

**REMOVAL OF MgO, CaO & OTHER IMPURITIES
FROM PHOSPHORIC ACID**

BY

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INTRODUCTION

Over the last few years, a considerable amount of work has gone into the development of a new process to remove various impurities from phosphoric acid. In this process, the phosphoric acid is treated in an ion exchange column which removes the magnesium oxide to whatever concentration is required as well as the calcium oxide and many of the other metallic impurities found in the feed acid. In this system, a unique resin regeneration system has been developed that allows for the system to produce sulfuric acid from the regeneration section that is pure enough and strong enough to be reused in the phosphoric acid reaction step thereby virtually eliminating the consumption of H_2SO_4 for regeneration. This process has the capability of:

- (1) removing MgO from 30% P_2O_5 phosphoric acid to levels as low as 0.05% or lower;
- (2) reducing CaO levels to virtually zero;
- (3) producing a stable merchant grade phosphoric acid with only very minimal amounts of post precipitation;
- (4) providing recovery rates of the treated phosphoric acid in excess of 99%;
- (5) producing a 98% pure magnesium sulfate by-product;
- (6) extending some of the phosphate rock reserves by as much as 25%.

PROCESS DEVELOPMENT

American Pembroke, Inc. located in Bartow, Florida started work approximately 4 years ago on a system to remove magnesium from low strength phosphoric acid. As a result of this work, the Folded Bed Chemical Separation Process for the removal of magnesium and calcium has been developed. Three (3) consulting engineering firms, well-known to the phosphate industry, have reviewed the process and found it to be technically sound and economically viable. The pilot plant operation in Pembroke, Florida has shown that the process can reduce the magnesium content of a variety of phosphoric acids from initial levels of as high as 2.5% MgO to as low as 0.05%. Concurrently with this high degree of magnesium removal, the calcium content is reduced by approximately 99% of its level in the untreated acid. In addition in a typical Florida acid, 5 to 10% of the iron and aluminum present in the feed acid is removed. Also 20% to as high as 50% of the sodium and potassium is removed. The exact amount of these cations removed varies from acid to acid and must be determined by actual tests.

This new magnesium removal system for phosphoric acid is basically an ion exchange system utilizing a pulsed column. The resin used in this system is a strong acid macroporous polystyrene resin which removes the calcium and magnesium from the phosphoric acid and is later regenerated with sulfuric acid. A unique system of regeneration has been developed in the pilot plant which allows the regeneration sulfuric acid to be discharged from this system as 73% H_2SO_4 suitable for feed back to the phosphoric acid reaction system.

PROCESS DESCRIPTION

Flowsheet No. 1 shows the ion exchange side of the system. In this system,

PROCESS DESCRIPTION (Cont'd.)

the load column and regeneration column are pulsed simultaneously. A given quantity of resin is hydraulically moved into the bottom of the load and regeneration columns, and an equal amount of resin is expelled from each column. The expelled resin is then suitably washed, treated, and regenerated in the various receivers prior to arriving in the pulse chamber ready for the next pulse. While the resin is being treated in the receiver, raw phosphoric acid enters the top of the load column and moves countercurrent to the movement of the pulsed resin and exits the bottom of the load column as treated acid. In a similar fashion, the regeneration sulfuric acid enters the top of the regeneration column and exits the bottom of the regeneration column after regenerating the resin.

In the load column, the calcium and magnesium ions are removed from the phosphoric acid. It should be noted that only the cations, such as magnesium are removed; any phosphate associated with a cation is left in the treated phosphoric acid. This maintains the high P_2O_5 efficiency of the process.

When the phosphoric acid is contacted with regenerated resin to remove the magnesium, a small amount of dilution occurs. The amount of dilution is dependent on the amount of magnesium removed from the phosphoric acid. When the magnesium level in 30% P_2O_5 phosphoric acid is reduced from 0.9% to 0.15% MgO , the resulting product acid will be about 28% P_2O_5 concentration.

