# PECO HF PROCESS

by

Leif E Bouffard
Vice President
of
PHOSPHATE ENGINEERING & CONSTRUCTION CO.
Lakeland, Florida

and

G. Michael Lloyd Jr.
Research Director - Chemical Processing
of
FLORIDA INSTITUTE OF PHOSPHATE RESEARCH
Bartow, Florida

Presented at
American Institute of Chemical Engineers
Joint Meeting
Clearwater, Florida
May 25, 1991

# PECO HF PROCESS

## Table of Contents

# 1.0 INTRODUCTION

Phosphate Engineering & Construction Company, Inc. (PECO), founded in 1973 in Lakeland, Florida, is a diversified engineering and development company striving to assist companies in becoming more efficient and productive. Since its inception the company has performed services for several industries with principal involvement in the phosphate industry.

Recently PECO embarked on a research program that has resulted in the development of a new process which converts a process waste stream contaminant, fluorine, into several profitable fluoride products. The use of this process will make the reduction of fluorine in phosphogypsum cooling ponds an objective driven by profit motivation rather than by legislation.

PECO was awarded a grant from Florida Institute of Phosphate Research (FIPR) to perform bench and pilot plant scale investigations to verify the technical and economic viability of the PECO HF Process. This report is a nonconfidential summary of this investigation.

# 2.0 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 30,000 to 40,000 tons per year.

A market does exist for fluoride products; however, 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 HF Process could provide a significant additional profit to the phosphate producers and at the same time reduce the inventory of fluorine on the plant site.

## 2.1 Fluorine Availability

Wet process phosphoric acid is normally produced by chemically attacking the phosphate rock with concentrated sulfuric acid in a medium of phosphoric acid and calcium sulfate (gypsum). The fluoride fraction of the phosphate rock is converted in the reaction step to silicon tetrafluoride and hydrogen fluoride which are evolved during the subsequent concentration step. The fluorine evolved during the reaction step is typically absorbed into pond water in order to limit the quantity of fluorine emitted from the process and thus meet existing environmental standards. The fluorine evolved during the concentration step is either recovered as fluosilicic acid or is absorbed into the pond water used to condense the water vapor liberated during the evaporation process.

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 the 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.

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. Operating these systems in conjunction with PECO's closed loop cooling system would increase the amount recovered to approximately fifty percent.

## 2.2 Fluoride Market

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. Currently this market is not 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 HF Process separates the silica from the fluorine and opens up the more profitable fluoride chemical market to the phosphate industry.

### 2.2.1 Supply and Demand

Fluoride chemicals and chlorofluorocarbons (CFC) currently make up a three billion dollar United States market* and should reach six billion by 1994. Recent media attention has been focused on eliminating the ozone destroying CFCs and extremely high taxes have been imposed on their use. Major United States companies have developed replacements for these ozone destroying CFCs and their use will result in a large increase in the consumption of hydrogen fluoride. Because of this the market for hydrogen fluoride is expected to increase and the price is predicted to rise at the rate of 3.5% per year.

---

* All references to trends and prices were obtained from personal telephone quotes from various suppliers and numerous trade journals.

The table below shows the percent of the total market of hydrogen fluoride by areas of consumption. The bulk of this market is fluorocarbon production and amounts to 228,000 tons per year. Approximately 500 million dollars of the total market is directed to raw materials and specialty chemicals other than the CFCs.

PERCENT OF TOTAL U.S. MARKET OF HYDROGEN FLUORIDE

| Areas of Consumption of HF | Total Market Percent | Total Market Tons/Year |
|---|---|---|
| Fluorocarbons | 57 | 228,000 |
| Aluminum Fluoride | 17 | 68,000 |
| Fluorochemicals | 12 | 48,000 |
| Steel, Glass Metals (70% HF) | 7 | 28,000 |
| HF Alkylation | 4 | 16,000 |
| Uranium | 3 | 12,000 |

Chemical Profile 7/25/88, Chemical Marketing Reporter

Approximately 17% (68,000 tons per year) of the total hydrogen fluoride produced in the United States is used to produce aluminum fluoride necessary for the production of aluminum. Fluorochemicals comprise 12% of the market (48,000 tons per year). Surfactant uses include disbursements in paints, coatings and printing inks, and certain fine fluorochemicals are used as intermediates in the synthesis of such products as agricultural chemicals and pharmaceuticals. Applications for soil and water repellents include water proofing sports wear, making carpets stain resistant and grease proofing pet food bags. The fluorinated oils and fluids are used as lubricants for pump bearings in hostile environments such as liquid oxygen and as fluids for high performance vacuum pumps. An aqueous solution of 70% hydrogen fluoride (28,000 tons per year) is used in the steel and glass industries. The remaining 7%, or 28,000 tons per year, is consumed in the hydrogen fluoride alkylation process of the petroleum industry and uranium processing.

