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THE PECO P2O5/HF PROCESS

By

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PECO

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CONSULTING

ENGINEERING

LABORATORY

PILOT PLANT

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1.0 INTRODUCTION

Phosphate Engineering & Construction Company, Inc. (PECO), incorporated in 1973 in Lakeland, Florida, USA, is a process and product development organization for the phosphate and chemical industries striving to assist them in becoming more efficient, productive, and environmentally safe. Since its inception PECO has been concerned with the environmental issues surrounding the phosphate industry, as indicated by the areas of its research and resulting patents.

PECO has a well-equipped, Florida state certified, analytical laboratory, pilot plant, and process engineering group to perform research programs which have resulted in the development of several processes being offered to the industry on an exclusive worldwide basis. These processes include, but are not limited to, a patented closed loop system for the elimination of fluorine pollution from phosphoric acid plants by eliminating cooling ponds, and a patented P₂O₅/HF Process for the production of phosphoric acid and hydrogen fluoride from fluosilicic acid and phosphate rock.

1.1 BACKGROUND INFORMATION

Approximately 600,000 tons per year of fluorine are contained in the twenty million tons per year of phosphate rock consumed in the state of Florida for the production of phosphate fertilizers. Approximately 400,000 tons of this material could be recovered as fluosilicic acid; however, the present market for fluosilicic acid is only about 60,000 tons per year.

A market does exist for fluoride products; however, except for the PECO P₂O₅/HF Process no economical process is presently available to convert the total amount of fluorine evolved during the manufacture of phosphate products into these finished saleable products. This newly developed PECO P₂O₅/HF Process could provide a significant additional profit to the phosphate producers.

A limited number of phosphoric acid producers recover fluorine as fluosilicic acid. This is due to the relatively small market demand for fluosilicic acid or its products such as sodium silicofluoride, cryolite, and aluminum fluoride.

Because of this small demand, the bulk of the fluorine evolved during the manufacture of wet process phosphoric acid is absorbed into the cooling pond water.

The concentration of fluorine in cooling ponds can build up to levels of about 4,000 ppm (0.4%) for producers who recover fluosilicic acid and to about 12,000 ppm (1.2%) for producers who do not. Producers who have lined their cooling ponds and do not recover fluosilicic acid have encountered fluorine levels over 25,000 ppm (2.5%).

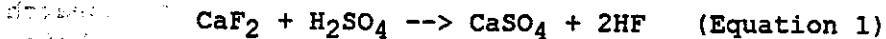
A sizeable market of 400,000 tons per year exists for fluorine in the United States and this market is predicted to increase to 500,000 tons per year by 2000. Historically this market has not been available to the

phosphate industry since its fluorine is tied up with silica and therefore not acceptable to the higher value fluoride consumers. The PECO P₂O₅/HF Process separates the silica from the fluorine and opens up the fluoride chemical market to the phosphate industry.

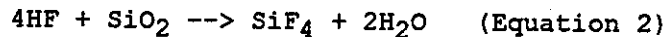
1.2 FLUORINE CHEMISTRY

The field of fluorine chemistry is very complicated and one of the more complex subjects in the field of inorganic chemistry. It is not necessary to totally understand the complex reactions of the molecule fluorine, however a brief discussion of this area of chemistry is presented below to assist the reader in following the logic in some of the basic designs used by the practicing chemical engineer.

Fluorine is obtained from the mineral fluorapatite. In most cases phosphate rock contains approximately 3% to 3.5% fluorine. When the phosphate rock is reacted with sulfuric acid in the production of phosphoric acid, the calcium fluoride present in the phosphate rock produces hydrogen fluoride according to the following equation:

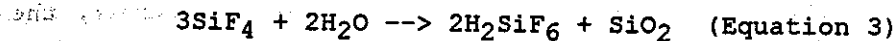


As soon as the hydrogen fluoride is formed it attacks the silica present in the phosphate rock. Although the amount of silica in phosphate rocks varies, there is normally an excess of silica available to react with all the hydrogen fluoride generated by equation 1. The attack by the hydrogen fluoride of the silica follows the equation given below.



