

FLUORINE CONTROL SYSTEMS

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FLUORINE CONTROL SYSTEM

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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 P_2O_5/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 P_2O_5/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 P_2O_5/HF Process could provide a significant additional profit to the phosphate producers and at the same time dramatically reduce the fluorine emissions from the plant site.

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.

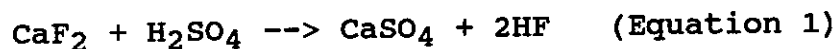
The concentration of fluorine in cooling ponds can build up to levels of about 4,000 ppm (0.4%) for producers who recover fluosilicic acid and to about 12,000 ppm (1.2%) for producers who do not. Producers who have lined their cooling ponds and do not recover fluosilicic acid have encountered fluorine 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 1994. 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

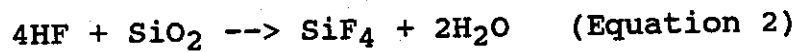
The field of fluorine chemistry is very complicated and one of the more complex subjects in the field of inorganic chemistry. It is not necessary to totally understand the complex reactions of the molecule fluorine, however a brief discussion of this area of chemistry is presented below to assist the 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:



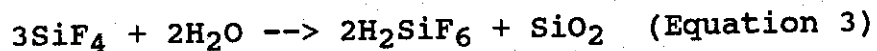
As soon as the hydrogen fluoride is formed it attacks the silica present in the phosphate rock. Although the amount of silica in

phosphate rocks varies, there is normally an excess of silica available to react with all the hydrogen fluoride generated by equation 1. The reader may recall that hydrofluoric acid is one of the few acids which will attack glass. Glass is primarily silica and therefore, hydrogen fluoride will attack and etch it quite easily. The attack by the hydrogen fluoride of the silica follows the equation given below.



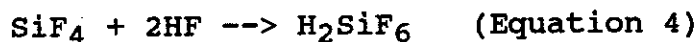
The product from this reaction is silicon tetrafluoride which is a gas at normal room temperature and pressure.

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:

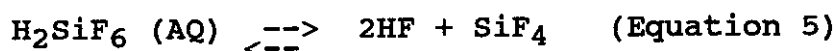


This is significant because when the fluosilicic acid is formed, insoluble silica is generated as a gelatinous material having the characteristic of plugging up fume scrubbers, fluosilicic acid recovery towers, and anything else that it comes in contact with. In some cases it makes many processes for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

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 (H_2SiF_6) 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 SiF_4 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 (SiF_4) 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 his 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 .

1.3 CONVENTIONAL COOLING POND OPERATION

Figure 1 depicts a normal abbreviated cooling pond operation of a conventional phosphoric acid plant. During the production of phosphoric acid large amounts of heat are generated by its exothermic reaction. This heat is removed by exposing the phosphoric acid liquor to a vacuum flash cooler, which evaporates

