production Tons/Day $H_3PO_4$	Liquid		Gas			
		Flow Rate GPM	Pressure PSIG	Temperature In of	Flow Rate ACFM	Pressure Drop Unit in $H_2O$	Temperature In of
11	650	4.0	3	74	858	19.2	159
12	650	5.1	6	74	815	23.0	160
13	650	6.5	10	75	755	29.9	158
14	650	7.8	14	76	780	33.7	160
15	650	9.0	20	78	722	41.2	162
16	650	7.2	11	77	760	31.8	161

TABLE 17 CONTINUED

Run No	Mean Fluoride Concentration		Fluoride Removal Efficiency Percent	Liquid/Gas Ratio		Number of Transfer Units	Contacting Power	
	MG/STD In	CU FT Out		GPM/M STD CFM	Ratio		HP/M STD CFM	Gas Liquid Total
11	132.6	13.12	90.1	5.46	2.31	2.22	0.01	2.23
12	125.7	10.92	91.3	7.35	2.44	2.52	0.03	2.55
13	127.3	6.29	95.0	10.07	3.00	3.04	0.06	3.10
14	138.5	7.34	94.7	11.76	2.94	3.52	0.10	3.62
15	159.2	5.89	96.3	14.69	3.30	3.98	0.17	4.15
16	121.3	10.91	91.0	11.13	2.41	3.34	0.07	3.41

APPENDIX II  
CALCULATIONS

## II CALCULATIONS

### Fluoride Removal

$$\text{mg F}^-/\text{std cu ft} = \frac{(H)(V)(18.99)}{(Q_{SD})\left(\frac{T_m}{T_s}\right)\left(\frac{P_m}{P_s}\right)}$$

where:

H = molarity of impinger solution, determined  
from calibration curve, moles F<sup>-</sup>/liter

V = volume of impinger sample, ml

18.99 = molecular weight of fluorine

Q<sub>SD</sub> = corrected volume of dry effluent gas sampled,  
cu ft

= total volume sampled  $\left[1 - \left(\frac{\text{Vapor pressure at } T_m}{P_m}\right)\right]$

T<sub>m</sub> = absolute temperature at the dry gas meter, °R

T<sub>s</sub> = standard temperature, 68°F + 460° = 528°R

P<sub>m</sub> = absolute pressure at the dry gas meter,  
inches Hg

P<sub>s</sub> = standard pressure, inches Hg

$$\text{mg/std cu m} = (\text{mg/std cu ft})(35.314)$$

$$\text{Removal efficiency} = \left(\frac{C_i - C_o}{C_i}\right) \times 100$$

where:

C<sub>i</sub> = inlet concentration, mg/std cu ft

C<sub>o</sub> = outlet concentration, mg/std cu ft

Number of Transfer Units

$$\text{Number of transfer units} = \ln \left[ \frac{1}{1 - \left(\frac{E}{100}\right)} \right]$$

where:

E = removal efficiency

Contacting PowerLiquid Phase Contacting Power

$$HP_L = \frac{(H_P)(\text{gpm})}{(1714)(Q_S)}$$

where:

$HP_L$  = contacting power in liquid phase,  $HP_L/m$   
std cfm

gpm = liquid flow rate

$H_P$  = pressure of liquid, psig

1714 = conversion factor

$Q_S$  = corrected effluent gas flow rate at 29.92  
inches Hg and 68<sup>o</sup>F, m std cfm

Gas Phase Contacting Power

$$HP_G = (0.1575)(Q_S)(P)$$

where:

$HP_G$  = contacting power in gas phase,  $HP_G/m$  std  
cfm

$Q_S$  = effluent gas flow rate at standard condi-  
tions of 29.92 inches Hg and 68<sup>o</sup> F, m  
std cfm

$P$  = pressure drops across scrubber, inches  $H_2O$   
0.1575 = conversion factor

Total Contacting Power

$$HP_T = HP_G + HP_L$$

where:

$HP_T$  = total contacting power,  $HP_T/m$  std cfm

$HP_G$  = gas contacting power,  $HP_G/m$  std cfm

$HP_L$  = liquid contacting power,  $HP_L/m$  std cfm

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## BIOGRAPHICAL SKETCH

John Munro Craig was born in Chicago, Illinois, July 23, 1938. He received his elementary education in the public schools of Illinois and Ontario, Canada, and graduated from high school in Sarasota, Florida, in June 1956.

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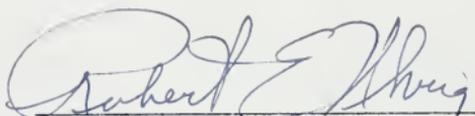
From September, 1967, to the present the author has attended the University of Florida pursuing studies in the field of Environmental Engineering.

The author is a member of Air Pollution Control Association and American Society of Heating, Refrigerating, and Air Conditioning Engineers. He has been awarded the 1963 ASHAE - Homer Addams award from the American Society of Heating, Refrigerating, and Air Conditioning Engineers. He is a registered Engineer in Florida and Tennessee.

His family includes his wife, Jo, and his three children, John, Linda, and Kimi.

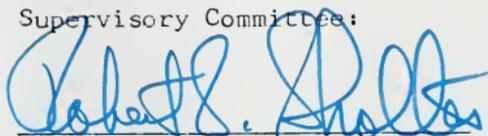
This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

March, 1970

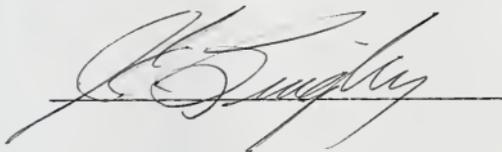
  
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