

IMPROVED METHOD FOR THE MANUFACTURE
OF WET PROCESS PHOSPHORIC ACID

PRESENTED AT AICHE CLEARWATER ANNUAL
JOINT MEETING ON MAY 27, 1989

BY

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INTRODUCTION

The wet process manufacture of phosphoric acid has been used for many years. The wet process involves the reaction of phosphate raw materials with sulfuric acid to form a reaction media of monocalcium phosphate, calcium sulfate, phosphoric acid and sulfuric acid. The designations of the three types of processes for the manufacture of phosphoric acid by the wet process are based on the by-product calcium sulfate degree of water of hydration; namely, the gypsum or dihydrate process, the hemihydrate process, and the anhydrite process. The type of the by-product is dependent on a number of factors, most importantly the temperature of the process system and the P_2O_5 concentration of the liquid phase of the slurry. For better control of that reaction temperature, P_2O_5 concentration in the slurry, and higher P_2O_5 yields, it has been a common practice to pre-dry the phosphate rock before grinding to the proper reaction size. Moisture introduced with the phosphate rock reduces the filter cake wash water and lowers P_2O_5 yields since evaporation of water is limited by the associated heats of reaction and dilution.

The high energy costs and more rigid environmental standards have and are causing the phosphate industry to change to a practice of wet grinding of the phosphate rock. The present method of wet phosphate rock grinding typically results in a phosphate rock slurry of about 65% solids and 35% water. With this increased water quantity to the phosphoric acid plant, the water balance problem even for the dihydrate processes results in a limit to the concentration of P_2O_5 in the

liquid phase of the reaction slurry. Many dihydrate plants have had to be satisfied with a filtrate P_2O_5 concentration of 26-27% P_2O_5 to maintain P_2O_5 yields. Plants, employing wet phosphate rock grinding, have had to reduce the wash water to the filter in an effort to increase the concentration of the filtrate phosphoric acid. But this decrease in wash water input results in lower P_2O_5 yields as the water balance within the process becomes critical.

This process improvement to be described therefore has the prime objective to provide a method where increased inputs of water, either from undried phosphate rock, wet grinding of phosphate rock, dilute sulfuric acid or from other sources will not interfere with associated high P_2O_5 yields, lower concentration of filtrate phosphoric acid and/or unbalance the zero steam requirements.

This process also has the embodiment to enhance the environmental operations of the phosphate complex by reducing the need for non-contact cooling water at the sulfuric acid plant. The volume of process water for sulfur trioxide hydrolysis is also greatly reduced and replaced by pond water recycle in the phosphoric acid plant.

It is obvious to one skilled in the phosphate business that production of a higher concentration phosphoric acid filtrate results in thermal savings. The energy presently used to concentrate the phosphoric acid to levels of P_2O_5 necessary for manufacture of MAP, DAP and merchant grade acid can be used elsewhere within the fertilizer complex.

EMBODIMENT OF PROCESS

The first step in the manufacture of phosphoric acid after the grinding of the phosphate rock is to react the aforementioned phosphatic materials with strong sulfuric acid (usually 93% strength) and digest into a slurry therein. This sulfuric acid is typically obtained from an adjoining sulfuric acid plant where the gaseous reaction product of sulfur trioxide is hydrolyzed with water. The large heat of dilution is normally lost to a non-contact water cooling stream. This heat of dilution could be made use of in the phosphoric acid plant where available heat is at a deficit.

This proposed process improvement teaches the use of a mixture of gaseous sulfur trioxide and strong sulfuric acid to react with the phosphatic materials in the phosphoric acid digester vessels. The proportion of the $\text{SO}_3/\text{H}_2\text{SO}_4$ mixture is dictated by the energy requirements of the particular reaction system. Thus, water laden phosphate rock is now able to be processed without drying or wet phosphate rock grinding can be employed. Even of greater importance with this process improvement; the present dihydrate chemistry for the manufacture of phosphoric acid can be changed to the hemihydrate chemistry which brings with it much higher yields of P_2O_5 (98.5%) and more concentrated filtrate phosphoric acid (50%). Without this process improvement, wet grinding of phosphate rock would not be economically feasible with the practice of the hemihydrate phosphoric acid process. Even present dihydrate operating phosphoric acid complexes

can benefit by this process improvement as additional wash water can be used on the filter and the present water balance difficulties associated with wet ground phosphate rock can be alleviated.

