

PHOSPHATE PROCESSING

2001

By

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I. ABSTRACT

It is now the year 2001. Economic and environmental pressures have forced the phosphate industry to significantly change practices developed 25 years ago. Direct acidulation of matrix was instituted to expand the reserves, reduce water requirements, and eliminate slime holding ponds. Impurities such as magnesium and toxic cadmium are being removed from the crude acid using ion exchange technology. The magnesium impurities are being sold as a micronutrient. Closed loop cooling systems which eliminate cooling ponds and prevent the emission of fluoride pollutants have been incorporated into and are an integral part of the operating facility. The fluorine recovered from this cooling system is being processed into a highly profitable hydrogen and aluminum fluoride compounds. Phosphoric acid is being converted into a high analysis monopotassium phosphate containing 80 units of plant nutrients which can be stored indefinitely as a solid, or applied as a solution when required, due to its high water solubility.

This is what the fertilizer industry looks like in the year 2001; however, the technological breakthroughs that laid the foundation for it occurred in the year 1990.

II. INTRODUCTION

Over ten years have passed since the Florida Sections of the American Institute of Chemical Engineers held their Joint Meeting in Clearwater, Florida. As predicted in the January 1990 issue of the Chemical Processing Magazine the growth of the Chemical Processing Industry has been limited by the availability of raw materials such as oil, gas, potash, phosphate rock, sulfur as well as electricity. Historically, low raw material prices and abundant supplies earned producers substantial profits by converting these materials into primary chemicals. But increased governmental control of these primary materials drove prices into rapid escalation and disrupted supply. This forced the industry to find new ways to enhance the value of their products to maintain profitability. In addition to these economic pressures, increasing pressure from society at large and the government in particular pushed companies to accept responsibility and assume liability for producing hazardous chemicals, generating hazardous wastes, consuming precious water and other negative impacts upon the environment.

Fortunately for the Fertilizer Industry, technology was already available for this time of transition.

Phosphate Engineering and Construction Company (PECO) had been engaged in developing new processes anticipating the needs of the

fertilizer industry in the 1990's and beyond. Some of the processes commercialized by PECO over the last ten years are:

1. Producing phosphoric acid from unbeneficiated phosphate ore.
2. Removing magnesium and cadmium from phosphoric acid.
3. Producing low chloride monopotassium phosphate from phosphoric acid and potash.
4. Eliminating fluoride pollution from phosphoric acid plants using a closed loop cooling system .
5. Producing phosphoric acid and hydrogen fluoride from phosphate rock and fluosilicic acid.
6. Producing potassium sulfate from waste metallic sulfate streams.

III. PCS/PECO ACIDULATION PROCESS

A. GENERAL

The use of chemical fertilizers derived from phosphoric acid has increased greatly during recent decades with most of the increased production of finished products coming from North Africa. While there continues to be a strong worldwide need for fertilizers and phosphate chemicals, many of the high grade easily mined phosphate rock deposits were depleted, leaving only lower grade ores with higher levels of impurities. Conventional beneficiation techniques resulted in increasingly lower recoveries of phosphates thereby decreasing the supply of raw material.

Many deposits, too poor to be practically upgraded or containing impurities which could not be mechanically separated from the phosphate ore, could no longer be used in conventional phosphoric acid reaction systems.

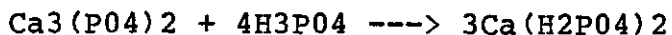
The introduction of a PCS/PECO acidulation process in the early 90's increased the amount of phosphates recovered as product acid from fifty pounds of P_2O_5 per one hundred pounds of P_2O_5 mined from the deposit to eighty-five pounds.