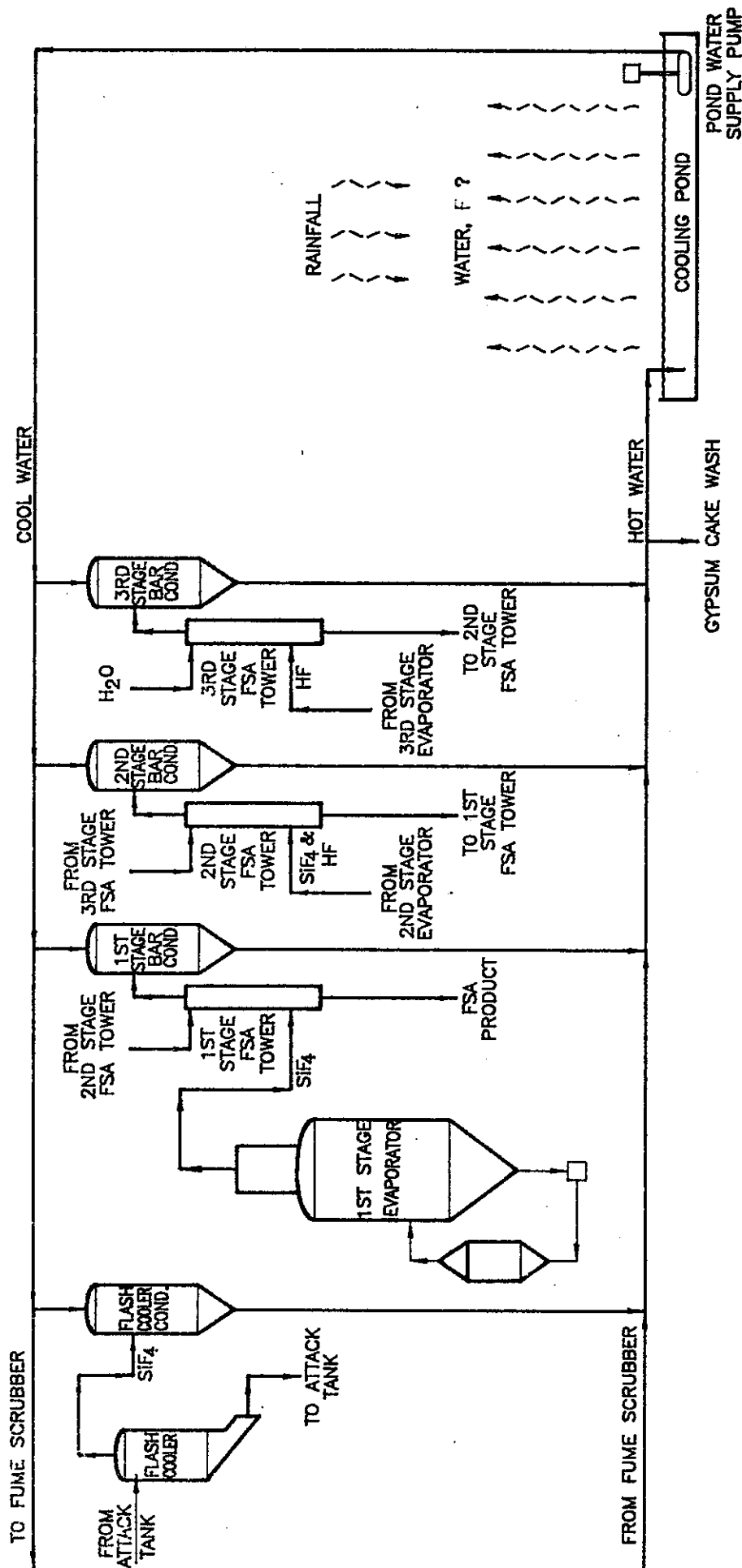


FIGURE 1



FLUOR DANIEL ENGINEERING & CONSTRUCTION CO., INC.
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CONVENTIONAL PHOSPHORIC ACID PLANT
 COOLING POND SYSTEM

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water and liberates SiF_4 and a small amount of hydrogen fluoride from the liquor thus producing a cooling effect to maintain the desired temperature. This evaporated water and liberated fluorine compounds are then condensed with pond water which is sent to the cooling pond. The cooled pond water is then pumped back to the barometric condenser of the flash cooler so as to condense more vapors and pick up more fluorine from the flash cooler.

About 10% to 15% of the fluorine entering the phosphate complex is liberated at the flash cooler. No company is currently attempting to recover the fluorine liberated at this point due to the fact that a severe silica deposition problem is anticipated since no hydrogen fluoride rich fluosilicic acid streams are available.

Generally the same type of operation is used in the evaporator section of the plant where the phosphoric acid is concentrated from 28% P_2O_5 on up to 40% or 52% P_2O_5 . The vapors from the evaporator section are condensed in barometric condensers by direct contact with cool pond water. The warm pond water is then sent to the cooling pond where it is cooled by evaporation and recirculated back to the barometric condenser to condense more vapor and pick up more fluorine compounds.

The barometric condensers require large quantities of pond water to condense the vapors from the evaporators and the flash cooler. Because of the large volume of water, the silica which

precipitates in the pond water is so dilute that it does not have an opportunity to precipitate out in lines and plug up the large pond water pipes. Consequently, the precipitation of silica in the barometric condenser is hardly any problem at all because any precipitated silica is washed away and transported to the cooling pond where it settles out.

