

REMOVAL OF MAGNESIUM AND OTHER IMPURITIES FROM PHOSPHORIC ACID VIA PULSED BED ION EXCHANGE - THE PEMBROKE PROCESS

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Today, rising phosphate rock magnesium concentrations threaten Florida fertilizer producers. Although some deposits with acceptable P_2O_5 and moderate impurities exist today, few deposits will offer low magnesium in the future. Of course, producers can reduce high magnesium content with heavy media beneficiation to approximately 1% to 1.5% MgO followed by blending with low MgO rock. This approach temporarily avoids magnesium problems; however, this approach also progressively demands more and more low magnesium rock to maintain a constant feed analysis to the attack system. Unfortunately, despite beneficiation and blending, producers still incur high P_2O_5 losses, increased freight and tank cleaning costs, lower DAP grade (or adding "grade enhancers"), onerous sludge handling, and more operating cost. These problems do not exist if producers remove magnesium from dilute (25 - 40% P_2O_5) phosphoric acid.

Although many impurities occur in wet process phosphoric acid, magnesium may be the most serious because magnesium can:

- slow the attack system by increasing phosphoric acid viscosity and decreasing gypsum filtration rates.
- limit DAP grade by occupying potential phosphate ammoniation sites.
- cause sludge precipitation from merchant acid in railcars and storage tanks. This precludes long term acid storage by preventing sequestration (dissolution) of other impurities. The impurities precipitate as metallic impurity phosphates causing high P_2O_5 losses, high freight costs, excessive tank cleaning, and expensive sludge handling.
- require additional purifications for super acid and liquid fertilizer production. Ion exchange reduces additional purifications, P_2O_5 losses, sludge handling, short evaporation cycles, and excessive freight costs.

For some time, American Pembroke and Swenson Process Equipment researched solutions to the magnesium problem. In 1983, 1985, and 1987 papers, Swenson reported promising results to the AIChE. Today, we will describe some recent process improvements and review the current technology status.

PROCESS DEVELOPMENT

After performing considerable concept testing and bench scale process development, American Pembroke installed a small, one liter per minute pilot plant in Bartow, Florida. This pilot plant successfully processed many phosphoric acid samples from central Florida, northern Florida, North Carolina, and Tunisia. In 1987, following pilot plant tests, Swenson designed a 13,000 MT/Yr P_2O_5 magnesium removal facility for installation by Spie Batignolles at an existing phosphoric acid plant located in Sfax, Tunisia. This plant successfully treated 0.9% MgO phosphoric acid to 0.15% MgO phosphoric acid for several months.

As originally developed, the Pembroke-Swenson MgO Removal Process regenerated loaded ion exchange resin with once-through concentrated sulfuric acid. Regeneration efficiency was excellent; however, wash water diluted the sulfuric acid spent regenerant to 50 - 70% H_2SO_4 . Since optimum efficiency demanded concentrated sulfuric acid, the process recycled spent regenerant to the reactor. Sfax successfully demonstrated this sulfuric acid recycle; however, our American clients preferred that Swenson develop an alternate approach which eliminates any sulfuric acid recycle. We succeeded in 1989. Today, we will report our improved magnesium removal process to the AIChE.

Our improve process regenerates loaded resin by replacing some sulfuric acid hydrogen ions with other anions, such as NH_3 . This approach depresses impurity solubilities and allows return of fresh regenerant solution to the regen chamber. In addition to eliminating the sulfuric acid purge, we also eliminated equipment, simplified controls, increased reliability, and reduced costs.

CURRENT PROCESS

The current Pembroke-Swenson MgO Removal Process removes magnesium, calcium, and monovalent and divalent impurities from dilute phosphoric acid. Our process combines the superior resin regeneration offered by folded-bed ion exchange (also called pulsed-bed ion exchange) while using common, familiar raw materials. The process features eight major equipment items: a load column, a resin metering chamber, a regeneration chamber, two wash chambers, a pulse chamber, crystallizer, and filter. Figure 1 shows a schematic flowsheet of the Pembroke-Swenson MgO Removal Process equipment.