This improvement in recoveries increased the recoverable reserves by 50% or more and was achieved through efficient recovery of the P_2O_5 values normally lost with the slimes and tailings fractions

of the beneficiation process. What made the PCS/PECO acidulation process so novel was the way it treats the mixture of coarse and fine solids and recovers these lost phosphates. In the process the coarse solids flow counter-current to the flow of recycle acid thereby contacting progressively stronger acid as they move through the reactors finally contacting the strongest acid (recycle acid from the gypsum crystallizer) just prior to leaving the reaction system. The fine solids move co-current with the flow of recycle acid both from the point of entry of the ore to the system and from the point of formation due to dissolution of the larger particles. This combination greatly enhances solubilization of the tricalcium phosphate. Consequently, it also results in effective washing of the different rejected solids in order to recover soluble product.

B. PROCESS DESCRIPTION

The process involves reacting unbeneficiated phosphate ore with phosphoric acid to produce a monocalcium phosphate/phosphoric acid solution as shown by the following equation:



Subsequently, the monocalcium phosphate is converted to phosphogypsum and phosphoric acid by the reaction of monocalcium phosphate and sulfuric acid as shown by the following equation:



A simplified process flow diagram of the acidulation process is shown in Figure 1.

ORE FEED PREPARATION

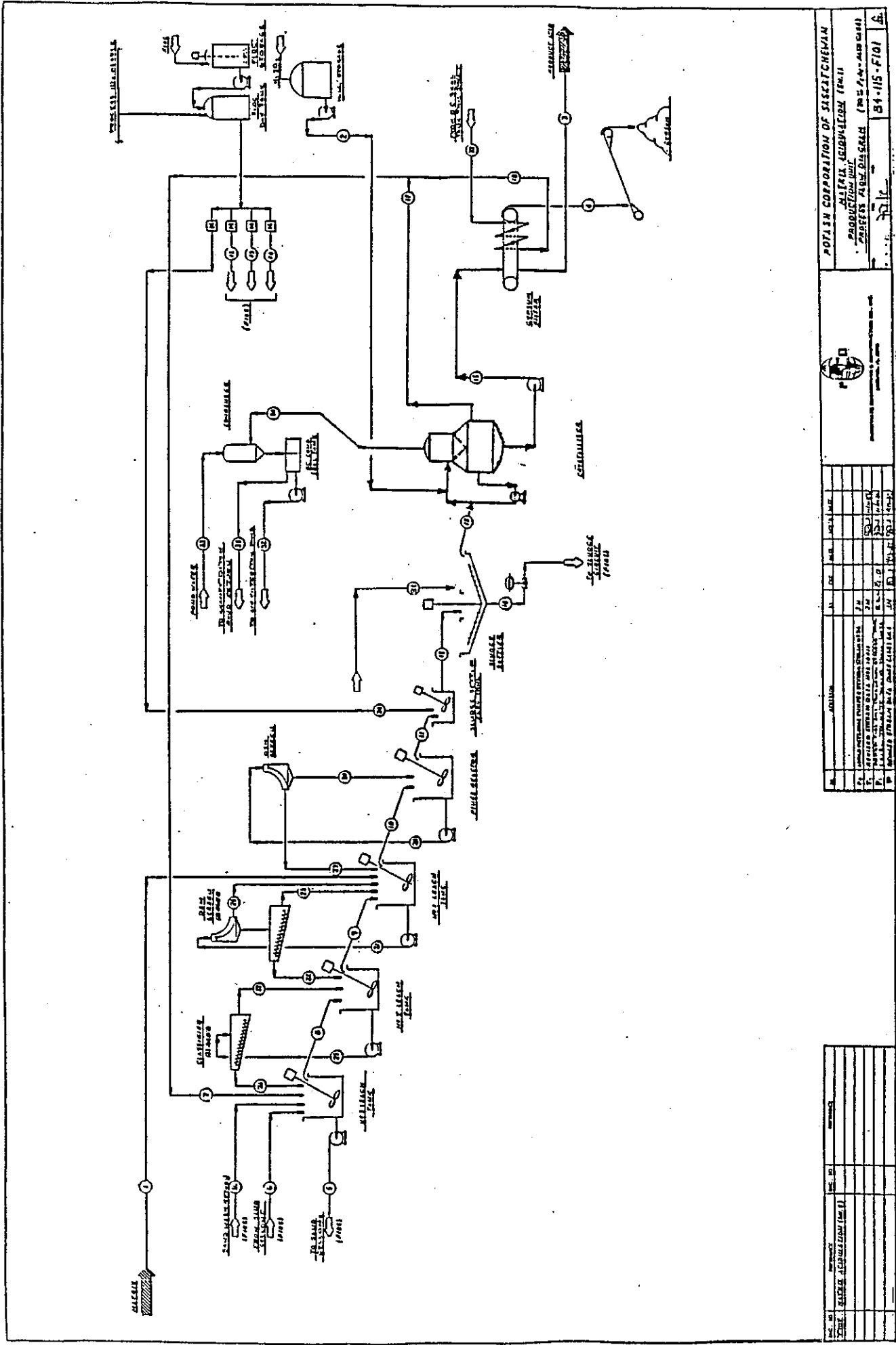
Unbeneficiated phosphate ore is received from storage and placed in surge bins. The ore, dewatered through dewatering panels located on the surge bins, is screened to separate the oversize (+1/4 inch) fraction which then is crushed in a hammermill and rescreened. The unground on-spec materials are conveyed to the ore leaching area. The oversize from the second screening operation is returned to the surge bin for reprocessing. This results in a substantial savings of electrical power previously consumed by the requirement to grind the rock prior to acidulation.