All of the aforementioned silica problems could be corrected by the addition of a hydrofluoric acid solution, as stated earlier, to the fluosilicic acid scrubbing circuit. Again, this is not economically justifiable, however, if it could be justified approximately 2.4 pounds of fluosilicic acid could be produced per pound of hydrogen fluoride added.

The cooling ponds associated with a normal size phosphoric acid plant can vary in size from 100 to 400 acres in size. This size is necessary to provide the evaporative surface required to cool the pond water to approximately 90° F in the summer which is low enough to condense the vapors from the evaporators and the flash cooler.

Because of the vastness of the ponds, large amounts of water are deposited into the pond water system during adverse weather conditions, especially a hurricane. A very strict water management program has been adopted by all phosphate producers to accommodate this large input of water during the rainy season. However, should several hurricanes occur in a short period of time liming and treatment facilities are provided to treat the

water before it is discharged off the plant site. The installations have done an excellent job of eliminating the possibility of any contaminated water leaving the plant site. Virtually all plant operators have been able to operate their ponds in such a way that normally no water is discharged from the cooling pond to the surrounding environment. Monitoring wells have been installed around the pond to detect any seepage of pond water into the ground water and in most cases this has shown that very little, if any, seepage does occur.

The pond water is used as a source of water to wash the gypsum on the gypsum filter in the phosphoric acid plant thus putting back into the phosphoric acid product that amount of fluorine, as well as phosphoric acid, which is associated with this wash water.

In addition, pond water is used to hydraulically place the gypsum on the gypsum stack. Since this transport water is in intimate contact with the gypsum, phosphoric acid is transferred from the gypsum to the pond water, building up to 2.0% to 2.3% P_2O_5 .

Because of this, the lowest concentration of P_2O_5 in the liquid associated with the gypsum is that of the pond water containing 2.0% to 2.3% P_2O_5 . If the plant water balance were to allow the use of fresh water, or water with no P_2O_5 in it, to wash the gypsum, the P_2O_5 in the gypsum could be significantly reduced.

Generally speaking, the concentration of fluorine in the cooling pond will reach a level of approximately 10 to 12 thousand ppm and will be stabilized at that level. Many studies have been

conducted to determine the actual amount of fluorine released from a cooling pond and in most cases the studies have been inconclusive. It is assumed that a great deal of the fluorine in the pond water becomes associated with the gypsum and deposited on the gypsum stack. For every 100 pounds of fluorine contained in the phosphate rock shipped into a phosphate complex, 20 pounds is shipped out in the phosphate product and 20 pounds reports to the gypsum waste product. The remaining 60 pounds is absorbed by the cooling pond system in plants that do not recover fluorine. Approximately 25% of the fluorine contained in the rock is recovered by producers that collect fluosilicic acid.

2.0 PECO CLOSED LOOP SYSTEM

The first attempt by PECO to eliminate the fluorine pollution problem resulted in the issuance of U.S. Patent # 3,811,246, entitled "Closed Loop System for the Elimination of Fluorine Pollution from Phosphoric Acid Plants". The elements of this patent are illustrated in Figure 2.

The emission of fluorine to the atmosphere is eliminated by simply eliminating the cooling pond. The cooling function of the pond is replaced by the installation of a cooling tower which removes the heat from the phosphate complex. Since any fluorine in the cooling tower water would be stripped out by the air flow through the tower and eventually end up in the atmosphere, no fluorine can be allowed to get into the cooling tower water. To accommodate this a heat exchanger is inserted between the cooling tower and the barometric condensers of the flash cooler and evaporator.

Having inserted this exchanger the water condensed in the barometric condenser, as well as the fluoride vapor picked up by the cooling water, is then contained in a closed loop. Now a system has to be worked out to get rid of this condensed water, as well as handling the fluorine compounds contained in the closed loop.