Temperature of the feed acid has little effect on the efficiency of the ion exchange system. In the pilot plant, the process has been run at temperatures from 90°F to 160°F, with little effect on the overall kinetics of the resin loading and regeneration characteristics. Since the resin has a maximum operating temperature of 250°F, the actual limiting temperature may be set by materials of construction. This system has no temperature excursions in the process and would use the phosphoric acid at the temperature existing in the 30% storage tank.

Now that the resin has been loaded with the impurities from the phosphoric acid, it must be regenerated before it can be reused. In this process, elevated concentrations of sulfuric acid, rather than the conventional dilute sulfuric acid are used to regenerate the resin.

The use of high strength sulfuric acid has several advantages. For example, the use of a 50% sulfuric acid regeneration solution would present only 1/10th the volume of spent regeneration solution as compared to the use of a 5% regeneration solution. This greatly reduces the problem of treating and disposing this spent regeneration solution waste stream. Historically, this has been a severe deterrent to the use of ion exchange systems. We have also found that high strength sulfuric acid prevents the fouling of the resin by organic matter present in black phosphoric acid.

Early attempts to use high strength sulfuric acid met with the problem that the solubility of calcium sulfate is very low so that when the calcium leaves the resin, it forms a precipitate in the regeneration column which will plug

PROCESS DESCRIPTION (Cont'd.)

up the regeneration column. This plugging problem can be overcome by using high velocities of regeneration solution in the column, thus preventing any plug up, but then high consumption of regenerated solution is encountered and low concentrations of MgO in the regeneration solution make treatment of the spent regeneration solution, to remove the MgO, difficult.

These problems are solved, by this process, in the first stage regeneration system. In this stage, sulfuric acid is recirculated very rapidly past the resin, so that when the CaO leaves the resin and forms a precipitate, the velocity is high enough to prevent any plug up. The precipitated calcium sulfate is then swept from the system and removed by a thickener and may be disposed of on the main gypsum filter. This system has the added advantage of washing the resin of any sand, dirt, and other insoluble components present in the feed acid.

Essentially all of the CaO is stripped from the resin in this stage and the CaO leaves the system in the settled underflow as calcium sulfate. Little, if any, MgO is stripped from the resin. Since the MgO is very soluble in sulfuric acid, its concentration is allowed to build up to an equilibrium concentration wherein any MgO stripped from the resin is replaced by MgO from the first stage regenerant due to its high MgO concentration, usually about 1.5% MgO.

The resin at this point is stripped of CaO, which would cause plugging and loaded with MgO. It enters the regeneration column where it is stripped of MgO, by small quantities of high strength sulfuric acid, thus producing a spent regeneration solution of small volume and high MgO content.

When using sulfuric acid of high concentrations, special care must be taken to prevent osmotic shock and cracking of the resin. Severe cracking of the resin will occur if a resin, which has been exposed to water, is suddenly exposed to sulfuric acid of 55% concentration. However, if the resin which has been exposed to water then encounters a 30% sulfuric acid, before being exposed to 55% sulfuric acid, the amount of cracking is virtually eliminated. The pilot plant has used the same resin for well over a year, under this system, with the amount of cracking too small to measure.

Having removed the impurities from the phosphoric acid and regenerated the resin, we are now faced with the age-old problem of "What do we do with the spent regeneration solution?". Fortunately, our problem, volume-wise, is only about 1/10th that which we would have had if we had used the normal 5% sulfuric acid regenerate instead of the 55% solution. However, we do have a spent regeneration solution of about 35% sulfuric acid containing 1.5% MgO and very little CaO, for which we have to find a use.

We have learned that if the sulfuric acid concentration is raised to approximately 73%, the solubility of the MgO drops to about 0.2% and the MgO precipitates as magnesium sulfate. Fortunately a phosphoric acid complex uses large quantities of sulfuric acid and, therefore, concentrated sulfuric acid is available to mix with the 35% sulfuric acid from the regeneration column to raise the spent regeneration solution to approximately 73% sulfuric acid.

PROCESS DESCRIPTION: (Cont'd.)

This 73% sulfuric acid is then used in the attack tanks of the phosphoric acid plant to react with the phosphate rock. Flowsheet No. 2 illustrates how the regeneration solution is treated to make it suitable for recycling to the phosphoric acid reactor.