Another important feature of this process is the reduced water of hydrolysis necessary at the sulfuric acid plant. Pond water at the phosphoric acid plant will replace the high quality process water presently used to hydrolyze the SO_3 at the sulfuric acid plant.

Still another important feature is the reduced cooling water requirements at the sulfuric acid plant for removing the associated heat of dilution. This heat of dilution is presently discarded to the cooling medium and lost to the complex.

In summary, therefore this process improvement is logical from the following standpoints:

1. The heat of absorption of the SO_3 is recovered at the phosphoric acid plant where the heat input is badly needed.
2. Not good engineering design to expend effort at the sulfuric acid plant to hydrolyze the sulfur trioxide from the gaseous stream when it can be taken direct at the phosphoric acid plant. An analogous situation might be the condensation of ammonia at the ammonia plant site and re-evaporation at the nitrogen product complex.

PROCESS DISCUSSION

Please refer to Figure 1.

With the present innovation it is now possible to practice wet process phosphoric acid manufacture, produce high concentrations of filtrate phosphoric acid directly and still maintain high P_2O_5 yields without upsetting the plant water balance.

The first step in producing phosphoric acid by the wet process is to mix the ground phosphate rock with a recycle phosphoric acid stream and then react or digest the phosphate rock with concentrated sulfuric acid - strength ranging from 75 to 98%.

It is now proposed that, if instead of using concentrated sulfuric acid as a reactant, sulfur trioxide is substituted for part of that acid normally used, a higher heat of reaction results which is able to evaporate off excess water present.

It is quite a simple operation to take a slip stream of SO_3 gas from the exit of the sulfuric acid economizer and transport this stream to the phosphoric acid plant reactor. A booster blower is all that is required to accomplish this transfer of SO_3 gas to the phos acid plant. In addition it probably will be necessary to install another scrubber fan to be used in parallel with the existing scrubber fan. Depending on the capacity of the existing phosphoric acid plant scrubber, it may be necessary to add another small scrubber for parallel

operation. This is all that is required; no fancy and very high capital cost dewatering apparatus; i.e. filter, clarifier, etc. This entire gas transfer can be accomplished at only a fraction of the capital cost required for dewatering operations.

An important feature of this proposed innovation is that no flash cooler is required for removing heat of reaction and/or heat of dilution released during the reaction of acids with phosphate rock. For the case where flash coolers already exist in a phos acid plant being retrofitted or converted to the hemihydrate technology, these coolers can be used for the hydration or crystallization step. Thus no capital need be expended on new flash coolers for a plant conversion as necessary with the other methods of phosphate rock dewatering devices.

Still another feature of this proposed innovation is that a waste sulfuric acid stream of lower concentration (50-60% H_2SO_4) can be used to digest the phosphate rock without upsetting present yields or phosphoric acid filtrate concentrations. Obviously, other methods of phosphate rock dewatering would have no application with the usage of spent sulfuric acid streams.

Yet another important feature and probably very attractive for the phosphoric acid manufacturer is that he can vary the concentration of phosphoric acid filtrate produced and still maintain present yields, by varying proportions of sulfuric acid and sulfur trioxide gas passed to the phos acid plant reactor. The maximum filtration concentration, of course is dictated by the type of phosphate chemistry being practiced;

i.e. 50% P_2O_5 for the hemihydrate process and 30% P_2O_5 for the dihydrate process. For example, the phosphate manufacturer could readily obtain 50% P_2O_5 filtrate for merchant acid sales, 46% P_2O_5 filtrate for MAP manufacture, and 40% P_2O_5 filtrate for DAP manufacture using hemihydrate chemistry.

It is obvious that this process improvement will allow the maximum generation of electric power from those complexes employing co-generation.

HEAT THEORY

The heat of reaction of sulfuric acid with phosphate rock is known to be about 417 BTU/# of 68 BPL phosphate rock. The heat of reaction for the hydrolysis of sulfur trioxide is 696 BTU/# of SO_3 . The sensible heat for the gaseous sulfur trioxide stream is about 271 BTU/# of SO_3 assuming cooling from 450 F to 190 F. Thus the total heat release for the use of sulfuric trioxide in place of sulfuric acid to digest phosphate rock is 1066 BTU/# of 68 BPL phosphate rock. This represents an increase in reaction heat of 2.56 times or 156% of that for present practiced phosphoric acid manufacture.

