



PHOSPHATE ENGINEERING & CONSTRUCTION CO., INC.

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REMOVAL OF CATIONIC IMPURITIES
FROM WET PROCESS PHOSPHORIC ACID

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Presented at
American Institute of Chemical Engineers
Joint Meeting
Clearwater, Florida
May 28, 1988

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INTRODUCTION

Phosphate Engineering & Construction Co. (PECO) is a diversified engineering and development company offering services in the areas of:

Process Engineering/Development

Project Engineering/Management

Environmental Engineering

Laboratory Services

PECO was founded in 1973 in Lakeland, Florida. Since its inception, the company has performed services for several industries with principal involvement in the phosphate industry.

In recent years, considerable development work has led to the following patent applications:

1. Removal of Cationic Impurities from Inorganic Solutions.
2. Matrix Acidulation.
3. Low Chloride Monopotassium Phosphate Production from Phosphoric Acid and KCl.
4. Potassium Sulfate Production from Waste Metallic Sulfate Streams.
5. Closed Loop System for the Elimination of Fluorine Pollution from Phosphoric Plants.

REMOVAL OF CATIONIC IMPURITIES
FROM WET PROCESS PHOSPHORIC ACID

BACKGROUND

Low impurity phosphate reserves are being depleted in Florida with much of the remaining reserves containing significantly higher levels of magnesium and other impurities. Current ore beneficiation methods are not effective or economical in reducing the magnesium from the ore prior to producing wet process phosphoric acid.

When phosphate rock is reacted with sulfuric acid to produce phosphoric acid, most of the impurities that are in the rock are dissolved in the acid. These impurities are principally iron, aluminum, fluorine, magnesium, calcium, sodium, potassium and cadmium.

These impurities create problems in processing the acid and in converting it into phosphatic fertilizer products. The impurities react to form sludges when the acid is concentrated thereby increasing superphosphoric acid viscosity, storage problems in ammoniated liquid fertilizers and grade problems in DAP.

As the impurity levels increase in the phosphate rock, these problems will become more severe requiring some degree of treatment.

The fortunate producer, who experiences intermittent supplies of high impurity rock feed, need only to treat the filter acid during the time he is processing low grade ore. For the unfortunate producer, who will be

receiving only high impurity or low grade rock, the problem will be daily and he will have to treat the filter acid continually. The PECO Acid Purification Process, which is an ion exchange process, lends itself to either application.

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 a suitable regeneration solution. The process has transferred the magnesium from the phosphoric acid to the regeneration solution.

In most cases, the removal of the magnesium from the regeneration solution is a more severe problem than the removal of the magnesium from the phosphoric acid.

One approach to the problem is to add sufficient 93% sulfuric acid to the regeneration solution to raise its concentration to 75% sulfuric acid, which then causes the magnesium to become insoluble and precipitate as a $MgSO_4 \cdot H_2SO_4$ double salt. This requires the use of extremely large quantities of 93% sulfuric acid which is returned to the phosphoric acid plant at 75%. Cations such as cadmium are at such a low level in the sulfuric acid regeneration solution that even with addition of concentrated 93% sulfuric acid the cadmium cannot be caused to precipitate.

PECO has developed a process which will allow for the removal of the cationic impurities from the phosphoric acid without using large quantities

of sulfuric acid to treat the regeneration solution to cause the cationic impurities to precipitate.

The PECO Acid Purification Process utilizes conventional fixed bed ion exchange methods of contacting the solution with the resin. This technology is well understood and has been practiced for some thirty to forty years. It is simple and has a very low capital cost when compared to other systems.

The PECO regeneration system is a closed loop and the only materials leaving the regeneration loop are the precipitated impurities and the evaporation of the water of dilution when high levels of magnesium are encountered in the feed phosphoric acid. It has been found that the magnesium precipitated from the regeneration loop has a market value, which in some cases, may be sufficient enough to totally offset the cost of the operation.

During the development of the PECO Acid Purification Process, it was noted that cadmium was removed from the phosphoric acid to levels as low as 2ppm in 30% P2O5 phosphoric acid. It was also noted that the cadmium, once removed from the phosphoric acid, would then enter the regeneration loop and it would also be precipitated along with the magnesium. This process forms the basis of a method to remove cadmium from phosphatic fertilizers to acceptable ecological levels.