NATURE OF PROBLEM

The manufacture of phosphoric acid by the wet process results in an acid that contains the majority of the impurities that were found in the phosphate rock. For years, manufacturers essentially ignored the effect of all of the impurities except for the iron and aluminum. In more recent years, considerable attention has been paid to the other impurities that are in the acid and this has been especially true of the magnesium. At the present time, the phosphate fertilizer industry is having to consider using lower grade phosphate rock as high quality reserves are becoming depleted in many parts of the world. The production of presently accepted products from the lower grade rock will require some purification of the phosphoric acid produced from it, particularly removal of magnesium. Thus it appears that the American Pembroke process meets an industry need.

PHOSPHATE ROCK SUPPLIES

It has been well documented that the U.S. supply of high quality phosphate rock permitting the production of products containing relatively modest amounts of impurities is decreasing rapidly. The continued maintenance of our phosphatic fertilizer industry and its growth will depend on an ability to use lower grade rocks and still make products generally acceptable and competitive throughout the world. One of the principal impurities that has been receiving increasing attention lately because of its impact on rock processing and the product is magnesium. The newer deposits being commercialized in Florida as well as many of those in the Western and Carolina areas of the country contain substantially increased percentages of magnesia, up to about 5% instead of the customary 0.5% or less which can be obtained in many of the high grade central Florida materials. New beneficiation methods are being developed to cope with part of this problem and will probably be used to bring the magnesia content of the south Florida materials down to approximately 1%. While this is a substantial improvement, the 1% is still too high for the production of acceptable products in a cost-effective processing scheme with current technology.

This gradual reduction in grade with time is an increasingly serious problem and is particularly serious for the integrated producers who market rock as well as consume rock. Those people in the industry who are rock purchasers, both domestic and foreign, buy on specifications that allow them to bypass the magnesium problem, at least for the time being. The impact of this, however, on the rock producer is that he is faced with putting more and more of the high quality rock into external sales. However, even with blending, since the ratio of magnesium to P_2O_5 is gradually increasing, the problem cannot be evaded forever. This means that his own captive consumption must be based on using lower and lower quality rock, facing higher production costs, and difficulty in the production of competitive products.

MANUFACTURE OF DAP & TSP (Cont'd.)

When phosphoric acid containing high levels of magnesium is used in the production of DAP or TSP, considerable problems can result. The installation of a magnesium removal process would considerably minimize the sludge utilization problems associated with the manufacture of these products. The need to utilize the sludge currently produced by the clarification of phosphoric acid in addition to that normally settling in the tanks places restrictions on the relative ratios of merchant grade phosphoric acid, di-ammonium phosphate, and triple-super phosphate that can be produced in a plant and still achieve product grade and quality. Use of a cleaner acid would allow far greater production flexibility and obviously lead to potential savings in inventory cost and the ability to be more flexible in meeting market changes and relative product demands.

In production of DAP, ammonia is reacted with phosphoric acid to make a standard grade of DAP containing 18% nitrogen and 46% P₂O₅. The phosphoric acid used to manufacture DAP must be of a quality such that enough ammonia can react with the phosphoric acid to maintain the 18% nitrogen. There are various factors used to determine the combination and level of impurities (iron, aluminum, and magnesium) that can be tolerated. These impurities effectively neutralize the phosphoric acid thereby reducing the amount of ammonia that can be absorbed by the acid. Consequently, a problem occurs in that the DAP is low in nitrogen content.

Now that substantial quantities of iron, aluminum and magnesium are expected, the problem with making DAP containing 18% nitrogen is magnified. It appears that in order to make grade in DAP the feed rock to the system should contain less than 0.6% MgO.

It has also been demonstrated that the use of high magnesium content acid for the production of triple-super phosphate can lead to major increases in hygroscopicity of the product and severe stickiness quality control problems. The product is similar to that caused by a high free acid content. One method used to combat this issue is to produce a lower grade triple, such as 0-44-0 rather than a standard 0-46-0. While apparently this material has been accepted in the domestic market place, it can lead to freight penalties.