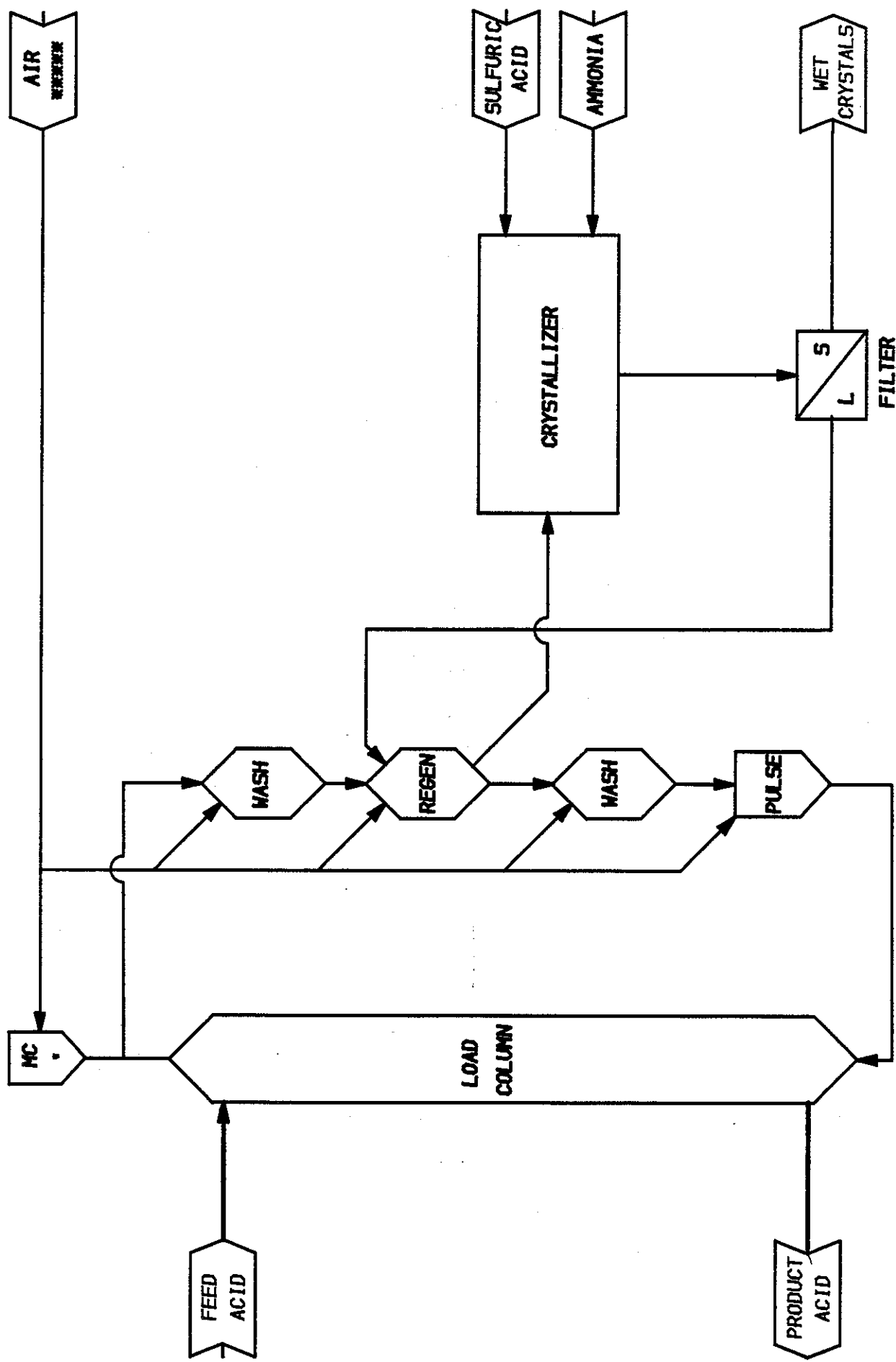


FIGURE 1- PEMBROKE SWENSON MGO REMOVAL PROCESS
SCHEMATIC FLOWSHEET

In the process, dilute impure phosphoric acid flows through a load column packed with anion exchange resin. Magnesium and other impurities replace H^+ and NH_4 ions in the resin. Feed acid flow in the column is countercurrent relative to the resin. Periodically, the process controller cycles the ion exchange system by: 1) interrupting acid flow; 2) transferring (pulsing) a small measured volume of fresh (regenerated) resin from a pulse chamber to bottom of the load column; 3) simultaneously fluidizing and transferring an equal volume of loaded resin from the top of the load column to a wash chamber; and 4) resuming acid flow. Each pulse typically transfers 10% to 20% of the load column volume.

In the wash chamber (Wash Chamber A), compressed air forces entrained phosphoric acid from the loaded resin voids. After conditioning, loaded resin is transferred into a regeneration chamber (Regen Chamber B). During regeneration, massive amounts of fresh regenerant solution (Fresh Regen) react with loaded resin to replace magnesium and calcium ions in the resin with hydrogen and ammonium ions. Saturated fresh regenerant solution contains sulfuric acid, ammonia, and magnesium and calcium sulfate. During regeneration, the spent regeneration solution becomes slightly supersaturated with magnesium and calcium sulfate.

Regeneration process and equipment design is crucial for any successful phosphoric acid purification process since the regenerant is almost always saturated with magnesium and calcium. These ions precipitate as hard sulfate crystals in very undesirable locations unless controlled by careful screen design, by limiting spent regenerant travel time (particularly within the regeneration chamber), and meticulously engineered supersaturation relief. Fortunately, pulsed bed ion exchange eases this formidable design challenge.

A major advantage of pulsed-bed ion exchange processing is that regeneration only treats a small part of the total resin inventory during each cycle. Therefore, loaded resin can be much more intensively treated with considerably more regenerant solution than with other ion exchange technologies. By applying massive regenerant volume (relative to resin volume), spent regenerant slightly supersaturates which minimizes premature precipitation. Moreover, intensive regeneration also reduces travel time between supersaturation creation in the Regen Chamber and supersaturation relief in the Crystallizer. With knowledgeable process engineering and careful attention to equipment geometry (to minimize solution transit time), one can surmount the regeneration design challenge.