PROCESS DESCRIPTION

Ion Exchange Area

A simplified process flow diagram of the ion exchange process is presented in Figure 1. Clarified filter acid is received via pipeline from the phosphoric acid plant and is stored in the agitated feed acid storage tank.

The acid is then metered under flow control to the load cycle of the fixed bed ion exchange unit for transfer of the cation impurities (CaO, MgO, Fe₂O₃, Na₂O, K₂O and Cd) from the phosphoric acid to the cation exchange resin. A fixed 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 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.

The cations loaded on the resin are then stripped from the resin by the regeneration solution. The process has then transferred the cations from the acid to the regeneration solution producing the pregnant mother liquor. Sufficient regeneration solution is passed through the loaded resin so that all of the cations removed from the acid are transferred to the pregnant

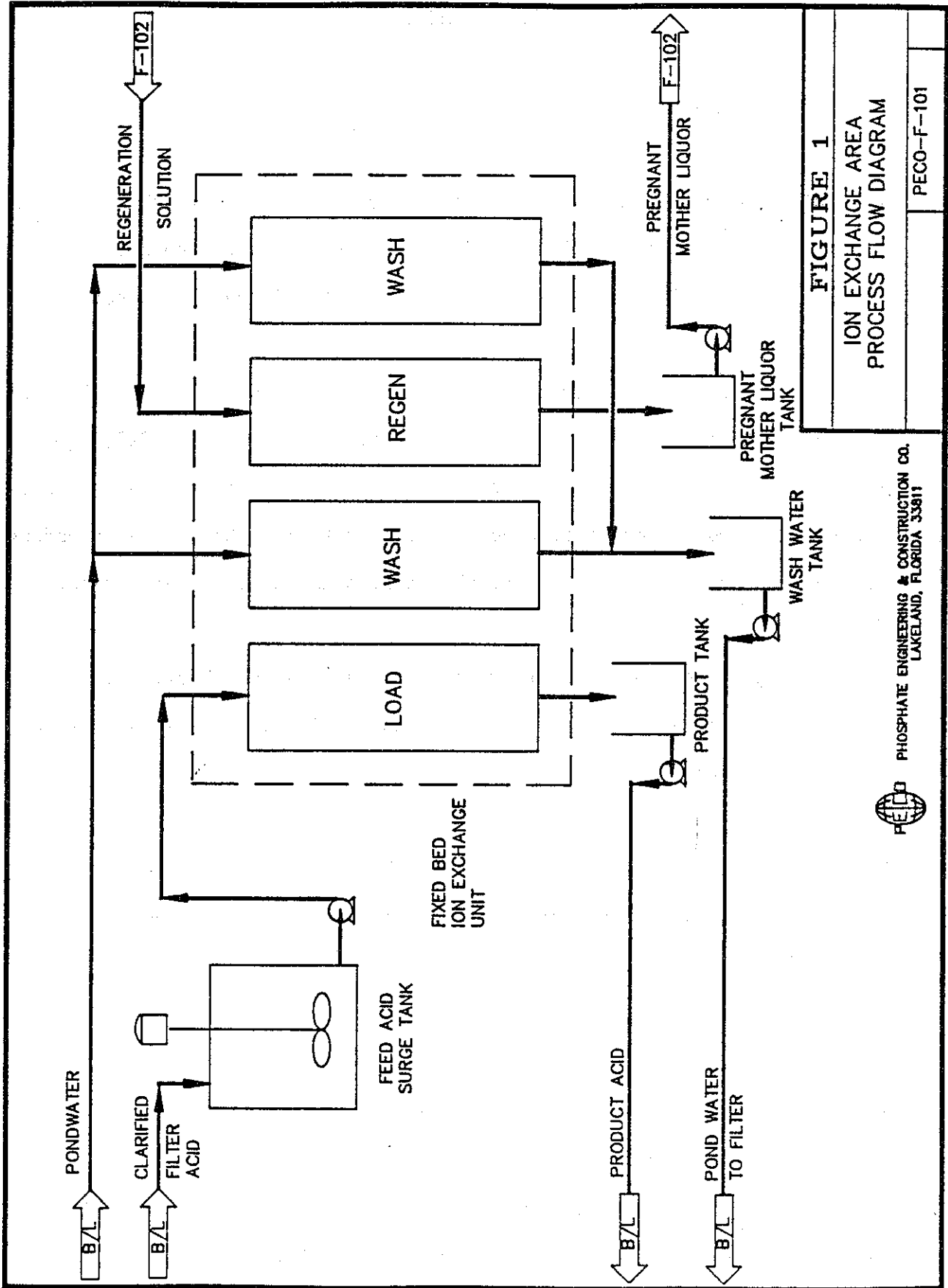


FIGURE 1
ION EXCHANGE AREA
PROCESS FLOW DIAGRAM

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PECO-F-101

mother liquor thereby providing a fully regenerated resin bed for the next load cycle.

After a sufficient amount of recirculating regeneration solution has passed the resin, it is diverted to a loaded chamber and a stream of pond water is used to displace the volume of regeneration solution remaining in the ion exchange resin bed.

The pregnant mother liquor and a small portion of the pond water is returned to the vacuum 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 to the phosphoric acid plant for use as filter cake wash water.

Regeneration Solution Production Area

A simplified process flow diagram of the production of regeneration solution and the recovery of cationic impurities is presented in Figure 2. Pregnant mother liquor from the fixed bed ion exchange unit is pumped to the vacuum crystallizer along with metered amounts of reagents A and B which are commonly used by phosphate producers.

The crystallizer is operated under vacuum so the recirculated slurry is constantly being exposed to the vacuum removing the heat of reaction and