ORE LEACHING

The phosphate ore is metered into a leach circuit where it is contacted with a circulating mass of phosphoric acid containing a nominal 20% P_2O_5 . The coarse material moves counter-current to the gravity flow of the leach acid and the fines move co-current with the flow of the leach acid.

The undigested sand fraction of the ore exits the No. 3 leach tank for subsequent separation of the sand and acid.

The fines, or slimes, fraction of the ore exits the fines reactor for concentration in the sludge settler.



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 СИСТЕМА СИСТЕМАТИКА
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Figure 1

SLUDGE CIRCUIT

The overflow from the fines reactor and the return acid from the sludge separator operation are gently mixed with flocculant in the sludge flocculator tank and then flows to a settler equipped with a rake. The sludge laden underflow from the settler is pumped to a series of centrifuges for separation of the solids and is water washed to recover water soluble P_2O_5 . Approximately 75% of the P_2O_5 in the slimes fraction of the feed ore is recovered in this circuit. The clear overflow from the sludge settler is pumped to vacuum crystallizers for conversion of monocalcium phosphate to gypsum and phosphoric acid. The fine material, generally clays or slimes, discharged from the process contains the same approximate moisture content and physical characteristics as phosphogypsum. This eliminates the enormous amounts of water retained by the clays associated with beneficiation. This not only resulted in a reduced demand for water but also eliminated the land requirements needed for large above ground slime holding ponds.

CRYSTALLIZATION

The clear overflow from the sludge settler is mixed with 98% sulfuric acid and transferred to two vacuum forced circulation crystallizers. Gypsum slurry from the crystallizers is pumped to the gypsum filter for recovery of product acid.

Clear overflow from the crystallizer is mixed with the No. 2 filtrate from the gypsum filter and returned to the No. 3 leach tank to repeat its cycle.

AREA 05 GYPSUM FILTRATION

The gypsum/phosphoric acid slurry from the crystallizer is filtered on a vacuum filter with a three-stage counter-current wash. The No. 1 filtrate is the product acid from the process. The wash filtrates are mixed with the crystallizer overflow providing the recycle leach acid. An excess of free sulfuric acid is required to precipitate the gypsum from the recycle acid. This free sulfuric acid results in the formation of gypsum in the leach circuit. Approximately 20% of the total gypsum formed is removed from the process along with the slimes. Most of the radioactive nuclei co-precipitates in the gypsum formed in the leach circuit. As a consequence, the gypsum separated on the gypsum filter is virtually free of radioactive material. This gypsum could be used directly or reprocessed into sulfuric acid and cement.