WATER BALANCES

To illustrate the water balances which can accompany this process improvement, Figures 2,3,4 & 5 are here presented. The double filtration hemihydrate phosphoric acid technique is illustrated as this type of technology realizes the ultimate to be expected; namely,

... Concentrated phosphoric acid without energy input

... High yields of phosphate (P_2O_5)

Figure 2 is the water balance for a typical double filtration hemihydrate phosphoric acid plant with predried phosphate rock. Figure 3 is for the same double filtration plant using a wet ground phosphate rock slurry of 65% solids and 35% water. Figure 4 is for the same plant where the 35% water ground phosphate slurry has been dewatered on a vacuum filter to 20% water filter cake prior to use in the phosphoric acid plant. Finally, Figure 5 presents the water balance where 80% H_2SO_4 is used in place of the customary 93-98% strength sulfuric acid.

LABORATORY INVESTIGATION

This innovative method for the manufacture of phosphoric acid has been satisfactorily demonstrated in the laboratory. The phosphate rock was completely digested by the mixture of sulfuric acid and sulfur trioxide.

PROCESS ECONOMICS

The substitution of an SO_3 gaseous stream for part of the sulfuric acid feed to the phosphoric acid reactor appears to be a much lower cost alternate to the dewatering of wet ground phosphate rock slurry. Let's assume a 600 ST/D dihydrate phosphoric acid operating with a phosphoric acid filtrate concentration of 26% P_2O_5 in the liquid phase. Theoretically, this plant could operate at a phos acid concentration of 30% P_2O_5 , if economically feasible. The difference in water content between concentrations of 26% & 30% P_2O_5 is about 26,000 #/hr which presently must be removed by steam condensation at the phos acid plant evaporator station. The energy necessary for this P_2O_5 concentration could be used elsewhere within the fertilizer complex.

A sulfur trioxide gaseous stream of about 22,000 SCFM from the sulfuric acid economizer would furnish sufficient heat to remove the aforementioned 26,000 #/hr of water.

It is difficult to estimate what the capital cost would be to install the necessary facilities to handle the usage of an SO_3 gaseous stream from the sulfuric acid plant. A small booster fan and possible modifications to the existing phos acid digester scrubber system might prove necessary. An estimated modification cost might be in the range of \$75 - \$150,000.

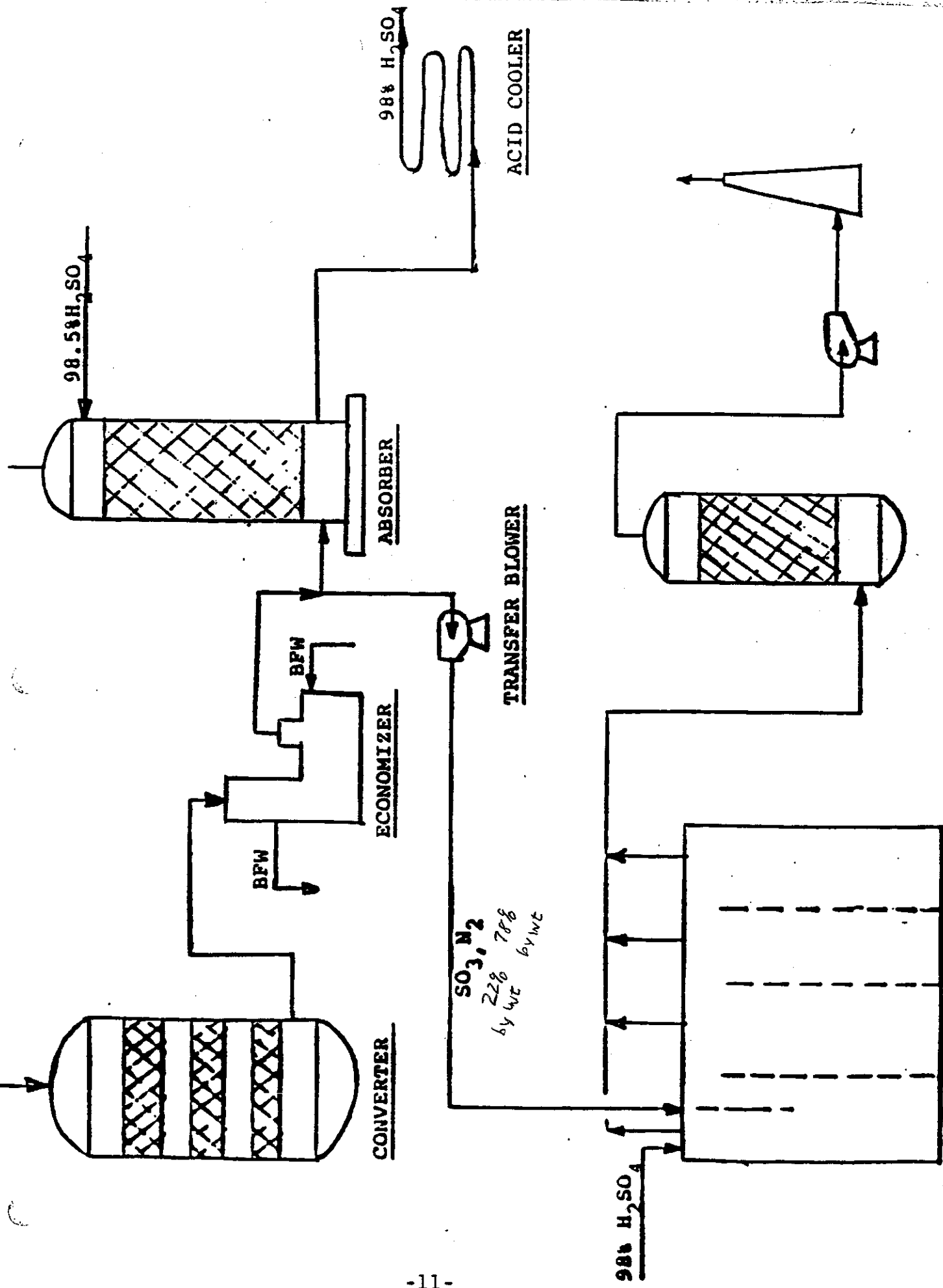
If the alternate dewatering approach is considered for the P_2O_5 concentration, the present 35% H_2O content ground phosphate rock