MANUFACTURE OF PHOSPHORIC ACID - MERCHANT 54% & SUPERPHOSPHORIC ACID 70%

In the manufacture of both merchant grade and superphosphoric acid, it has been well recognized that high levels of magnesium in phosphoric acid from the filter lead to greatly increased rates of scaling in the evaporators. Apparently this is, to a considerable extent, the result of the formation of various magnesium fluosilicate chemicals. There has been considerable indication that high levels of magnesium limit fluorine evolution, thus even further enhancing the reduced scaling in evaporators. Thus, the use of a magnesium removal process with its ability to remove both magnesium and calcium at the stage of filter acid would result in the equivalent of increased evaporator capacity because of the reduced fouling and necessary boilout times.

MANUFACTURE OF PHOSPHORIC ACID - MERCHANT 54% & SUPERPHOSPHORIC ACID 70%

(Cont'd.)

To the manufacturer of superphosphoric acid, the reduced magnesium content is becoming of primary importance even based upon the rock available today. High magnesium contents in superphosphoric acid lead to very high viscosities and to the formation of ammonium magnesium phosphate compounds which can render the final products unsaleable. In addition, magnesium pyrophosphate precipitates in the acid resulting in sludge problems and reduction of the polyphosphate content of the acid. Currently in superphosphoric acid contracts that are being negotiated on a worldwide basis, a maximum level of magnesium is being stipulated at 0.6% MgO. Using current technology, this level can be achieved only by a combination of selection of raw material rock and an extensive clarification process resulting in low yields of ultimately saleable superphosphoric acid as compared to what might be achieved if the magnesium could be removed from the acid before concentration.

MANUFACTURE OF LIQUID FERTILIZERS

Liquid fertilizers are the consumer product with the most pressing current need for low magnesium content. High magnesium superphosphoric acids used in their manufacture lead to short shelf lives, in the order of a few weeks or less in many cases. The liquid fertilizer industry has indicated that they would like to have much longer shelf life available to them, hopefully in the neighborhood of 9 months and possibly even 12 months. The value that the liquid fertilizer producers place on this aspect of this superphosphoric acid is evidenced by their willingness to generally pay a premium for low magnesium superphosphoric acid material.

CHEMICAL CONSUMPTION

In a general discussion of this process, it is very difficult to arrive at a cost per ton for treatment of the acid. This is because the cost is affected by a number of factors, such as the size of the plant, the analysis of the feed acid and the required analysis of the product acid. However, we can assume a typical feed acid composition and on that basis determine the consumption of sulfuric acid and P₂O₅ losses for a typical plant. We will assume that the acid fed to the system would have the following composition:

P ₂ O ₅	27.5%
MgO	0.9%
CaO	0.46%
H ₂ SO ₄	2.5%

Acid with this composition would result in a product acid from the system which would contain:

P ₂ O ₅	25.7%
MgO	0.15%
CaO	0.08%
H ₂ SO ₄	3.8%

CHEMICAL CONSUMPTION (Cont'd.)

Based on these feed and product analyses, we can now estimate that the pounds of sulfuric acid consumed by the process per pound of P_2O_5 produced by the process would be 0.16. This sulfuric acid consumption includes the sulfate that is required for the calcium and magnesium as well as the sulfuric acid that ends up in the product acid. We can also estimate that the pounds of sulfuric acid which would be recycled to the reactor as 73% sulfuric acid would be 2.0 to 2.4 pounds H_2SO_4 per pound of P_2O_5 produced. P_2O_5 losses from the system would be equal to 0.0036 pounds of P_2O_5 per pound of P_2O_5 in the product.

In most cases, the dilution of the acid should not result in any additional cost in the production of the acid as the total pounds of water evaporated should not be increased. Flowsheet No. 3 illustrates the water evaporated to produce 100 tons/day of P_2O_5 as 54% merchant grade acid both from treated and untreated acid. You will note that it is necessary to feed approximately 120 tons/day of untreated P_2O_5 to the evaporator train and evaporate 206.4 tons/day of water if you wish to end up with 100 tons/day of 54% P_2O_5 merchant grade acid. The additional P_2O_5 in the feed is to take care of the various clarification losses through concentration and storage. This is compared to only slightly over 100 TPD of treated acid fed to the system with 203.9 TPD of water evaporated to achieve the same production when clarification is eliminated.