SAND CIRCUIT

The sand slurry from the No. 3 leach tank is pumped to a bank of cyclones to concentrate the sand before filtration. The clear overflow from the cyclones is returned to the No. 3 leach tank, while the 60% solids underflow is filtered on a horizontal vacuum belt filter equipped with a three-stage counter-current wash. Approximately 95% of the P_2O_5 in the sand fraction of the feed

ore is recovered in this circuit. The product and wash filtrates are combined and returned to the No. 3 leach tank. The coarse fraction, generally sand is discharged from the process separate from the fine residue. Separate discharge of the coarse and fine wastes made it possible to use the wastes more selectively. For example, in land reclamation the coarse and fine material could be placed separately or together.

IV. PECO ACID PURIFICATION PROCESS

A. GENERAL

In addition to the acidulation process the PECO acid purification process also resulted in a significant increase in the usable phosphate reserves because its ability to process high magnesium ore (1% to 2% MgO) into phosphoric acid has, in some cases, doubled the mineable phosphates reserves. In other cases ores previously considered unmineable with existing beneficiation methods, could now be profitably processed.

When phosphate rock is reacted with sulfuric acid to produce phosphoric acid, most of the impurities in the rock dissolve in the acid creating problems both in processing the acid and in converting it into phosphatic fertilizers. These impurities increase superacid viscosity, result in storage problems in ammoniated liquid fertilizers, and grade problems in DAP.

The PECO acid purification process utilizes conventional fixed bed ion exchange methods of contacting the solution with the resin to remove these impurities. This technology is well understood and had been practiced for some forty to fifty years. It is simple and has a very low capital cost when compared to other ion exchange systems.

It is well known that cationic resins can be used for the removal of cations from phosphoric acid. A cation, magnesium for

example, is loaded onto the resin from the phosphoric acid and then stripped from the resin by PECO's patented ammonium sulfate regeneration solution.

The PECO regeneration system is a closed loop and the only materials leaving the regeneration loop are the precipitated impurities. It was found that the magnesium precipitated from the regeneration loop had a market value, which in some cases, was enough to offset most of the cost of the operation. The process is also being used to control toxic cadmium levels in product acids and by-product gypsum.

B. PROCESS DESCRIPTION

Ion Exchange Area

A simplified process flow diagram of the ion exchange process is presented in Figure 2. Clarified filter acid is received via pipeline from the phosphoric acid plant and is stored in the agitated feed acid storage tank.

Then the acid is metered under flow control to the load cycle of the fixed bed ion exchange unit for transfer of the cation impurities (CaO , MgO , Fe_2O_3 , Na_2O , K_2O and Cd) from the phosphoric acid to the cation exchange resin. A specified volume of feed acid is passed through the resin depending on the type and concentrations of the cations in the acid being treated.

At this point, the feed acid flow is diverted to another fully regenerated chamber and a stream of pond water is used to

displace the volume of acid remaining in the first ion exchange resin bed.

The treated acid and a small portion of the pond water is returned to the phosphoric acid plant for further processing into concentrated acids or complex fertilizers while the cations loaded on the resin are stripped from the resin by the regeneration solution. This process transfers the cations from the acid to the regeneration solution producing the pregnant mother liquor. Enough regeneration solution must be passed through the loaded resin so that a complete transfer is accomplished providing a fully regenerated resin bed for the next load cycle.

When the recirculating regeneration solution accomplishes its purpose, it is diverted to another loaded chamber and a stream of pond water displaces the volume of regeneration solution remaining in the ion exchange resin bed.

The pregnant mother liquor and a small portion of the pond water returns to the crystallizer for precipitation of the cations removed from the treated acid.

The bulk of the pond water used to wash the resin after the load and regeneration cycles is pumped into the phosphoric acid plant for use as filter cake wash water.