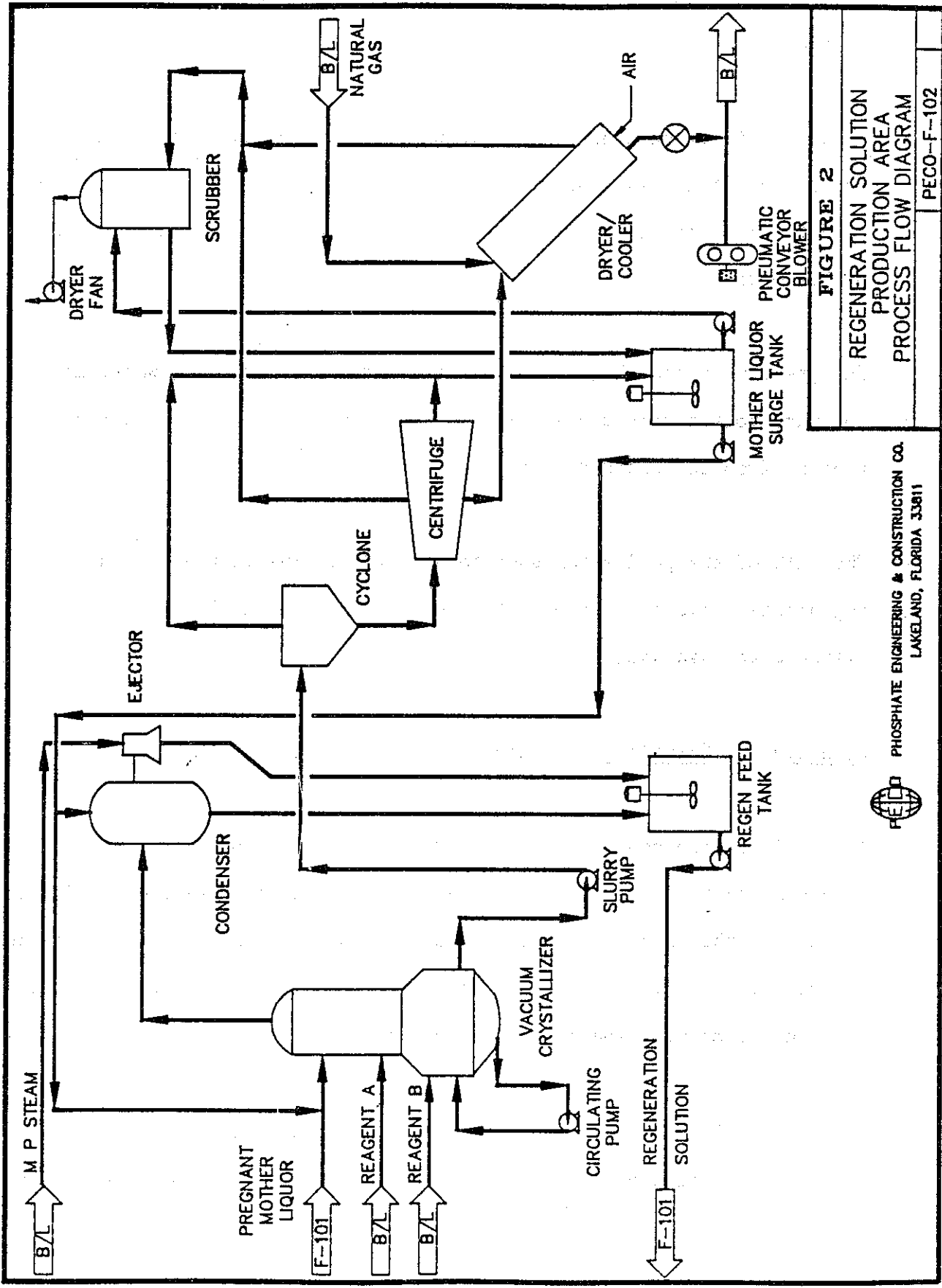


FIGURE 2
REGENERATION SOLUTION
PRODUCTION AREA
PROCESS FLOW DIAGRAM
 PECO-F-102

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cooling the slurry to a temperature at which the cationic salts are relatively insoluble.

The precipitation of the cations removed from the feed acid is necessary to prohibit these cations from loading back onto the resin during the regeneration cycle. This would reduce the resin exchange capacity, which would in turn reduce the amount of acid which can be treated by a given amount of resin.

The slurry containing the precipitated cations overflows the crystallizer at about 25% solids to the slurry pump which pumps it to a set of cyclones where the slurry is concentrated to 50% solids. The cyclone underflow is fed to a pusher type centrifuge for solids separation from the regeneration solution.

The solids are dried and cooled and pneumatically conveyed to storage.

The centrate from the centrifuge along with the overflow from the cyclones flows to the barren mother liquor surge tank.

A portion of the barren mother liquor or regeneration solution is pumped to the crystallizer barometric condenser.

The latent heat of condensation heats the saturated regeneration solution to a temperature which ensures that the regenerating cations are in solution during the regeneration cycle. The regeneration solution is

pumped under flow control to the regeneration cycle of the ion exchange unit.

A recycle stream of barren mother liquor is pumped to the crystallizer in order to control the solids concentration in the crystallizer.