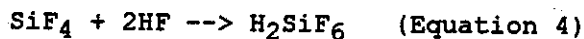
The product from this reaction is silicon tetrafluoride which is a gas at normal room temperature and pressure.

Since most phosphoric acid processes are conducted in an aqueous phase, the silicon tetrafluoride, as soon as it is produced, forms fluosilicic acid and silicon dioxide according to the following:

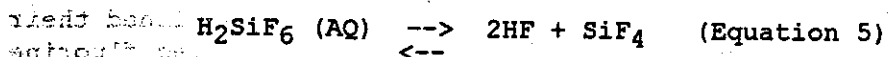


This is significant because when the fluosilicic acid is formed, insoluble silica is generated as a gelatinous material having the characteristic of plugging up fume scrubbers, fluosilicic acid recovery towers, and anything else that it comes in contact with. In some cases it makes many processes for the recovery of fluorine inoperable because of the large deposits of the silica gel in the operating equipment.

This problem can be avoided by using an aqueous solution of hydrogen fluoride to react with the silicon tetrafluoride producing fluosilicic acid, according to equation 4.



Fluosilicic acid (H₂SiF₆) can only exist in the aqueous phase; that is to say it exists only when it is in a water solution. As soon as the fluosilicic acid is vaporized from the water solution, it turns into SiF₄ and hydrogen fluoride according to equation 5.



It has been noted that silicon tetrafluoride is normally released earlier than hydrogen fluoride. In most cases the vapors coming from phosphoric acid at concentrations below 40% are very rich in silicon tetrafluoride (SiF₄) and lean in hydrogen fluoride. Therefore when this vapor

is scrubbed with water the silicon tetrafluoride reacts with the water in accordance with equation 3 producing fluosilicic acid, as well as generating the silica gel, again creating the problem of clinging to any surface and plugging up almost all equipment.

When the concentration of phosphoric acid is much over 40%, the vapors coming from that evaporator are generally rich in hydrogen fluoride and lean in silicon tetrafluoride. No silica is deposited when the vapors are scrubbed since the excess hydrogen fluoride reacts with SiO_2 in accordance with equations 2 and 4 producing H_2SiF_6 in water rather than precipitating the silica gel.

The chemical engineer, in designing a fluosilicic acid unit, will use a counter current operation so as to have a vapor rich in hydrogen fluoride scrubbed first and then use that liquor to scrub the SiF_4 from lower concentration evaporators. This keeps the mole ratio proper and prevents the formation of silica. The only alternative to this is to scrub the vapors rich in SiF_4 and add a pure stream of hydrofluoric acid to it so as to keep the mole ratio correct and thereby eliminate the precipitation of silica. However hydrofluoric acid is very expensive making it not economical to use as a regulator in a fluosilicic acid recovery system to keep the mole ratio constant.

The above explanation also illustrates why it is necessary to concentrate phosphoric acid to the higher concentration so as to obtain a hydrogen fluoride rich solution to be used in scrubbing the vapors from the lower P_2O_5 evaporator concentration stages. When a manufacturer is producing only 40% phosphoric acid, the vapors from that system do not contain enough hydrogen fluoride to be in equilibrium with the excess silicon tetrafluoride coming from the lower evaporators. Therefore it is extremely difficult to put in fluosilicic acid recovery units which will not precipitate silica, when evaporating phosphoric acid only to 40% P_2O_5 .

2.0 PECO P_2O_5 /HF PROCESS

The objective of the research program was to develop a process which would produce phosphoric acid by reacting fluosilicic acid and phosphate rock and convert the fluorine into a nonvolatile compound.

The process worked quite well producing phosphoric acid without using sulfuric acid, however, it had one drawback: while separating the phosphoric acid from the acid insolubles and precipitated solids, the silica associated with the fluosilicic acid reported to the solids as expected, the fluorine associated with the fluosilicic acid stayed with the phosphoric acid unexpectedly.

The dilemma proved to be short lived when PECO found that the fluorine is readily converted to hydrogen fluoride and easily liberated from the acid. The hydrogen fluoride vapors are then recoverable as a concentrated solution or as an anhydrous hydrogen fluoride. The domestic market demands for hydrogen fluoride and aluminum fluoride are sufficient to absorb over half of the hydrogen fluoride that could be produced by the phosphate industry.