V. PCS/PECO MKP PROCESS

A. GENERAL

The use of PCS/PECO matrix acidulation and PECO magnesium removal technology increased the supply of low cost raw material allowing some producers to earn a profit the old fashion way. But the PCS/PECO MKP process also provided a new way to add value to their products in order to increase profits while operating in a very competitive global market.

The production of an 0-50-30 monopotassium phosphate fertilizer product from wet process phosphoric acid and agricultural grade potash was a significant economic breakthrough. Prior to its introduction, MKP was produced from furnace grade phosphoric acid and potassium hydroxide at a cost which prohibited its use as a chemical fertilizer.

The analysis of the product now produced by this process is presented on Table 1 showing its general high purity.

The primary market for MKP is in the preparation of clear liquid fertilizers. When 10-34-0 liquid fertilizers were found to cause nitrogen ground water contamination, 0-50-30 MKP replaced it as a base material in liquid fertilizers preparation. Two other advantages of the 0-50-30 material were its extended shelf life (by a factor of years) and its increased units of plant food per ton of product.

Table 1

MONO-POTASSIUM-PHOSPHATE TYPICAL ANALYSIS

<u>Element</u>	<u>Analysis - %</u>
P2O5	51.42
K	28.54
CL	0.0160
SO4	0.7900
FE	0.0019
AL	0.0090
MG	0.0012
F	Less than 0.0050

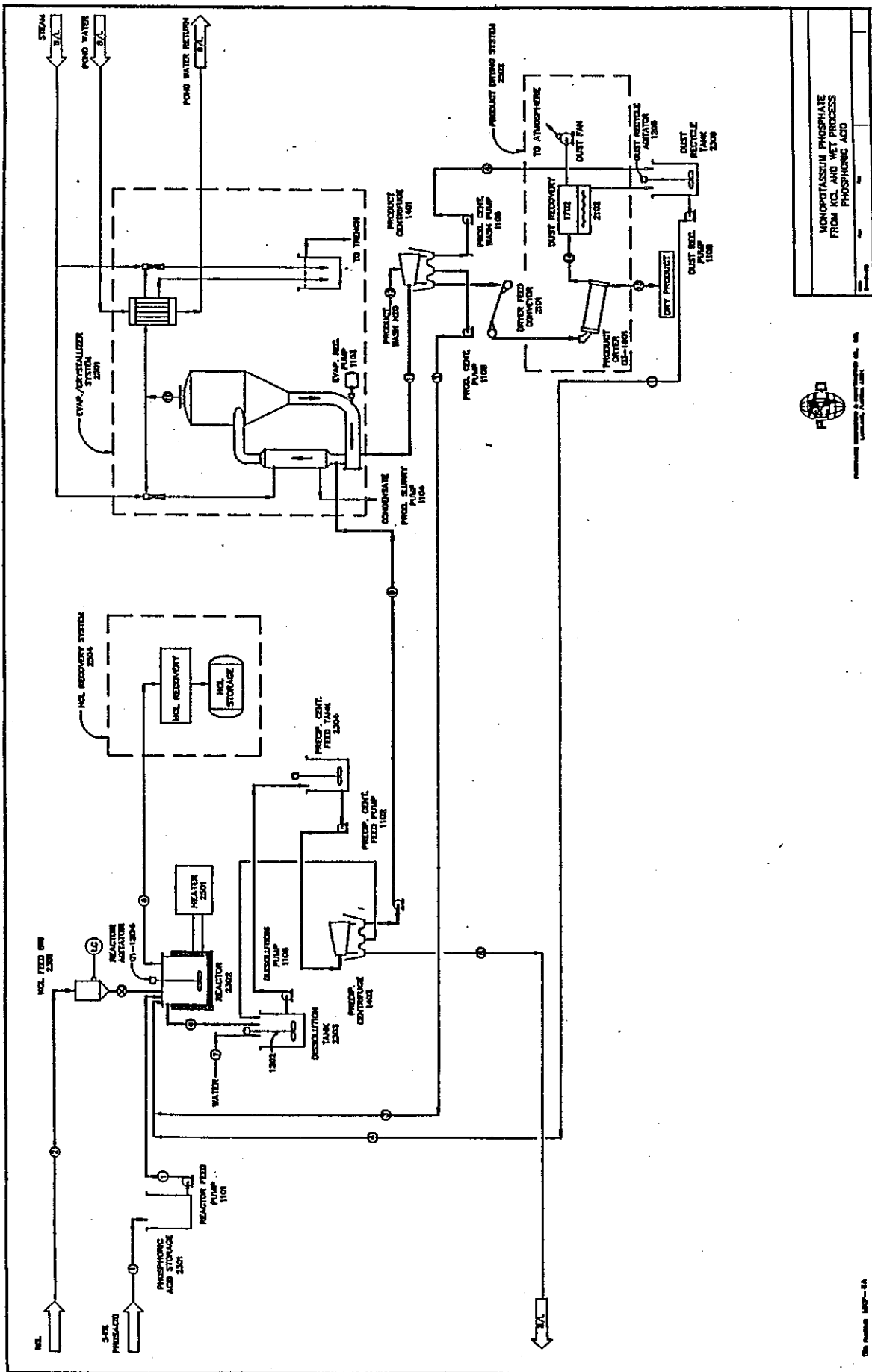
And since more can be done with less because of the high nutrient content of the 0-50-30 material, shipping and storage costs were significantly reduced. So this high concentration fertilizer was shipped throughout the world as the most economical way of supplying the necessary plant nutrients to a global community.