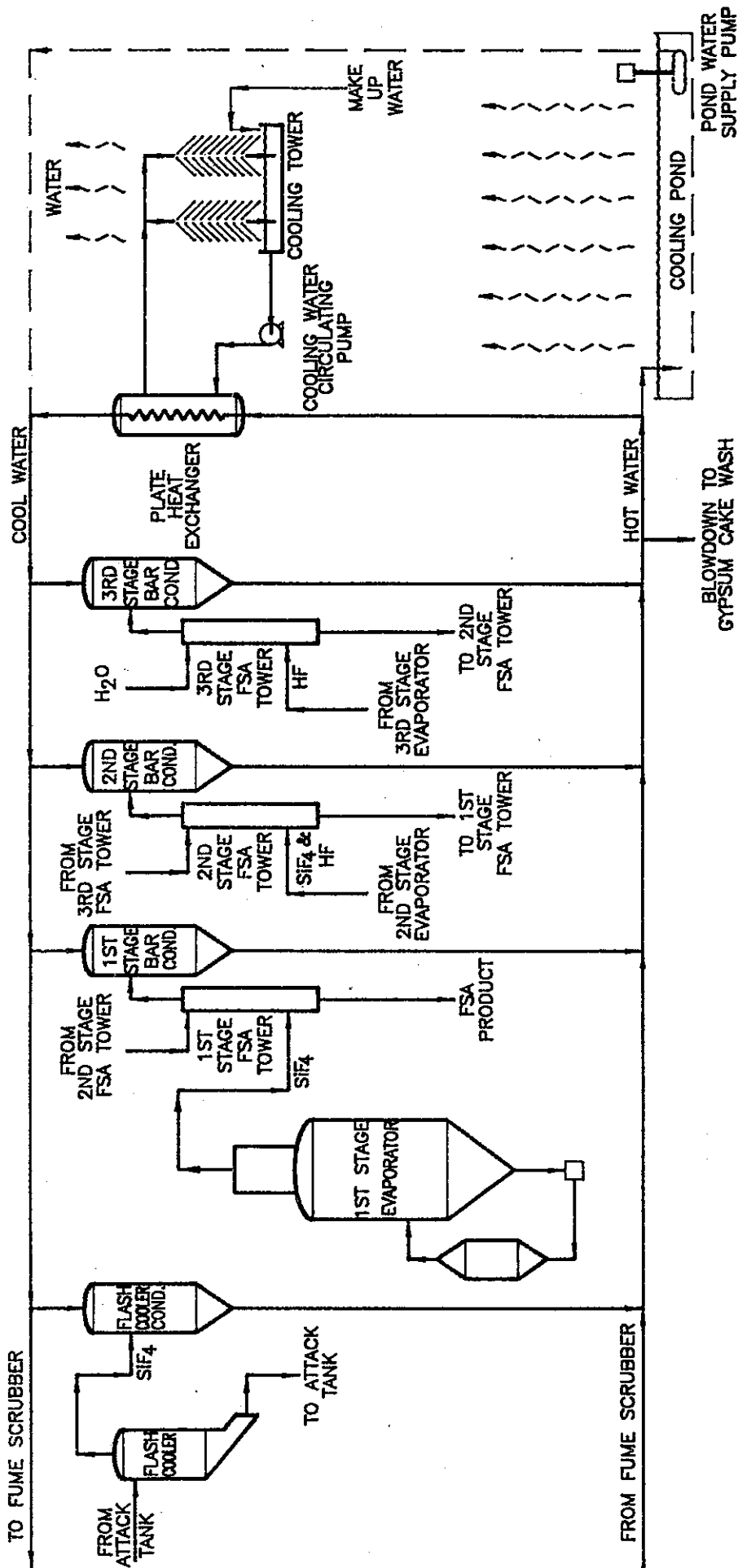


FIGURE 2



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 MIAMI, FLORIDA 33111

PECO CLOSED LOOP
 COOLING WATER SYSTEM

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The amount of fluorine entering the closed loop water is kept to a minimum by recovering it using conventional fluosilicic acid recovery systems before the vapors are condensed. By doing so, the amount of fluorine in the closed loop water is kept to an absolute minimum. However, this does generate large quantities of fluosilicic acid.