The initial invention of the PECO/ P_2O_5 HF Process occurred in August of 1989. This invention was registered with PECO's patent attorney who did a preliminary patent search and determined that this was definitely new technology and would not infringe on existing or past patents. The process then moved to a bench scale evaluation of the various chemical reactions and data obtained to design a continuous pilot plant. A continuous pilot plant was installed at PECO's research headquarters in Lakeland, Florida, and operated for some six months to verify the process on a pilot plant scale and

to obtain data for design of a commercial unit. Samples of the material were obtained at the various stages throughout the operation and analyzed by third parties who indicated that the process chemistry was correct and the process technology viable.

On January 19, 1993, the United States Department of Commerce Patent and Trademark Office issued Patent #5,180,569 covering this process. Based on this United States patent, foreign patents have been obtained in several critical countries throughout the world. Since that time two additional patents have been issued.

E.I. DUPONT DE NEMOURS & COMPANY (INC.) has been granted an exclusive license to use this process for the production of hydrogen fluoride for use in the manufacture of organic compounds, while PECO retains the right to use this process in the inorganic field.

PECO has completed a Process Engineering Design Package (Front End Engineering) and a definitive capital cost for the first commercial installation of the PECO P₂O₅/HF Process to be built and operated by PECO. The design basis for this facility is summarized in Table 3.

TABLE 3
DESIGN BASIS

FSA Consumed (100% Basis)	18,000 STPY
Plant Utility	7,440 HRS/YR
P ₂ O ₅ Produced	15,635 STPY
CaF ₂ Produced	24,830 STPY
HF Produced (100% Basis)	11,250 STPY

2.1 PROCESS DESCRIPTION

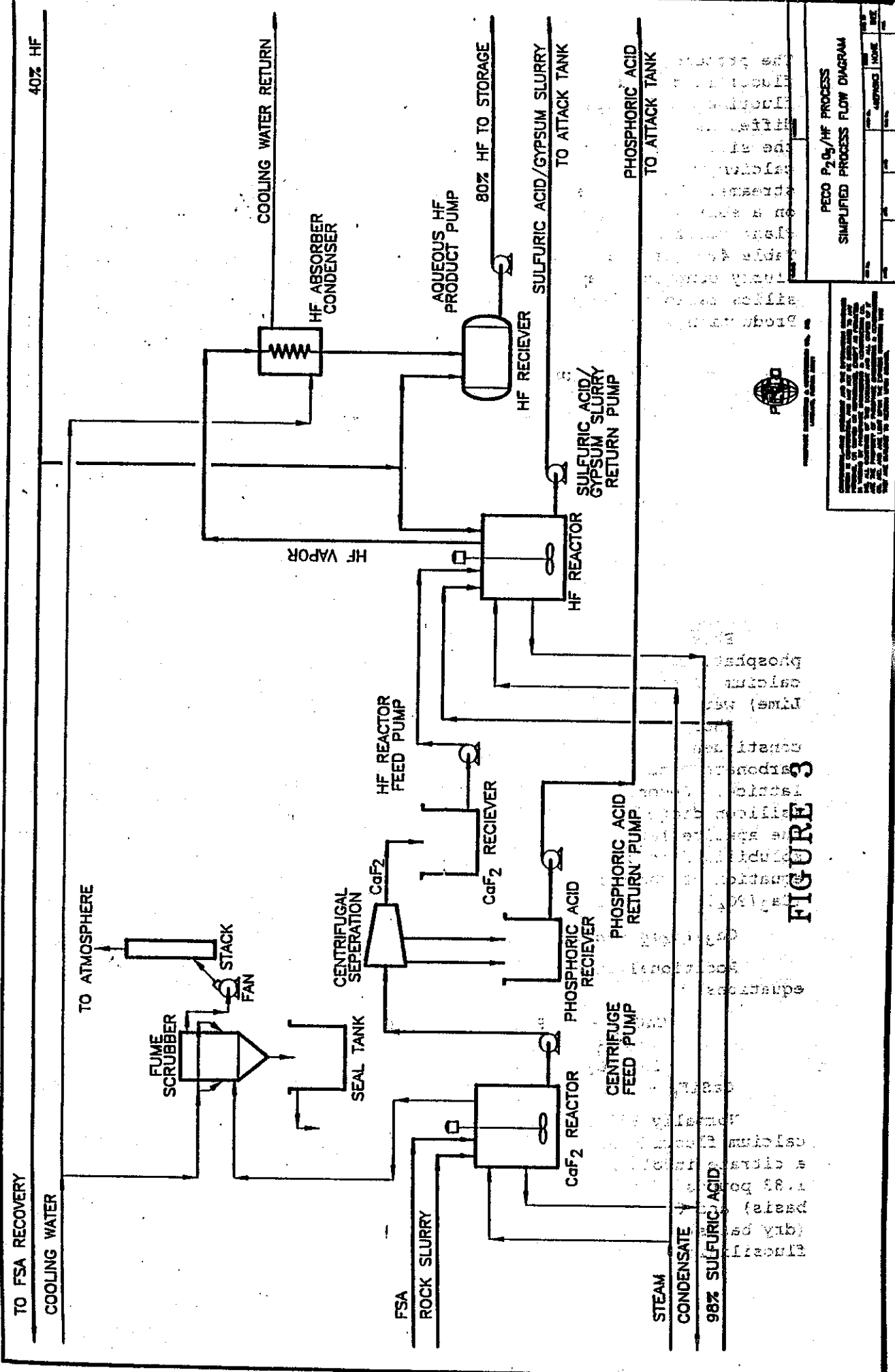
The PECO P₂O₅/HF Process produces wet process phosphoric acid by reacting phosphate rock and fluosilicic acid and subsequently recovering the fluorine as hydrogen fluoride is shown in Figure 3.