Also, the high purity MKP has proved to be excellent base material for building tetrapotassium pyrophosphate material in the detergent industry at a cost competitive with sodium tripolyphosphate.

B. PROCESS DESCRIPTION

A simplified process flow diagram of the MKP process is shown in Figure 3. Wet process phosphoric acid is mixed directly with potassium chloride and heated for a sufficient time and under conditions which allow evolution of the resulting hydrogen chloride from the melt as a gas. The resulting melt is mixed with water, centrate from the product recovery centrifuge, and wash solution from the filtration step. This forms a solution of soluble product monopotassium phosphate, unreacted potassium chloride, and double salt, plus a precipitate derived from the impurities in the phosphoric acid.

The precipitate is separated from the solution by any suitable means, such as filtration. The filter cake is washed to recover product and unreacted ingredients. The wash solution is recycled for dissolution of the reaction melt. The final washed cake exported from the process is a low grade potassium phosphate



MONOPOTASSIUM PHOSPHATE
 FROM HCL AND WET PROCESS
 PHOSPHORIC ACID

FIG 3

material containing the metallic impurities from the phosphoric acid feed. Approximately 0.1 to 0.3 tons of this 0-50-15 material is produced for each ton of MKP.

The filtrate solution is evaporated to produce a slurry of solid product monopotassium phosphate and barren mother liquor. This slurry is separated by any suitable means, such as centrifuge. The product crystals receive a light wash in the centrifuge to remove residual mother liquor. The centrate is returned to the reactor section to be mixed with additional quantities of feed ingredients. The wash from the centrifuge is returned to the melt dissolution system.

The wet product solids from the centrifuge is dried in any suitable dryer, such as a fluid bed or rotary dryer. Product dust from the drying system is captured either by a dust collector or wet scrubber and returned to the melt dissolution system.

The resulting dried product solids will typically contain from 0.1% to 1.0% chloride when produced from a solution containing from 3.0% to 5.0% chloride. The actual value can be varied by varying the reaction conditions to develop more or less conversions of potassium chloride and remove more or less hydrogen chloride from the reactor.

The hydrogen chloride gas and water vapor from the reactor are recovered in a two stage condenser. All the hydrogen and part of the water is condensed in the first stage to produce a

concentrated hydrochloric acid. The remaining water vapor is condensed in the second stage condenser as hot water to be used as a source of energy to preheat the feed to the reactor.