A simplified overall water balance for a phosphoric acid complex is given in Table 1. As can be seen the water balance for the production of phosphoric acid and subsequently producing DAP is negative. That is to say it is necessary to consume water to maintain the plant water balance due to the loss of water to the gypsum stack.

TABLE 1

PHOSPHATE COMPLEX WATER BALANCE

Basis 1.0 Ton P₂O₅ Produced

	<u>Input Tons</u>	<u>Output Tons</u>
Rock Slurry	1.65	
H ₂ SO ₄ Free	0.06	
Bonded	0.11	
DAP		0.04
Gypsum Free		1.78
Bonded		1.0
Makeup Water (By Difference)	1.00	
	----	----
Total	2.82	2.82

The flow of water entering the closed loop circuit is provided in Table 2. This table is based on concentrating enough P₂O₅ from

28% to 52% P₂O₅ to be blended with 28% P₂O₅ acid to produce a 38% P₂O₅ feed acid to the DAP plant.

TABLE 2

PHOSPHATE COMPLEX WATER BALANCE

Closed Loop Condensate
Basis 1.0 Ton P₂O₅ Produced

	<u>Input Tons</u>	<u>Output Tons</u>
Flash Cooler	1.0	
Evaporator (1)	0.94	
DAP (2)	1.06	
Blowdown (By Difference)		3.0
	----	----
Total	3.0	3.0

- 1) 0.57 Tons Concentrated from 28% to 52% P₂O₅
- 2) Blend Acid to DAP 38% P₂O₅
 DAP Product 2% H₂O

Overall 3 tons of water vapor enters the closed per ton of P₂O₅ produced. The condensed steam, has to be used in parts of the plant, otherwise it will accumulate very rapidly. Fortunately there are several areas where water containing very low amounts of fluorine and no P₂O₅ can be used throughout the plant. Some of the areas are:

- Gypsum filter wash water
- Makeup to the water used for gypsum disposal
- Makeup to the fluosilicic acid recovery units
- Makeup to the cooling tower
- Water for wet rock grinding

The predicted analysis of the closed loop water, as compared to conventional pond water, is as follows:

<u>Component</u>	<u>Conventional Pond Water</u>	<u>Closed Loop Water</u>
P ₂ O ₅	2.20%	0.00
F	1.10%	0.60
SO ₄	0.70	0.00
N	0.20	0.00

Normally 4 tons of wash water per ton of P₂O₅ produced is required to wash the gypsum cake. The closed loop requires 3 tons of water be remove per ton of P₂O₅ in order to maintain process inventory. Therefore 1 ton of makeup water per ton of P₂O₅ is required to meet both the demands of the gypsum filter and the process.

The makeup water can be either cooling pond water or fresh water. Using cooling pond water allows the existing cooling ponds to be reduced in volume and the P₂O₅ in the pond to be harvested over a period of time. Once the cooling pond is eliminated fresh water would be used to makeup the water deficit. The land area associated with the cooling pond would be available for building a new gypsum stack on contaminated land rather than virgin soil.

Use of the closed loop water to wash the gypsum filter cake will certainly reduce the acidity and P₂O₅ losses associated with the disposal of the gypsum waste. Whether the pH of the water used for hydraulically placing the gypsum will be raised high enough to negate the need for neutralization of this water can only be determined by laboratory and plant tests. If any lime is

required to raise the pH to an acceptable level, it will certainly be reduced by use of the closed loop. Obviously, washing the cake with water containing little or no P_2O_5 is the most effective and direct way of reducing P_2O_5 losses associated with the gypsum disposal operation.

In some cases it may be necessary that the closed loop water be treated before it can be used; for example, ion exchange, reverse osmosis, or a chemical treatment. This will certainly be necessary before the water can be used as makeup to the cooling tower. This will allow large quantities of closed loop water to be evaporated having a positive effect on the plant water balance. Shifting some of the blowdown from the closed loop to the cooling tower as makeup allows for more cooling pond water to be utilized as gypsum cake wash water. Sending 1 ton of closed loop water per ton of P_2O_5 produced to the cooling tower increases the makeup of cooling pond water to 2 which cuts the time necessary to eliminate the pond in half.