slurry would have to be reduced to about 28% H₂O. This would probably entail the installation of high speed thickeners which might involve a capital outlay of \$500 - \$600,000. In addition, the reported necessity for organic flocculation agents, to enhance the dewatering operations, would add to the operating costs.

CONCLUSIONS

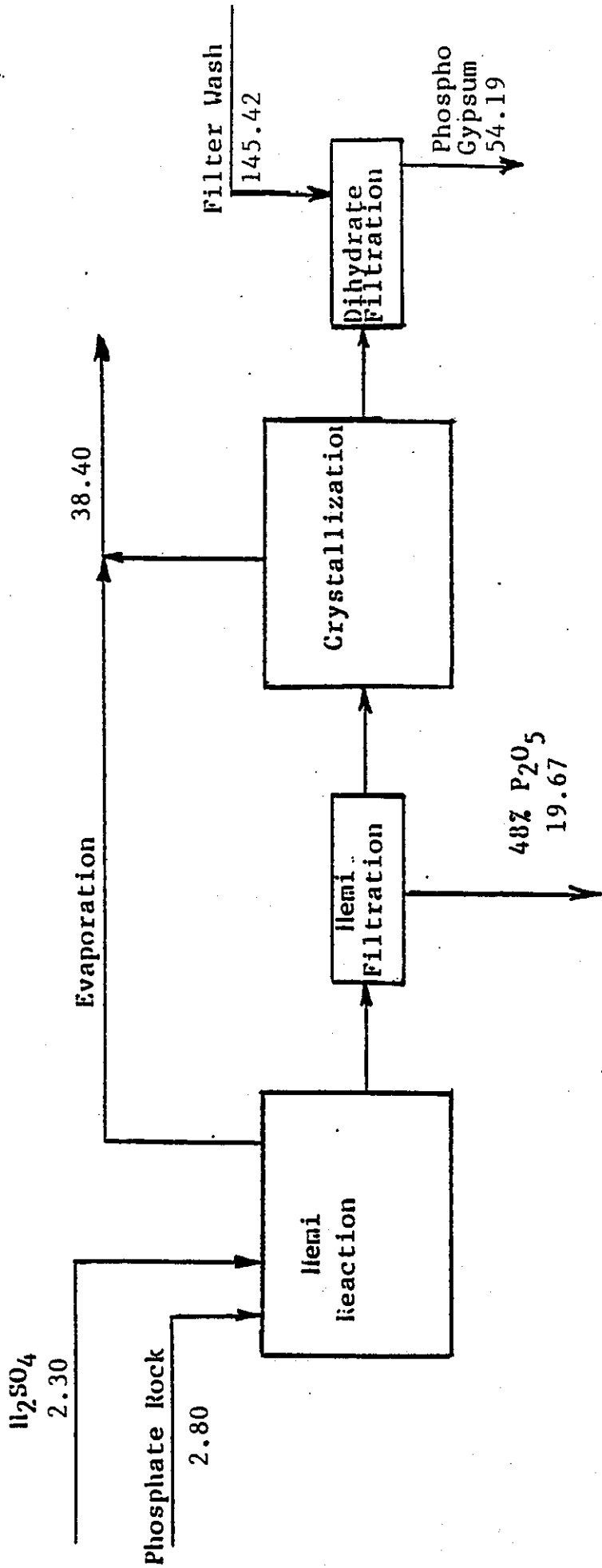
The usage of a gaseous sulfur trioxide stream provides the phos acid operator with a wide range of flexibility. This process innovation has application both to the dihydrate and hemihydrate types of phosphoric acid chemistry.