In the first step phosphate rock and fluosilicic acid are reacted and the resulting reaction slurry is filtered or centrifuged to separate the phosphoric acid and calcium fluoride, with a fluoride concentration of 12% to 15%, from the undigested rock and silica (Phosphoric Acid/Calcium Fluoride Production Area). In the final step vapors, containing 90% hydrogen fluoride are recovered from the silica free phosphoric acid and calcium fluoride. The vapors from this step are condensed to form a water solution of concentrated hydrogen fluoride (Hydrogen Fluoride Production Area). The phosphoric acid, having been separated from the hydrogen fluoride, is returned to the phosphoric acid plant for further processing. The concentrated hydrofluoric acid can either be sold directly or processed further using existing technologies to produce saleable fluoride salts or anhydrous hydrogen fluoride.

2.1.1 Phosphoric Acid/Calcium Fluoride Production Area

The Phosphoric Acid/Calcium Fluoride Production Area for the PECO P₂O₅/HF Process includes the following:

- P₂O₅/CaF₂ Reaction System
- CaF₂ Separation and Concentration System



40% HF

TO FSA RECOVERY

COOLING WATER

TO ATMOSPHERE

FUME SCRUBBER

SEAL TANK

CENTRIFUGAL SEPARATION

CaF₂

HF REACTOR FEED PUMP

FSA

ROCK SLURRY

CaF₂ REACTOR

CENTRIFUGE FEED PUMP

PHOSPHORIC ACID RECIEVER

PHOSPHORIC ACID RETURN PUMP

STEAM

CONDENSATE

98% SULFURIC ACID

HF VAPOR

HF ABSORBER CONDENSER

COOLING WATER RETURN

AQUEOUS HF PRODUCT PUMP

80% HF TO STORAGE

HF RECIEVER

SULFURIC ACID/GYPSUM SLURRY TO ATTACK TANK

SULFURIC ACID/GYPSUM SLURRY RETURN PUMP

PHOSPHORIC ACID TO ATTACK TANK



PECO P₂O₅/HF PROCESS
SIMPLIFIED PROCESS FLOW DIAGRAM

FIGURE 3

THIS DIAGRAM IS A SIMPLIFIED REPRESENTATION OF THE PROCESS AND IS NOT TO BE USED FOR DESIGN OR CONSTRUCTION PURPOSES. THE PROCESS IS SUBJECT TO CHANGE WITHOUT NOTICE. THE PROCESS IS SUBJECT TO PATENT PROTECTION.