CONCLUSIONS

It is apparent from the above that the removal of magnesium will result in considerable advantages to the phosphoric acid manufacturer. The ability to remove magnesium significantly increases the phosphate rock reserves by allowing the miner to mine rock with high magnesium levels which are currently bypassed. The removal of magnesium will also allow easier making of grade in the manufacture of DAP and TSP and will also result in a better quality superphosphoric acid. In a number of cases, the viscosity of treated superphosphoric acid has been reduced by a factor of 10 when compared to superphosphoric acid produced from untreated acid.

In addition to the improvements noted above, it has been found that phosphoric acid concentrated from acid treated in the Pembroke system tends to have a much better stability than the untreated acids. It is believed that the 40% clarification step could be eliminated during concentration of the acid as virtually all of the calcium values have already been removed in the ion exchange system. In addition, merchant grade 54% P_2O_5 acid has shown stability after many weeks of storage. Samples of acid that have been stored for over a year show virtually no precipitation of solids at the end of this time. In this way, 54% clarification could also be avoided along with the resultant costs of recycling sludge back to other fertilizer steps.

The benefits of the installation of a Pembroke MgO removal system can be summed up as follows:

1. Ability to use lower grade rocks in the manufacture of phosphoric acid

CONCLUSIONS (Cont'd.)

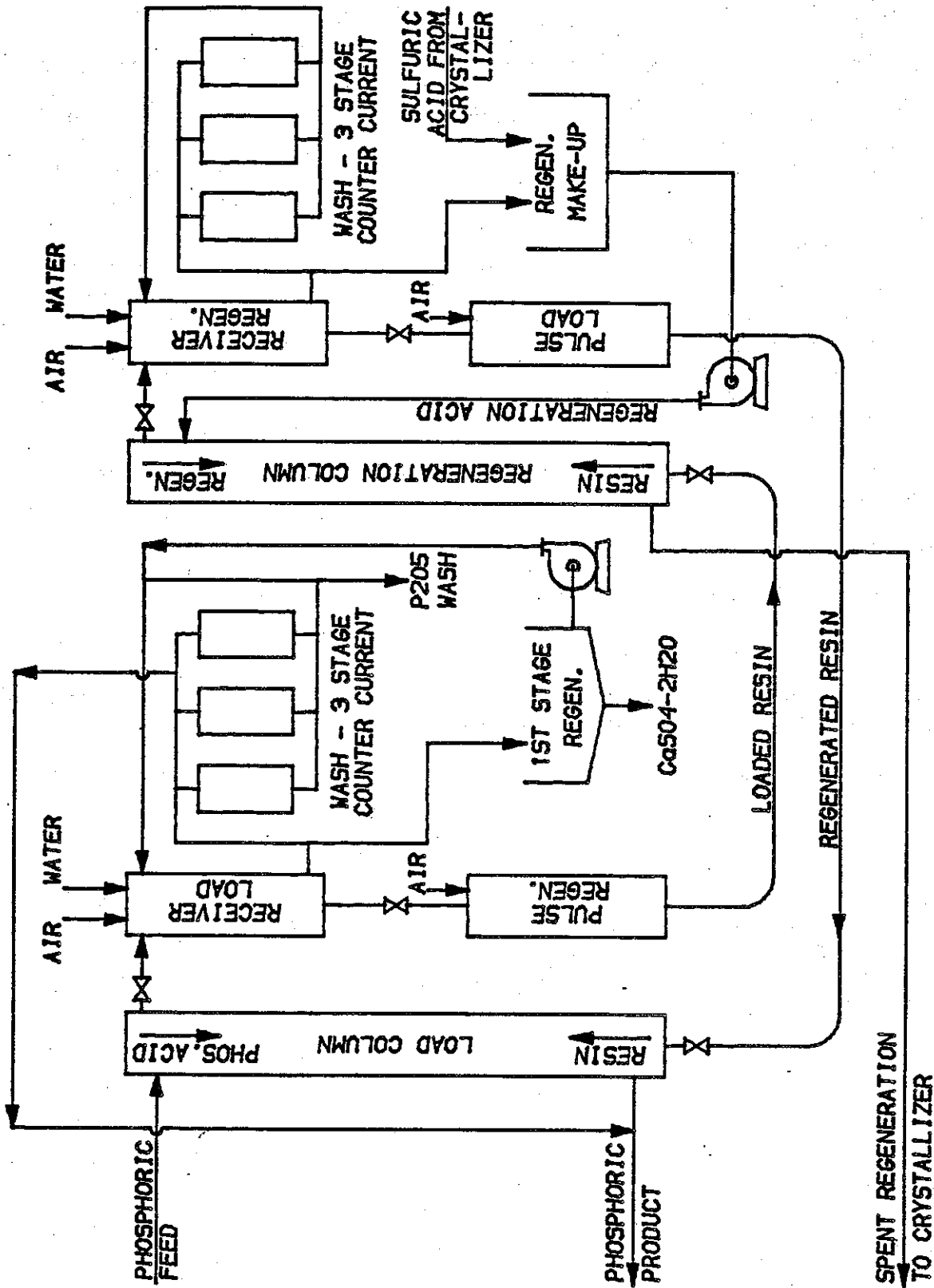
2. Better ability to make grade in the production of DAP and TSP
3. Production of stable merchant grade acid, thereby eliminating the need for clarification
4. Production of more stable, less viscous superphosphoric acid that will be generally fluid at room temperature
5. Longer evaporator cycles, thereby reducing maintenance costs in evaporation.