Use of the closed loop water for the above applications eliminates the need to discharge any water from the phosphate complex to the surrounding area thereby maintaining the water balance in the plant. The use of the closed loop system will also eliminate the need for facilities to accommodate the influx of water from any weather conditions.

The biggest problem associated with the use of the closed loop, is: "What do you do with the large amounts of fluosilicic acid generated?"

The market for fluosilicic acid is currently about 60,000 tons per year of 100% fluosilicic acid. This market could be totally satisfied by one or two plants producing fluosilicic acid, depending on their size, not allowing the rest of the industry to economically employ such a route to answer the fluorine and its related emission problems. Therefore it was really not a viable solution.

Another alternative to selling fluosilicic acid would be to completely neutralize it with lime stone and/or lime. This is an extremely costly answer to the problem for it would cost a 1,000 TPD P_2O_5 phosphoric acid unit approximately \$12,500 per day to maintain a pH of 3.5 in these systems. In addition, there is not enough lime production capacity in all of Florida to handle the requirements of maintaining a pH of 3.5% in the conventional cooling pond and gypsum loop of the plants located in Florida.

In conclusion the PECO Closed Loop System does resolve the problem of fluorine emission to the atmosphere and contamination of the ground water. However, due to the limited market for the fluosilicic acid produced it was not economically viable in and of itself.

Recognizing this, in 1989 PECO embarked on a program to develop a use for fluosilicic acid which would expand the market and create a demand for the large amount of fluosilicic acid capable of being produced by the phosphate industry.

3.0 PECO P2O5/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 aluminum fluoride. The market demands for hydrogen fluoride and aluminum fluoride are sufficient to absorb most of the hydrogen fluoride that could be produced by the phosphate industry.

The initial invention of the PECO/P₂O₅ HF Process occurred in August of 1989. This invention was registered with PECO's patent attorney of Dowell and Dowell in Washington DC. Mr. Ralph Dowell 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.

The bench scale testing and pilot plant operation of the P_2O_5 /calcium fluoride portion of the PECO P_2O_5 /HF Process was conducted under a loan provided by the Florida Institute for Phosphate Research.

On July 20, 1992, the United States Department of Commerce Patent and Trademark Office issued a Notice of Allowance to PECO for thirty-three claims of the thirty-eight claims requested. The patent was formally issued on January 19, 1993. Based on this United States patent, foreign patents have been obtained in several critical countries throughout the world.

This new process converts a process waste stream contaminant and environmental pollutant, fluorine, into several saleable fluoride products. The use of this process will make the elimination of fluorine in phosphoric acid plant cooling ponds economically motivated rather than driven by legislative mandate.

Currently, PECO, under contract to FRS Partners, is about to complete 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 FRS Partners. The design basis for this facility is summarized in Table 3.