Water vapor exits from the crystallizer into a barometric condenser where condensable vapor is removed by direct contact with the barren mother liquor. The noncondensable gases from the barometric condenser are compressed to atmospheric pressure by a steam ejector and are discharged to the regen feed tank.

Scrubbing equipment is provided to ensure minimum emissions from the regenerating production and product recovery area.

PROCESS APPLICATIONS

Magnesium Removal

The PECO Acid Purification Process is capable of removing magnesium from wet process phosphoric acid intended for superphosphoric acid production. A magnesium concentration of 0.3% MgO in superphosphoric acid is desired to control viscosity of the acid and allow liquid fertilizer solutions with extended shelf lives to be produced.

The level of MgO in superphosphoric acid can be reduced by filtering magnesium phosphates from hot green acids. The filtering of superphosphoric acid requires excess evaporator capacity since the sludge fraction from this type of operation contains large percentages of very expensively produced superphosphoric acid. Conversely, black superphosphoric acid cannot be filtered and precipitation and clarification of the feed acids for magnesium removal are ineffective.

In order to produce a 68% P2O5 superphosphoric acid with 0.3% MgO requires that the filter acid, fed to the evaporation area and subsequently to the superphosphoric acid evaporator, be limited to 0.15% MgO.

As can be seen in Table 1, the acid had a relatively high MgO level which would result in a 1.26% MgO in superphosphoric acid, if untreated. The concentrations of P2O5, CaO, MgO, Fe2O3, Al2O3 and Cd in the acid before and after treating approximately three bed volumes of acid are presented in Table 1.