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The process produces three times the quantity of P₂O₅ per unit of fluosilicic acid as compared to other processes. In addition the fluorine and silica in the fluosilicic acid are precipitated as two different insoluble compounds which can be mechanically separated. Once the silicon dioxide has been removed from the phosphoric acid and calcium fluoride, this stream is further processed into two product streams. Two thirds of the product phosphoric acid containing 20% P₂O₅ on a solids free basis is exported to the wet process Phosphoric Acid Plant for further processing. The analysis of this product is give in Table 4. The second product stream, calcium fluoride/phosphoric acid slurry containing approximately 50% CaF₂ by weight with a fluorine to silica ratio of 100 to 1, is transferred to the Hydrogen Fluoride Production Area for conversion to hydrogen fluoride.

TABLE 4
PHOSPHORIC ACID TYPICAL ANALYSIS
(Solids Free Basis)

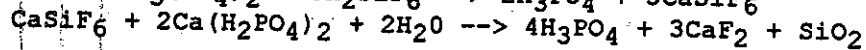
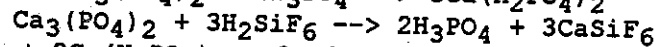
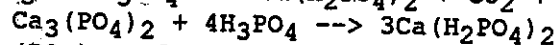
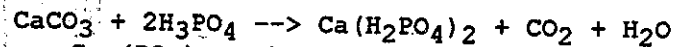
	% by wt
P ₂ O ₅	18.7
CaO	0.23
Al ₂ O ₃	0.012
Fe ₂ O ₃	0.26
MgO	0.20
F	0.47
SO ₄	0.15
SiO ₂	0.24

Phosphoric acid and calcium fluoride are produced by reacting phosphate rock and fluosilicic acid in a medium of phosphoric acid and calcium fluoride. The basic raw materials are 68 BPL (Bone Phosphate of Lime) wet ground phosphate rock slurry and 23% fluosilicic acid.

Phosphate rock is a complex material, the principal mineral constituent, fluorapatite, contains calcium, phosphate, fluoride, carbonate, and other elements or groups bound together in the crystal lattice. Secondary mineral constituents are organic matter and sand (silicon dioxide). When the rock is treated with a strong mineral acid, the apatite lattice is destroyed and the phosphate constituent is solubilized as orthophosphoric acid (H₃PO₄). The overall chemical equation of the principal reaction between the phosphate constituent (Ca₃(PO₄)₂) and fluosilicic acid (H₂SiF₆) is as follows:



Additional side reactions are represented by the following equations:



Normally 97% of the fluorine in the feed acid is converted to calcium fluoride and 90% of the P₂O₅ in the rock feed is converted from a citrate insoluble form to a water soluble form. The reaction yields 1.83 pounds of calcium fluoride per pound of fluosilicic acid (100% basis) and 0.28 pounds of water soluble P₂O₅ per pound of phosphate rock (dry basis) or 0.87 pounds of water soluble P₂O₅ per pound of fluosilicic acid (100% basis).

After mechanically separating the phosphoric acid and calcium fluoride produced by the process from the silicon dioxide and undigested portions of the phosphate rock, over 85 percent by weight of the P₂O₅ in the rock feed is recovered in the product phosphoric acid and calcium fluoride/phosphoric acid slurry in a water soluble form. Approximately 85.8% of the fluorine in the fluosilicic acid is recovered in the calcium fluoride/phosphoric acid slurry as calcium fluoride.

2.1.1.1 PECO P₂O₅/CaF₂ Reaction System

The PECO P₂O₅/CaF₂ Reaction System consists basically of a single reaction vessel with suitable agitation, heat exchanger, fume ventilation, raw material feed systems, and a reaction product surge and transfer system.