Extensive laboratory work on a computer operated prototype pilot plant has demonstrated the feasibility of the folded bed chemical separation process. In addition, this pilot plant has demonstrated that the chemical consumptions and P_2O_5 losses that are predicted above are easily attainable. Currently a 100 gpm demonstration plant is in the design phase and it is expected that this plant will soon be under construction. The laboratory and pilot plant testing have demonstrated that this process has several advantages over conventional extraction processes:

1. Minimal P_2O_5 loss - magnesium and calcium ions are removed as sulfate and not phosphate.
2. No hydrocarbon solvents are introduced into the plant
3. Virtually no interference with phosphoric acid production
4. Low sulfuric acid consumption
5. Increased evaporator capacity or availability because the cleaner acid increases the interval between washouts
6. It should be possible to reduce or eliminate clarification during concentration.
7. A potentially saleable product, magnesium sulfate, is produced.

The pilot plant is currently in operation and is available for testing on acids where there is an interest in seeing the effect of this system on specific acids. We would be pleased to discuss these applications in detail with any prospective users of the system.

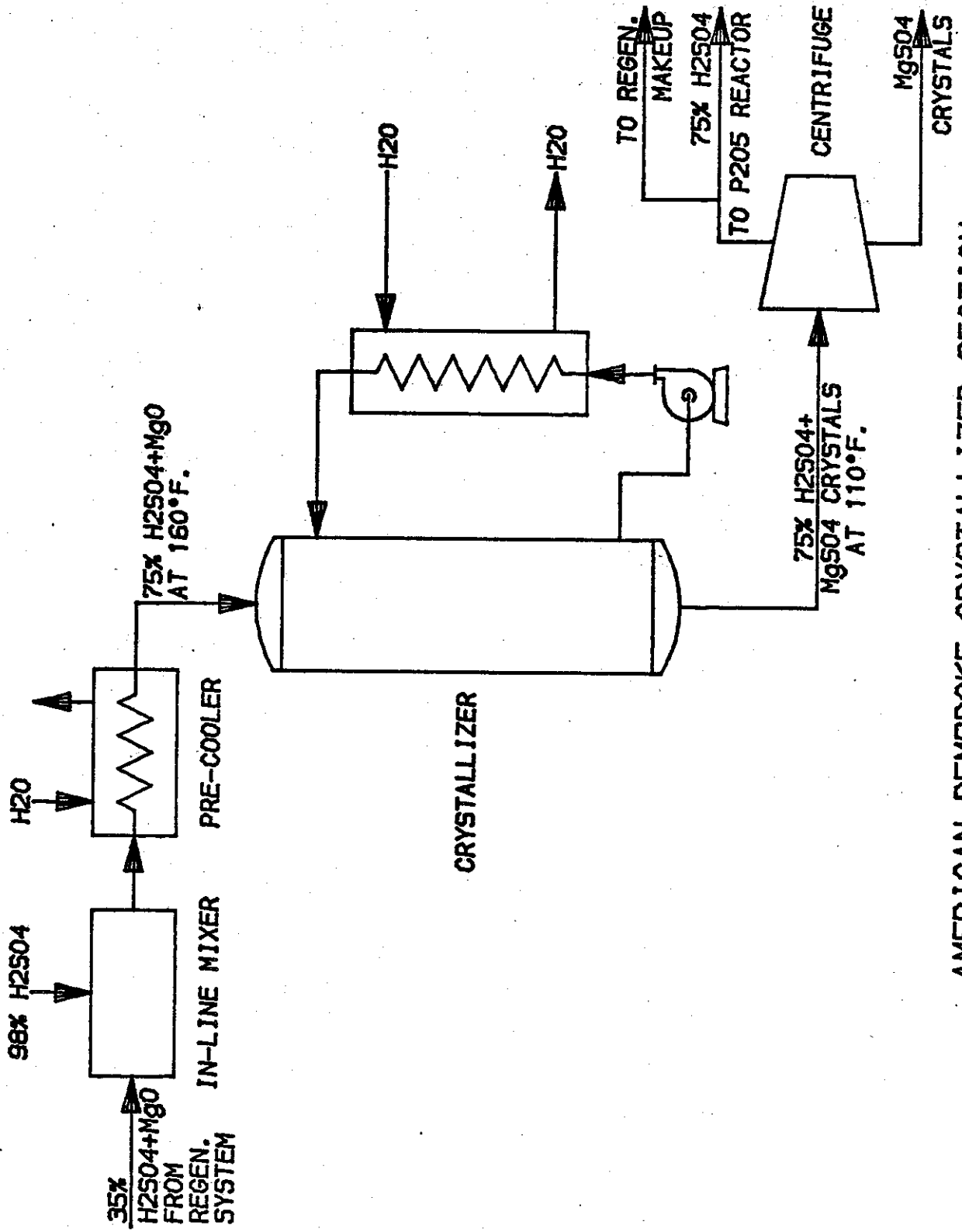
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AMERICAN PEMBROKE FOLDED BED PROCESS