TABLE 1

MAGNESIUM REMOVALFEED AND PRODUCT ACID ANALYSIS

	<u>Feed Acid</u> <u>% by Weight</u>	<u>Product Acid</u> <u>% by Weight</u>	<u>% Removed</u>
P2O5	28.5	27.3	-
CaO	0.08	0.0	100
MgO	0.63	0.15	75
Fe2O3	0.72	0.43	37.5
Al2O3	0.35	0.33	2
Cd	18ppm	3ppm	85

The concentration of MgO was reduced approximately 75% to 0.15%, which is the desired level. In addition, virtually all of the calcium and 37.5% of the Fe2O3 and 30% of the Na2O and K2O were also removed.

The acid was diluted from 28.5 to 27.3% P2O5 which would require approximately 385 pounds of steam per ton of P2O5 to return the treated acid to its original concentration.

The cost in reagents would be approximately \$7/ton of P2O5. It has been found that the magnesium precipitated from the regeneration loop has a market value, which in some cases may be sufficient to totally offset the cost of the operation. The net cost is considerably less than can be achieved by the filtration of superphosphoric acid with its inherently high cost due to the over production of superphosphoric acid.

A capital cost estimate has been prepared based on a typical process flow diagram and equipment list indicating a total capital cost of approximately \$3.5 million for a 500 TPD P2O5 plant.

Cadmium Removal

The PECO Acid Purification Process forms the basis of a method to remove cadmium from phosphate fertilizers to acceptable ecological levels.

In countries, especially in Europe, where legislation is being developed to remove or limit cadmium in the food chain, by setting a Cd/P2O5 ratio, it is desirable to economically reduce the cadmium in the phosphoric acid so the subsequent fertilizer product does not exceed the proposed limits.

As can be seen in Table 2, the acid treated had a relatively high cadmium level of 61ppm. The concentrations of P2O5, CaO, MgO, Fe2O3, Al2O3 and Cd before and after treating approximately three bed volumes of acid are given in Table 2.

TABLE 2

CADMIUM REMOVAL

FEED AND PRODUCT ACID ANALYSIS

	<u>Feed Acid</u> <u>% by Weight</u>	<u>Product Acid</u> <u>% by Weight</u>	<u>% Removed</u>
P2O5	30.41	29.4	-
CaO	0.09	0.0	100
MgO	0.43	0.11	74
Fe2O3	0.46	0.32	28
Al2O3	0.98	0.91	4
Cd	61ppm	9ppm	85

The cadmium was reduced from 61 to 9ppm (85% removed) or from 200ppm Cd/unit of P205 to 30ppm Cd/unit of P205 which meets all present cadmium standards.

The acid was diluted from 30.4% P205 to 29.4% P205 which would require 290 pounds of steam per ton of P205 to return the treated acid to its original concentration.

Greater reductions in cadmium (10ppm Cd/unit of P205) removal are achievable, should proposed regulations be adopted, which would require approximately twice the evaporation cost due to increased dilution of the product.

In addition, virtually all of the calcium and 75% of the magnesium and 28% of the iron were also removed from the acid. Here too, it may be possible to offset the operating costs by marketing the precipitated compounds from the regeneration loop. This would require a two step crystallization process whereby the cadmium precipitates would be separated from the magnesium solids.

The total cost in reagents would be approximately \$5/ton of P205. A capital cost for a 500 TPD P205 plant is estimated to be approximately \$3.5 million.

Cation Removal for Improved DAP Quality

The PECO Acid Purification Process can also be applied to remove cationic impurities from phosphoric acid in order to produce a high quality DAP. The treated acids presented earlier in Tables 1 and 2 indicate that typically 100% of the soluble CaO, 75% of the MgO, and 28 to 37.5% of the Fe₂O₃ can be removed from the filter acid.

In Table 3, the analysis of the feed acid to a commercial granulation plant is presented along with the low grade DAP analysis of the product made from that feed acid.