Again, compressed air dewateres regenerated resin before transfer to another wash chamber (Wash Chamber C). After transfer and further conditioning, the phosphoric acid sluices regenerated resin (Fresh Resin) into the Pulse Chamber for return to the load column.

Magnesium and calcium impurities, contained in a slightly supersaturated spent regenerant solution obtained from the Regen Chamber, precipitate as mixed calcium and magnesium sulfates in a forced circulation crystallizer. In the crystallizer design, the engineer must control supersaturation relief in the circulating magma and produce an filterable crystal slurry. Sulfuric acid and ammonia injections maintain optimum crystallization conditions and replace hydrogen, sulfate, and ammonium ions lost during resin regeneration and crystallization.

A pump continuously withdraws crystal slurry and feeds it to a filter. Wet calcium sulfate and magnesium acid sulfate crystals (Wet Crystals) leave the filter as by-product. Mother liquor (Fresh Regen) recycles back to regeneration.

PROCESS BENEFITS

Benefits of using treated phosphoric acid, produced in the Pembroke-Swenson MgO Removal Process, include:

- Increased phosphate rock reserves
- Meet merchant acid specifications
- Maintain DAP grade without adding "grade enhancers"
- Lengthen evaporator cycles
- Allow very intensive resin regeneration in small, inexpensive equipment
- Use conventional fertilizer raw materials
- Produce long-term storable phosphoric acid and liquid fertilizer without sludge precipitation
- Permit liquid fertilizer production directly from 60% acid
- Recover magnesium and calcium impurities as easily-handled, potentially-marketable sulfate crystals
- Use small plant site
- Need low capital investment

PATENT PROTECTION

Patent coverage of the Pembroke-Swenson MgO Removal Process technology and equipment is both extensive and comprehensive. Many United States and foreign patents are now in hand. American Pembroke filed a patent application covering the recent process improvements. Pembroke and Swenson have each been provided with an opinion of non-infringement by their respective patent attorneys.