Two major companies generate about 50% of the domestic hydrogen fluoride produced. The primary source of fluorine used in this production is mineral calcium fluoride. Ninety-five percent of the calcium fluoride required to satisfy the American market is being imported, primarily from Mexico with increasing amounts supplied by China and South Africa. A very insignificant tonnage of fluoride chemicals are currently being produced from the waste fluosilicic acid of the phosphate industry.

Approximately 600,000 tons per year of fluorine is contained in the phosphate rock processed in the state of Florida for phosphatic chemicals. Only 20,000 to 30,000 tons per year of this material is converted to sodium silicofluoride for use as a water fluoridation chemical and a very small amount is converted into aluminum fluoride.

### 2.2.2 Chemical Prices

The major United States producers report charging a list price of 68.75 cents per pound of anhydrous hydrogen fluoride ($1375 per ton) and say that rising demand is putting an upward pressure on pricing. Significant discounts are no longer being made to the list price.

Aluminum fluoride prices have been quoted at $1100 to $1200 per ton and many suppliers have indicated that the material is in extremely short supply. Ammonium bifluoride salts are selling for $1500 per ton in Texas where it is being used to reactivate low or non-producing oil wells. Sodium bifluoride is quoted at $1.02 per pound or $2,040 per ton. Conventional wisdom indicates that these prices will remain in effect for the foreseeable future.

| | %F |
| --- | --- |
| Gyp | 20 |
| Phosphate | 20 |
| Evolved | 60 |
| FSA | 25 |

100 lb FSA / T $P_2O_5$

28 - 54

60% of F after acid conc. to 54

## 3.0 PECO HF PROCESS

A grant was awarded by Florida Institute of Phosphate Research (FIPR) to Phosphate Engineering & Construction Company (PECO) for the purpose of conducting research to determine the technical and economical feasibility of producing phosphoric acid, hydrogen fluoride and/or fluoride salts from fluosilicic acid. This work was conducted in two phases. The first phase consisted of reacting the fluosilicic acid and phosphate rock to affect a separation of the fluoride and silica components of the fluosilicic acid on a bench scale. Once this separation was demonstrated the second phase of the contract was to conduct the reaction on a continuous basis and to subject the reaction products to separation tests on a pilot scale. Representative material from these pilot tests was then used to recover hydrogen fluoride in a bench scale program.

In the first phase the chemical reaction proceeded as stated and the silica was effectively separated from the fluorine. Parameters affecting the separation of the fluorine from the silica were also optimized. Phase two of this project optimized the production of phosphoric acid and maximized the recovery of fluorine.

## 3.1 Process Description

The PECO HF Process produces wet process phosphoric acid by reacting phosphate rock and fluosilicic acid and subsequently recovering the fluorine as hydrogen fluoride.

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 with a fluoride concentration of 12% from the undigested rock and silica. In the final step hydrogen fluoride vapors are recovered from the silica free phosphoric acid. The vapors from this step are condensed to form a water solution of concentrated hydrogen fluoride. The phosphoric acid stripped of hydrogen fluoride is returned to the phosphoric acid plant for further processing. The concentrated hydrofluoric acid can either be sold directly or processed further to produce high value fluoride salts using existing technologies.

## 3.2 Process Investigation Results

A. Fluosilicic acid can be reacted with phosphate rock to produce a nominal 18% $P_2O_5$ 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 0.75 ton phosphoric acid was produced for each ton of fluosilicic acid fed to the system. The quality of the phosphoric acid produced had an impurities to $P_2O_5$ ratio one-fourth of the current levels with a typical analysis of: 17.7% $P_2O_5$; 0.012% $Al_2O_3$; 0.26% $Fe_2O_3$; 0.20% MgO; and 0.72% F.