TABLE 3

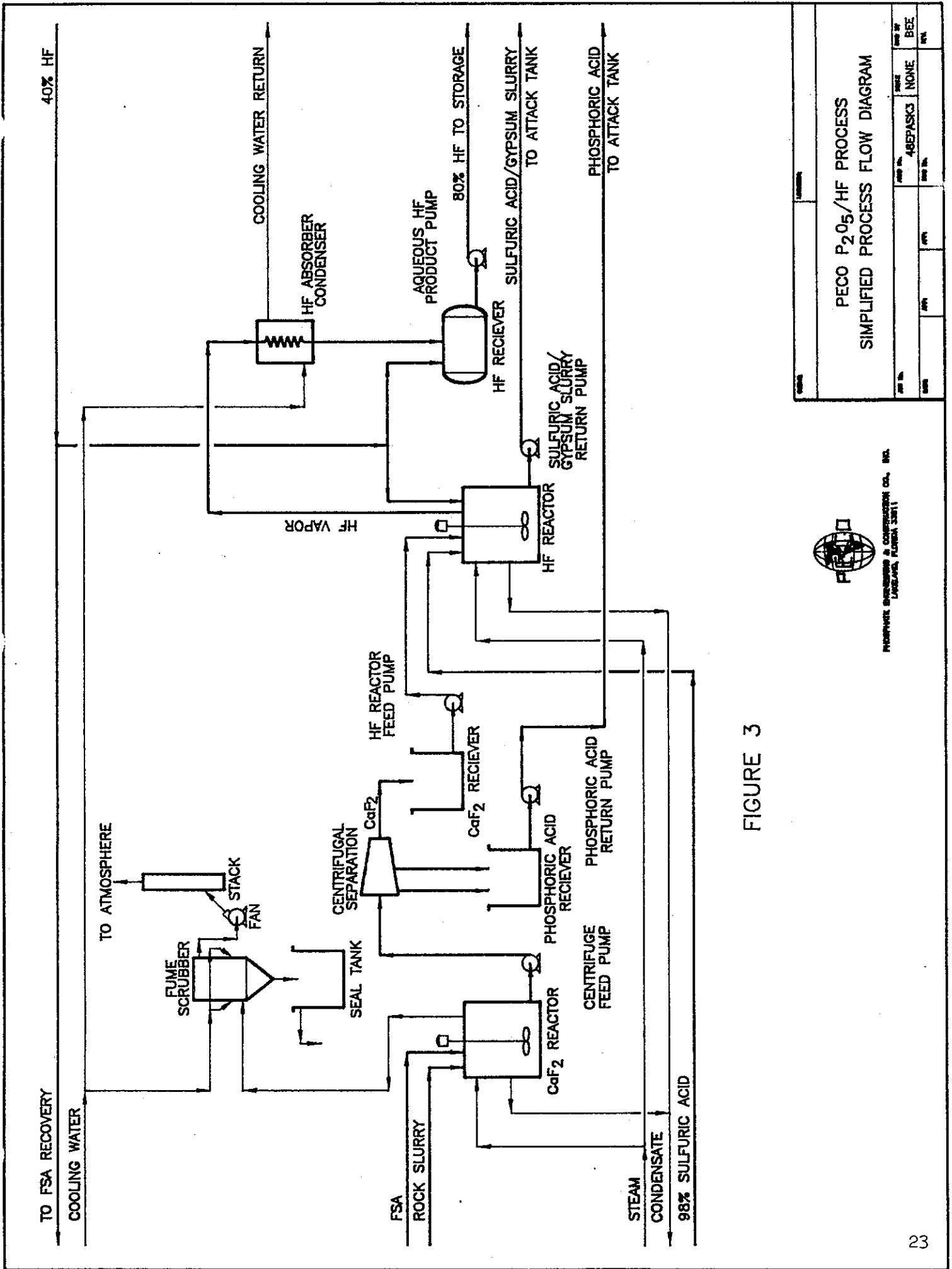
DESIGN BASIS

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

3.1 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



PECO P₂O₅/HF PROCESS
SIMPLIFIED PROCESS FLOW DIAGRAM

FIGURE 3

and silica (Phosphoric Acid/Calcium Fluoride Production Area).

In the final step hydrogen fluoride vapors 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.

The following description is of the first commercial PECO P_2O_5/HF Process currently under design.

3.1.1 Phosphoric Acid/Calcium Fluoride Production Area

The Phosphoric Acid/Calcium Fluoride Production Area for the PECO P_2O_5/HF Process includes the following:

P_2O_5/CaF_2 Reaction System

CaF_2 Separation and Concentration System

The process produces three times the quantity of P_2O_5 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 19% P_2O_5 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% CaF_2 by weight with a fluorine to silica ratio of 168 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_2O_5	18.7
CaO	0.23
Al_2O_3	0.012
Fe_2O_3	0.26
MgO	0.20
F	0.47
SO_4	0.15
SiO_2	0.24