CURRENT STATUS

At this time, Swenson Process Equipment offers proven improved Pembroke-Swenson MgO Removal Process for commercial application in phosphoric acid plants and liquid fertilizer plants. The process successfully treats feed acids, containing up to 1% MgO, to approximately 0.08% MgO. Dilution averages about 6% commercially, i.e. MgO removal may dilute a 28% P_2O_5 acid to about 26.5% P_2O_5 ; however, a few percent. The process eliminates all CaO and most MgO plus some monovalent and divalent impurities, such as ferrous iron. Treated acid exhibits excellent stability. We stored samples of 54% merchant acid and 10-34-0 liquid fertilizer both made from acid treated by the Pembroke-Swenson MgO Removal Process for years without impurity precipitation. We also produced super phosphoric acid from purified acid without precipitation despite the presence of sequestered iron, aluminum and other impurities. Apparently, removing calcium and most magnesium allows the remaining impurities to stay dissolved. Therefore, we believe that the Pembroke-Swenson MgO Removal Process finally eliminates the headaches and costs of sludge precipitation during storage and shipment.

Since the process uses closed equipment such as ion exchange columns, regeneration chambers, pumps, and tanks, environmental impacts are negligible. Some equipment and controls, such as air-actuated valves, vent compressed air streams to the atmosphere.

PRELIMINARY ECONOMICS

Capital Costs

Pembroke-Swenson MgO Removal Process capital cost varies with magnesium removal, feed acid composition, P_2O_5 throughput, existing facilities and layout, local utilities and conditions, client preferences, and many other factors. Therefore, estimating a "typical" capital cost is almost impossible since no plant is "typical." Based on 0.8% MgO acid feed and 0.2% MgO acid product, January 1990 dollars, existing acid storage, and utility and process connections by others, our recent budget quotations to Florida clients ranged from approximately \$7 million for an installed 100,000 ton per year P_2O_5 facility to about \$25 million for a 700,000 ton per year facility. Some plants will feature multiple-train ion exchange systems with single-train crystallization and filtration equipment.

Operating Costs

Again, operating costs for a "typical" Pembroke-Swenson MgO Removal Process plant are very difficult to estimate since each producer has unique cost evaluation methods. With this caveat and using January 1990 dollars and excluding depreciation, income taxes, and by-product credits, Swenson estimates approximate operating costs at a central Florida location range from approximately \$21 per ton P_2O_5 for a 100,000 ton per year plant to \$17 per ton P_2O_5 for a 700,000 ton per year plant. Larger facilities, particularly if constructed in progressively larger stages, may offer reduced costs.

FUTURE DEVELOPMENT

Previous tests with several phosphoric acids indicated that the Pembroke-Swenson MgO Removal Process also removes other undesirable anions from dilute phosphoric acid, including cadmium. Until recently, our research focused on perfecting magnesium removal. However, we expect future tests may confirm our process also removes other impurities at commercially attractive costs. We also expect any equipment and operating changes may be retrofitted into existing magnesium removal plants.

CONCLUSIONS

American Pembroke and Swenson Process Equipment developed a superior, cost effective process to remove magnesium, calcium, and other impurities from dilute phosphoric acid. This process, when installed by phosphoric acid producers, can eliminate sludge precipitation and grade problems. The process also can expand current phosphate rock reserves and permit long-term storage of acid and liquid fertilizers. American Pembroke and Swenson Process Equipment look forward to meeting the phosphate industry's magnesium removal needs now with a tested, proven technology.