C. Silica was separated from the fluorine such that the fluorine to silica ratio in the fluoride laden phosphoric acid was 100 to 150. The fluorine to silica ratio for commercially acceptable fluospar is 70 to 100.

D. Hydrogen fluoride was recovered at temperatures low enough to use plastics as materials of construction. This results in a low initial capital cost as well as low maintenance costs.

E. An overall recovery of 69% of the fluorine fed to the process as fluosilicic acid was recovered as a 70% to 80% hydrogen fluoride solution.

F. The hydrogen fluoride was produced as an 70% to 80% solution. Since this concentrated hydrofluoric acid is well above the 37% azeotrope, anhydrous hydrogen fluoride could be produced by a simple distillation process.

G. Sodium bifluoride was produced from the concentrated hydrofluoric acid.

H. The optimum amount of raw materials which achieved the best conversion of fluosilicic acid to hydrogen fluoride consistent with the maximum yield of hydrogen fluoride was determined.

I. Data was obtained for the design of a commercial unit for the production of the hydrogen fluoride solution. It is felt that existing technology currently practiced on a commercial basis can be used to produce anhydrous hydrogen fluoride, aluminum fluoride, sodium bifluoride, and ammonium bifluoride from the concentrated hydrofluoric acid produced by the PECO HF Process.

### 3.3 <u>Advantages of the PECO HF Process to the Operation of a Phosphoric Acid Complex</u>

The PECO 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 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 HF Process phosphate rock with very high impurity levels can be used in the PECO HF Process.

HF $1,375/#
$AF_3$ 1000-1200

$NH_3HF_2$ - $1500/ton
Na BiFl. - $2040

### 3.3.1 DAP Grade

The ratio of the magnesium, aluminum, and iron impurities as MgO, $Al_2O_3$, and $Fe_2O_3$, to $P_2O_5$ in the phosphoric acid produced by the PECO HF Process are 0.011, 0.0007, and 0.015 respectively. This is a reduction of approximately 75% of the impurities currently associated with wet process phosphoric acid produced in the Bone Valley.

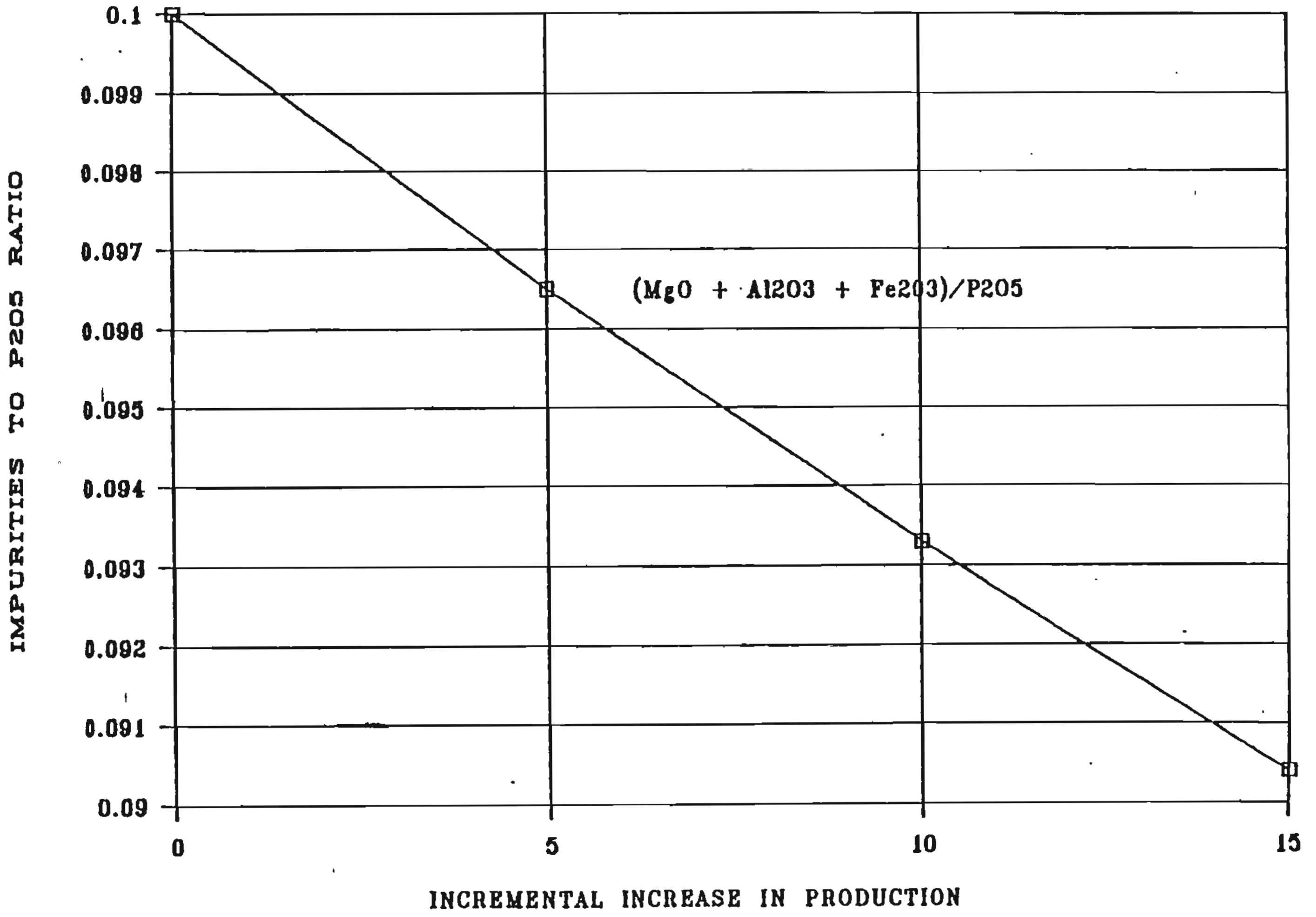
At this level of impurities the phosphoric acid produced by the PECO HF Process results in approximately a 0.70% decrease in the impurities ratio in the phosphoric acid produced by the complex for each percent increase in incremental production. This in turn provides for a corresponding proportional increase in DAP grade.