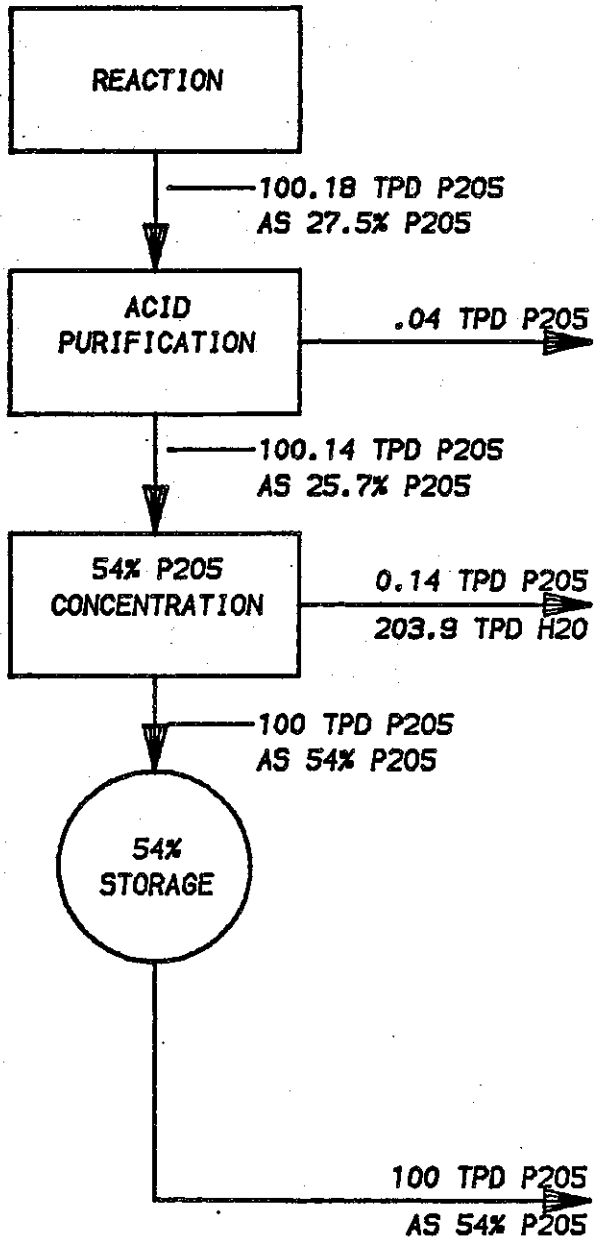
FLWSHEET NO. 1

SPENT REGENERATION
TO CRYSTALLIZER



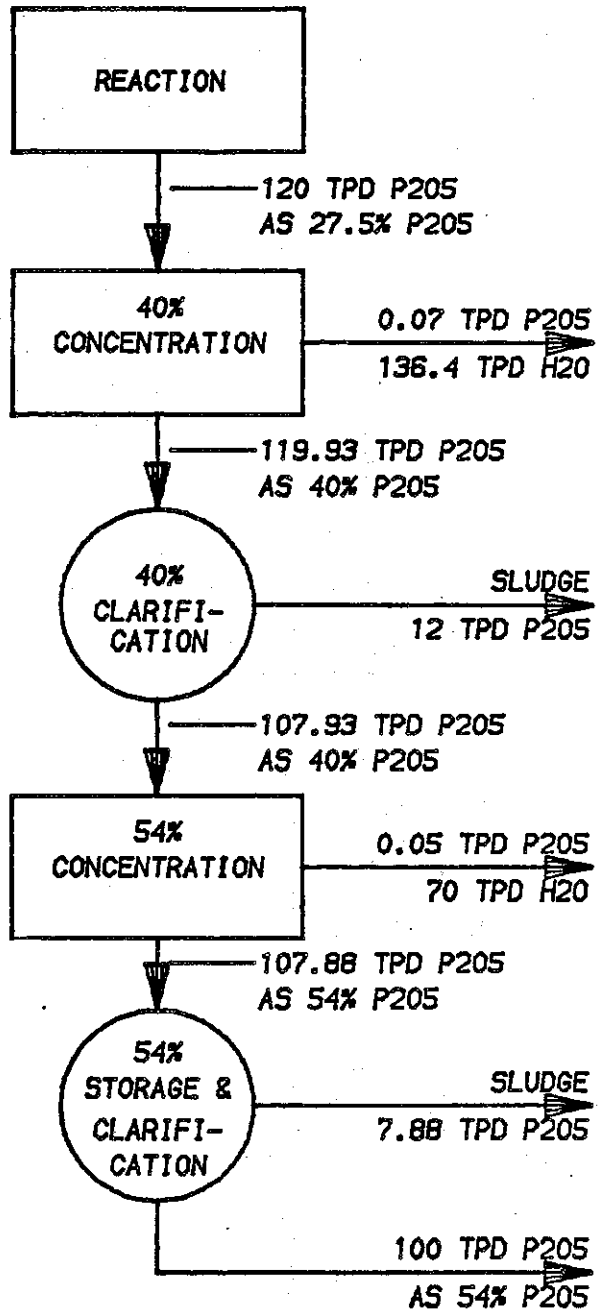
AMERICAN PEMBROKE CRYSTALLIZER SECTION

MERCHANT GRADE PRODUCTION
WITH PURIFICATION
(NO CLARIFICATION)



TOTAL EVAPORATION
REQ'D. = 203.9 TPD

MERCHANT GRADE PRODUCTION
WITH CLARIFICATION
(NO PURIFICATION)



TOTAL EVAPORATION
REQ'D. = 206.4 TPD