2.1.1.2 Calcium Fluoride Separation and Concentration System

In the PECO P₂O₅/HF Process the recovery of phosphoric acid and calcium fluoride is achieved through a two stage centrifugation step followed by a clarification step. The products having been separated from the waste products are further processed into phosphoric acid and calcium fluoride/phosphoric acid slurry by centrifugal separation. The phosphoric acid is returned to the fertilizer complex for conventional processing while the calcium fluoride/phosphoric acid slurry is transferred to the Hydrogen Fluoride Production Area.

2.1.2 Hydrogen Fluoride Production Area

The calcium fluoride/phosphoric acid slurry produced in the phosphoric acid/calcium fluoride production area is further processed into a concentrated solution of hydrogen fluoride.

The Hydrofluoric Fluoride Production Area for the PECO P₂O₅/HF Process includes the following:

- HF Reaction System
- HF Absorption System

This facility is designed to produce 11,250 short tons per year of hydrogen fluoride (100% basis) operating 7,440 hours per year. The facility produces a concentrated solution of hydrofluoric acid containing 80% HF which is transferred to the Aqueous HF Storage and Shipping Area. The analysis of this product stream is given in Table 5.

TABLE 5
PRODUCT HF TYPICAL ANALYSIS

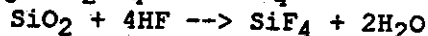
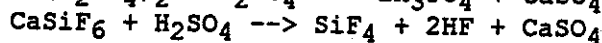
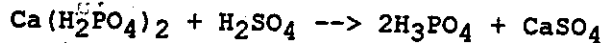
	% by wt
HF	80
P ₂ O ₅	0.24
SO ₄	0.24
SiO ₂	0.94

Hydrogen fluoride is produced by reacting the calcium fluoride/phosphoric acid slurry with concentrated sulfuric acid (93% to 98% H₂SO₄) in a medium of sulfuric acid/phosphoric acid and calcium sulfate. In the PECO P₂O₅/HF Process only 2.0 tons of sulfuric acid (100% basis) is consumed per ton of P₂O₅ produced.

The overall chemical equation of the principal reaction between the fluoride constituent (CaF₂) and sulfuric acid (H₂SO₄) is as follows:



Additional side reactions are represented by the following equations:



In order to convert 95% of the calcium fluoride to hydrogen fluoride a stoichiometric excess of sulfuric acid is reacted with the calcium fluoride. Additional sulfuric acid is added to increase the sulfuric acid content of the liquid portion of the hydrogen fluoride reactor slurry. This results in an increase in the evolution of the hydrogen fluoride and a higher concentration of hydrogen fluoride in the vapors exiting the reactor. Approximately 0.63 tons of HF (100% basis) is produced per ton of FSA (100% basis). The excess sulfuric acid containing phosphoric acid and calcium sulfate is exported to the Phosphoric Acid Plant reactor for utilization of the sulfuric acid and recovery of the phosphoric acid. The PECO P₂O₅/HF Process requires only 4.65 tons of sulfuric acid (100% basis) per ton of HF (100% basis) be returned to the attack system.

2.1.2.1 PECO HF Reaction System

The PECO hydrogen fluoride reactor system consists basically of a single reaction vessel with suitable agitation, heat exchanger, vapor transfer, raw material feed systems, and a reactor product surge and transfer system.

2.1.2.2 Hydrogen Fluoride Absorption System

Hydrogen fluoride vapors produced in the HF Reactor are recovered in the absorption system by circulating a stream of aqueous hydrogen fluoride solution containing 80% hydrogen fluoride. The absorption system which consists of a falling film condenser, circulating tank, circulating pump, and a tail gas scrubber, is housed in a totally enclosed building which is vented to a fume scrubber.

2.1.3 40% HF Utilization

A high purity aqueous hydrogen fluoride product containing 80% HF is exported from the facility. This material can be distilled to produce an anhydrous hydrofluoride suitable for conversion to high value fluoride products. The distillation process produces a 40% HF aqueous hydrogen fluoride solution containing the water and impurities present in the original 80% product. This dilute HF solution is returned to the PECO P₂O₅/HF Process Plant for recovery.