In Figure 1 the ratio of impurities (MgO, $Al_2O_3$, and $Fe_2O_3$) to $P_2O_5$ in the total production of phosphoric acid is plotted as a function of incremental capacity. The relationship is essentially linear with a base line ratio of 0.10. At a 5% increase in production the ratio reduces to 0.966 and at 10% reduces to 0.933.

The overall result benefits the phosphoric acid complex in two ways. First, it may allow a meaningful reduction in the use of urea necessary to achieve the mole ratios required for commercial DAP. Alternately, it may allow the use of phosphate rock with slightly higher impurities than is currently being used by a particular processor while

# FIGURE 1

RATIO vs PRODUCTION



maintaining current DAP grade. Both of these benefits can result in small reductions in production costs which when multiplied by the high volume typical of the phosphate fertilizer industry can result in measurable increases in profits.

### 3.3.2 Operating Factor

A major benefit of the PECO 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 HF Process is dependant on the operation of the phosphoric acid plant while the phosphoric acid plant operation is completely independent of the operation of the PECO HF Process. In addition, the operation of the evaporation circuits within the plant is not limited by the production of FSA since $P_2O_5$ contamination is not detrimental to the production of phosphoric acid by the PECO HF Process. In fact $P_2O_5$ currently lost during the evaporation step would be recovered in the FSA scrubbers and returned to the phosphoric acid plant in the acid produced by the PECO HF Process.

# 4.0 CAPITAL AND OPERATING COSTS

An order of magnitude capital cost estimate was prepared for a 14,000 tons per year sodium bifluoride production plant using the PECO HF Process. The commercial facility is estimated to cost four million dollars based on the data developed during the bench and pilot plant investigations of the PECO HF Process.

This capital estimate is based on a battery limits process plant and does not include storage of raw materials and products or waste disposal costs. It was assumed that utilities are available at battery limits at costs typical of the Florida phosphate industry. It was also assumed that space was available within the phosphoric acid complex to accommodate the commercial facility. Normal staffing for this operation would be one supervisor, operator, and assistant operator per shift.

The facility can produce either 14,000 tons per year of sodium bifluoride or 9,000 tons per year of concentrated hydrofluoric acid (100% basis). The process consumes 16,000 tons per year of fluosilicic acid, 55,200 tons per year of 68 BPL phosphate rock, and 26,240 tons per year of sulfuric acid (all on a 100% basis). In addition, the plant produces 12,000 tons per year of $P_2O_5$ as phosphoric acid of nominal 18% $P_2O_5$ concentration.