TABLE 3
CATION IMPURITY REMOVAL
DAP FEED ACID AND PRODUCT ANALYSIS

	<u>Feed Acid</u> <u>% by Weight</u>	<u>Actual DAP</u> <u>% by Weight</u>	<u>Predicted DAP</u> <u>% by Weight</u>
P205	38.0	45.8	45.7
CaO	0.65	0.71	0.78
MgO	0.37	0.43	0.45
Fe ₂ O ₃	1.71	2.03	2.06
Al ₂ O ₃	1.74	1.98	1.88
F	1.87	2.24	2.25
SiO ₂	0.46	0.72	0.26
Na ₂ O	0.21	0.26	0.25
K ₂ O	0.10	0.11	0.12
SO ₄	3.57	4.35	4.30
N	-	17.2	17.1
Moisture	-	1.74	1.74
Ratio	-	1.90	1.90

A DAP grade model was utilized to predict the DAP analysis based on the feed analysis and a relatively simple algorithm. The predicted DAP

analysis agrees very well to the actual analysis and is reasonably close enough for illustrative purposes.

The feed acid CaO (soluble), MgO and Fe₂O₃ concentrations were reduced to 0, 25 and 70% of these initial concentrations respectively and the resulting acid was then subjected to the same algorithm developed from the actual feed acid. The feed acid and resulting DAP grade are presented in Table 4.

TABLE 4
CATION IMPURITIES REMOVAL
DAP FEED ACID AND PRODUCT ANALYSIS
CaO, MgO AND Fe₂O₃ IN THE FEED ACID REDUCED

	<u>Feed Acid</u> <u>% by Weight</u>	<u>Predicted DAP</u> <u>% by Weight</u>
P2O5	38.0	46.4
CaO	0.12	0.14
MgO	0.09	0.11
Fe ₂ O ₃	1.20	1.46
Al ₂ O ₃	1.74	1.90
F	1.87	2.29
SiO ₂	0.46	0.27
Na ₂ O	0.21	0.26
K ₂ O	0.10	0.12
SO ₄	3.57	4.36
N	-	18.1
Moisture	-	1.74
Ratio	-	1.98

As can be seen, the DAP product was improved from an offgrade analysis of 17.2-45.8-0 (1.9 mole ratio) to an overformulated 18.1-46.4-0 (1.98 mole ratio).

The acid samples evaluated in Tables 1 and 2 had a fair percentage of the iron in the Fe+2 state resulting in the reductions in iron content in the treated acid. Since the level of reduced iron (Fe+2) in phosphoric acid produced in Florida is somewhat less, the feed acid to the DAP plant was also evaluated with the Fe2O3 being reduced 15%. Table 5 presents the feed and product analysis for this example.

TABLE 5
CATION IMPURITIES REMOVAL
DAP FEED ACID AND PRODUCT ANALYSIS
CaO, MgO AND Fe2O3 IN THE FEED ACID REDUCED

	<u>Feed Acid</u> <u>% by Weight</u>	<u>Predicted DAP</u> <u>% by Weight</u>
P2O5	38.0	46.2
CaO	0.11	0.14
MgO	0.09	0.11
Fe2O3	1.45	1.77
Al2O3	1.74	1.89
F	1.87	2.28
SiO2	0.46	0.26
Na2O	0.21	0.26
K2O	0.10	0.12
SO4	3.57	4.34
N	-	18.0
Moisture	-	1.74
Ratio	-	1.97

As can be seen, the analysis of the DAP increased to a 18.0-46-0 with a 1.97 mole ratio.

The cost per ton of DAP including evaporation and reagent costs are estimated to be \$2.50 to \$3 when removing all the soluble calcium, 75% of the magnesium and 15% of the iron in order to make grade. An estimate capital cost for a 500 TPD P2O5 is \$3.5 million.

SUMMARY

The advantages of the PECO Acid Purification Process are as follows:

1. Straight forward economical method for producing a low magnesium content phosphoric acid for superphosphoric acid production.
2. Cadmium can be reduced to meet all present and proposed limits.
3. Removing calcium and magnesium from the feed acids to be made into DAP improves off grade analysis to on grade specification.
4. The PECO regeneration system is a closed loop with normally only precipitated impurities leaving the loop.
5. No need for large quantities of concentrated sulfuric acid to be returned to the phosphoric acid plant in a dilute form.
6. Magnesium precipitated from the regeneration loop has a market value which in many cases offsets the total operating cost.
7. Cadmium can be precipitated along with the magnesium or precipitated separately.

8. Since the precipitated impurities have a market value, there is no need to burden other operations with sludge or to consume the impurities internally.

9. An overall reduction in the quantity of sludge generated during acid concentration and less scaling during filtration and evaporation.