VI. CLOSED LOOP COOLING SYSTEM

As pressures increased in recent years for producers to be accountable for the impact they had on the environment, technologies that eliminate or minimize the negative impacts of production became the way of life. Some, like matrix acidulation which conserves our most precious material resource, water, by eliminating large slime holding ponds, provide improved land utilization at the same time. Others, like PECO's patented closed loop cooling system which eliminates fluorine pollution from phosphoric acid plants, have proven necessary to maintain air and ground water quality.

The first commercial application of this technology was designed in 1989. As the technology was implemented throughout the industry due to regulatory pressures and economically attractive processes utilizing fluosilicic acid were developed, the situation improved until virtually no fluorides are emitted from a modern phosphoric acid facility.

The acidulation of phosphate rock, comprised primarily of tricalcium phosphate, calcium carbonate and calcium fluoride, produces carbon dioxide and hydrogen fluoride as by-products in addition to the desired phosphoric acid and gypsum. The carbon dioxide evolves out of the process while the hydrogen fluoride reacts with the silica or sand in the rock to produce silicon tetrafluoride. Fluorine evolves from the reaction step as

silicon tetrafluoride and was typically absorbed into pond water in order to limit the amount of fluorides emitted from the process to conform to environmental standards.

The fluorine evolved during later concentration steps as silicon tetrafluoride and hydrogen fluoride was either recovered as fluosilicic acid or was absorbed into the pond water used to condense water vapor liberated during the evaporation process.

In the PECO process the fluorine liberated during the reaction and concentration steps is recovered as fluosilicic acid using conventional technology. The recovery system works in conjunction with a closed loop aqueous condensing system. The water vapor and traces of fluorine exit the fluosilicic acid recovery system and enter the closed loop system where the water vapors are condensed and the fluorine vapors are absorbed by direct contact with the circulating water.

The circulating stream containing the condensed vapors is cooled, with most of the stream recycled to condense even more vapors. The cooling is accomplished by indirect exchange of heat with the fluorine containing condensate solution maintained in a closed system and isolated from the atmosphere. The heat duty is therefore transferred to the non-contaminated cooling water system which in turn is cooled by passage through a cooling tower. As a result, pollution of the atmosphere by fluorine vapors was completely eliminated along with the requirement for large cooling ponds.

VII. HYDROGEN FLUORIDE RECOVERY SYSTEM

Even though the closed loop cooling process eliminated large cooling ponds and associated air and ground water pollution problems, it had limited acceptance initially because the fluosilicic acid produced by the process had a limited market.

In 1989, PECO had already embarked on a development program to invent a process which would produce phosphoric acid by reacting fluosilicic acid and phosphate rock. Our goal was to produce phosphoric acid using fluosilicic acid 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. But 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 was readily converted to hydrogen fluoride and easily stripped from the acid. The hydrogen fluoride vapors were then recovered as a concentrated solution or as aluminum fluoride. The market demands for hydrogen fluoride and aluminum fluoride was sufficient to absorb the hydrogen fluoride produced from the evolved fluorine. Initially this new product added a value of

\$25.00 per ton of P_2O_5 produced; however, as time went on, producers continued to develop better methods of stripping and recovered increasingly greater amounts of fluorine from the phosphoric acid they produced thereby resulting in added values of more than \$60.00 per ton of P_2O_5 processed.

This process, in conjunction with the closed loop cooling system, converted a significant environmental pollutant into a highly profitable product.

VIII. CLOSING REMARKS

During the last ten years the phosphate industry evolved dramatically in order to maintain a viable role in the chemical process industry. The technologies of today, some of which were described in this paper, were made possible because of the pioneering efforts of the dedicated individuals who met in Clearwater, Florida, in 1990.

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PRESENTING AUTHOR BIOGRAPHY

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