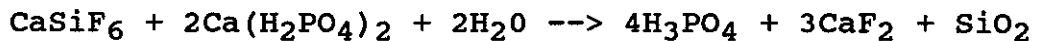
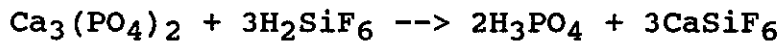
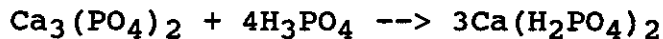
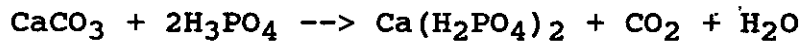
Phosphoric acid and calcium fluoride are produced by reacting phosphate rock and fluosilicic acid in a medium of phosphoric acid and calcium fluoride. The basic raw materials are 68 BPL (Bone Phosphate of Lime) ground phosphate rock slurry and 23% fluosilicic acid.

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 P_2O_5 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.

3.1.1.1 PECO P_2O_5 /CaF₂ Reaction System

The PECO P_2O_5 /CaF₂ Reaction System consists basically of a single reaction vessel with suitable agitation, internal heat exchanger, fume ventilation, raw material feed systems, and a reaction product surge and transfer system.

3.1.1.2 Calcium Fluoride Separation and Concentration System

In the PECO P_2O_5 /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.

3.1.2 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

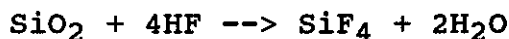
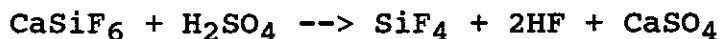
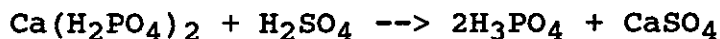
Hydrogen fluoride is produced by reacting the calcium fluoride/phosphoric acid slurry with concentrated sulfuric

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 P_2O_5 /HF Process requires only 4.65 tons of sulfuric acid (100% basis) per ton of HF (100% basis) be returned to the attack system.

3.1.2.1 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.

3.1.2.2 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.

3.1.3 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%.

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

3.2.1 Acid Quality

The PECO P₂O₅/HF Process provides an incremental increase in the production of phosphoric acid by profitably converting fluorine, 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.

3.2.2 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. In addition, the operation of the evaporation circuits within the plant is not limited by the production of fluosilicic acid since P₂O₅ contamination is not detrimental

to the production of phosphoric acid by the PECO P_2O_5 /HF Process. In fact, P_2O_5 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 P_2O_5 /HF Process.

3.3 PROCESS RESULTS

- A. Fluosilicic acid can be reacted with phosphate rock to produce a nominal 19% P_2O_5 phosphoric acid. Since phosphoric acid is produced by this process, relatively high levels of P_2O_5 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.
- B. 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 P_2O_5 ratio one-fourth of the current levels with a typical analysis of: 18.7% P_2O_5 , 0.23% CaO, 0.012% Al_2O_3 , 0.26% Fe_2O_3 , 0.20% MgO, 0.47% F, 0.15% SO_4 , and 0.24% SiO_2 .
- C. The PECO P_2O_5 /HF Process consumes only 2.0 tons of sulfuric acid per ton of P_2O_5 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.

- D. Silica is separated from the fluorine such that the fluorine to silica ratio in the calcium fluoride/phosphoric acid slurry is 168. The fluorine to silica ratio for commercially acceptable fluospar is 70 to 100.
- E. An overall recovery of 75% of the fluorine fed to the process as fluosilicic acid is recovered as an 80% hydrogen fluoride solution.
- F. 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 a simple distillation process.
- G. 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 P_2O_5 /HF Process.
- H. 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.

4.0 SUMMATION

As public awareness of the negative impact of fluorine on the environment increases, along with the recognition of the hazardous effects of fluorine on workers, the need to control and/or eliminate fluorine emissions to the atmosphere becomes even more important.

The best way to eliminate the fluorine emissions from the cooling ponds is to eliminate the cooling ponds themselves. This can be done with the installation of the PECO Closed Loop System. As more phosphate producers recover more fluosilicic acid, there will be a need for a larger market for this waste product. The PECO P2O5/HF Process fills that need by consuming the fluosilicic acid as a raw material to produce phosphoric acid and valuable hydrogen fluoride thereby providing a demand for large quantities of fluosilicic acid.