It was purposed for this economic analysis that 0.75 tons of $P_2O_5$ as phosphoric acid could be exchanged for one ton of fluosilicic acid valued at $60 a ton and 3.45 tons of phosphate rock (both on a dry basis). Using these assumptions the production cost of the concentrated hydrofluoric acid calculates to $188 per ton on a 100% basis. This figure includes labor and maintenance plus fixed costs such as overhead, taxes, insurance, and depreciation.

$\frac{12,000}{17,000}$ = $P_2O_5$ yield

Feeds

$H_2SiF_6$ 16,000

Phos Rock 55000

$H_2SO_4$ 26,000

Pos acid 12,000 @ 18% $P_2O_5$

HF 9,000

## 5.0 KEY POINTS

* The bench and pilot plant programs have demonstrated the technical capability of the PECO HF Process to produce phosphoric acid and hydrogen fluoride from phosphate rock and fluosilicic acid.

* The process provides a profitable method of reducing the fluoride content in phosphogypsum cooling ponds.

* Production costs for fluoride salts are low due to a credit for the phosphoric acid produced by the process and the low capital cost required to build a commercial production facility.

* The PECO HF Process produces over 0.75 ton $P_2O_5$ as phosphoric acid for each ton of fluosilicic acid (100% basis) input.

* The PECO HF Process can increase the production capacity of the phosphoric acid complex by five percent.

* The phosphoric acid produced by the PECO HF Process rejects much of the magnesium, aluminum, and iron in the rock resulting in a low impurity acid with an impurities to $P_2O_5$ ratio that is one quarter of current levels.

* The low impurity acid provides for a nearly linear reduction in the impurities level of the complexes entire production of $P_2O_5$ resulting in an increase in the mole ratio of DAP.

* Incorporating the closed loop cooling system can increase the recovery of fluorine and production of phosphoric acid by a factor of two.

* An overall recovery of 69% of the fluorine in the fluosilicic acid fed to the process can be recovered as a 70% to 80% aqueous hydrogen fluoride solution.

## 6.0 SUMMARY

The PECO HF Process is a low cost route to produce concentrated hydrofluoric acid, anhydrous hydrogen fluoride, aluminum fluoride, sodium bifluoride, and ammonium bifluoride. The primary raw material for the production of these fluoride products is fluosilicic acid recoverable by the phosphate producer from his phosphoric acid concentration step. This in conjunction with PECO's patented closed loop cooling system increases the recovery of fluorine by a factor of two. In addition it lowers the fluorine content in the pond water system to a level wherein the controversy surrounding fluorine becomes a mute point.

A domestic market has been documented at 400,000 tons per year of fluoride products and is predicted to increase to 500,000 tons per year by 1994. Ninety-five percent of the fluorine consumed in the United States is made from calcium fluoride imported from South Africa, China, and Mexico. If all the fluorine required for this market is supplied by the PECO HF Process, approximately 45 plants would be needed.

Each of these plants, capable of consuming 16,000 tons per year of fluosilicic acid (100% basis) at a capital cost of four million dollars, would be installed adjacent to a phosphate complex and would be sized to consume the fluorine recovered from a 1,000 tons per day $P_2O_5$ phosphate operation. The plant would be designed to accommodate the production of whichever fluoride salt the market demanded.

A second product of the PECO HF Process is phosphoric acid which would be returned to the phosphate producer for credit substantially underwriting the cost of the fluosilicic acid raw material. This credit for the phosphoric acid, combined with the low capital cost, makes the process an attractive, low cost method for producing valuable fluoride products.

Unlike the process developed by the US Bureau of Mines this process removes virtually all of the silica from the fluorine recovered from the fluosilicic acid. Other processes which produce phosphoric acid using fluosilicic acid are an integral part of the production of wet process phosphoric acid. The PECO HF Process is separate from the production of wet process phosphoric acid and does not negatively impact the efficiency or operating factor of the phosphoric acid plant. In addition to an incremental increase in production, another advantage is the extremely low impurities content of the acid which results in an almost directly proportional decrease in the impurities content of the phosphoric acid produced by the phosphoric acid plant.

The process has been demonstrated in a bench and pilot plant test program with the results providing a sound basis for engineering a commercial production unit. Patents have been applied for and a patent search indicated that the process does not infringe on any existing patents.