Alternatively, this material is available for use in the fluosilicic acid recovery process within the phosphoric acid plant. Every pound of hydrogen fluoride contained in the 40% HF solution utilized for the recovery of fluosilicic acid results in a net recovery of 2.4 pounds of fluosilicic acid (H₂SiF₆, 100% basis). The utilization of the 40% HF solution allows the fluosilicic acid recovery process to be operated with sufficient excess of hydrogen fluoride to maintain the

silicon dioxide in solution. The availability of this material allows for the recovery of concentrated fluosilicic acid from previously unavailable sources such as the phosphoric acid attack tank, flash cooler circuit, and fume scrubber. Heretofore these sources have been unavailable due to the precipitation of silicon dioxide.

The 40% HF solution available from the commercial installation can be used to eliminate the silicon dioxide precipitation problem and recover an additional 4,650 STPY of fluosilicic acid (100% basis) as a concentrated commercially valuable material. The use of this 40% HF solution results in a net increase in fluosilicic acid recovery of 25%.

2.2 ADVANTAGES OF THE PECO P₂O₅/HF PROCESS TO THE PHOSPHORIC ACID COMPLEX OPERATION

2.2.1 Acid Quality

The PECO P₂O₅/HF Process provides an incremental increase in the production of phosphoric acid by profitably converting fluorine as a contaminant in acid water streams into a low impurity phosphoric acid.

Since this phosphoric acid produced by the PECO P₂O₅/HF Process is lower in impurities than normal phosphoric acid, the effect of blending them makes it easier to produce DAP of acceptable quality.

It is speculated that because of the rejection of impurities by the PECO P₂O₅/HF Process phosphate rock with very high impurity levels can be used in the PECO P₂O₅/HF Process.

2.2.2 Operating Factor

A major benefit of the PECO P₂O₅/HF Process to the phosphoric acid production facilities is that it is not an integral part of the overall production of phosphoric acid. Hence, the operation of the PECO P₂O₅/HF Process is dependent on the operation of the phosphoric acid plant while the phosphoric acid plant operation is essentially independent of the operation of the PECO P₂O₅/HF Process.

3.0 SUMMARY OF PROCESS RESULTS

- 3.1 Fluosilicic acid can be reacted with phosphate rock to produce a nominal 20% P₂O₅ phosphoric acid. Since phosphoric acid is produced by this process, relatively high levels of P₂O₅ in the fluosilicic acid raw material are acceptable. Consequently, the evaporators in the phosphoric acid plant can be operated in the same manner as when fluorine is not being recovered. In fact, P₂O₅ currently lost during the evaporation step would be recovered in the fluosilicic acid scrubbers and returned to the phosphoric acid plant in the acid produced by the PECO P₂O₅/HF Process.
- 3.2 Over 0.87 tons of phosphoric acid is produced for each ton of fluosilicic acid fed to the system. The quality of the phosphoric acid produced has an impurities to P₂O₅ ratio one-fourth of the current levels with a typical analysis of: 18.7% P₂O₅, 0.23% CaO, 0.012% Al₂O₃, 0.26% Fe₂O₃, 0.20% MgO, 0.47% F, 0.15% SO₄, and 0.24% SiO₂.
- 3.3 The PECO P₂O₅/HF Process consumes only 2.0 tons of sulfuric acid per ton of P₂O₅ produced as compared to 2.75 normally consumed by wet process phosphoric acid plants and returns only 4.65 tons of sulfuric acid per ton of HF produced.

3.4 Silica is separated from the fluorine such that the fluorine to silica ratio in the calcium fluoride/phosphoric acid slurry is 100.

3.5 An overall recovery of 75% of the fluorine fed to the process as fluosilicic acid is recovered as an 80% hydrogen fluoride solution.

3.6 The hydrogen fluoride is produced as an 80% solution. Since this concentrated hydrofluoric acid is well above the 37% azeotrope, anhydrous hydrogen fluoride can be produced by distillation.

3.7 Existing technology currently practiced on a commercial basis can be used to produce anhydrous hydrogen fluoride, aluminum fluoride, and other fluoride salts from the concentrated hydrofluoric acid produced by the PECO P₂O₅/HF Process.

3.8 A 40% HF solution from the distillation process is available to be returned directly to the phosphate complex providing for a 25% increase in commercial strength fluosilicic acid recovery.