Co-generation
at 2¢/kw
Steam Valued at
\$3/ton ←



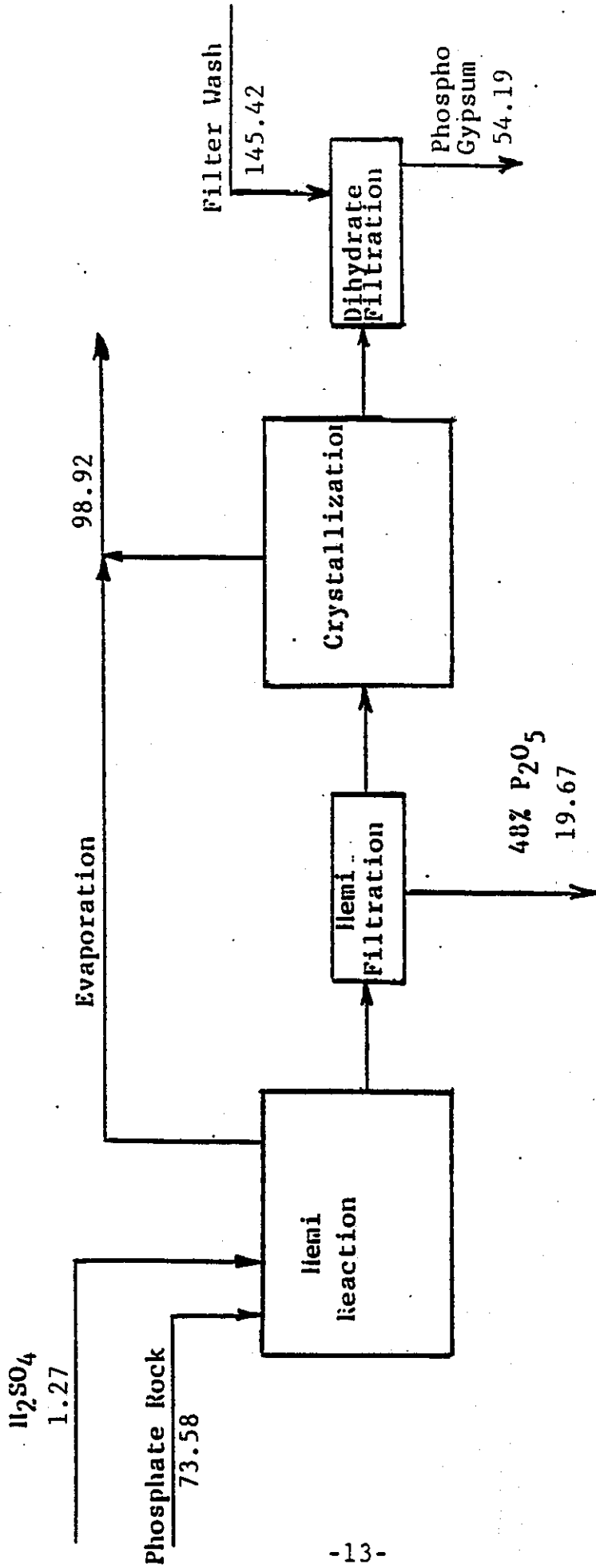
CONVERTER ECONOMIZER ABSORBER ACID COOLER PHOSPHORIC ACID REACTOR SCRUBBING TOWER EXHAUST FAN STP

Hemihydrate amt
1000 T/D of P₂O₅ as 48% P₂O₅
Water Balance
Tons/Hr



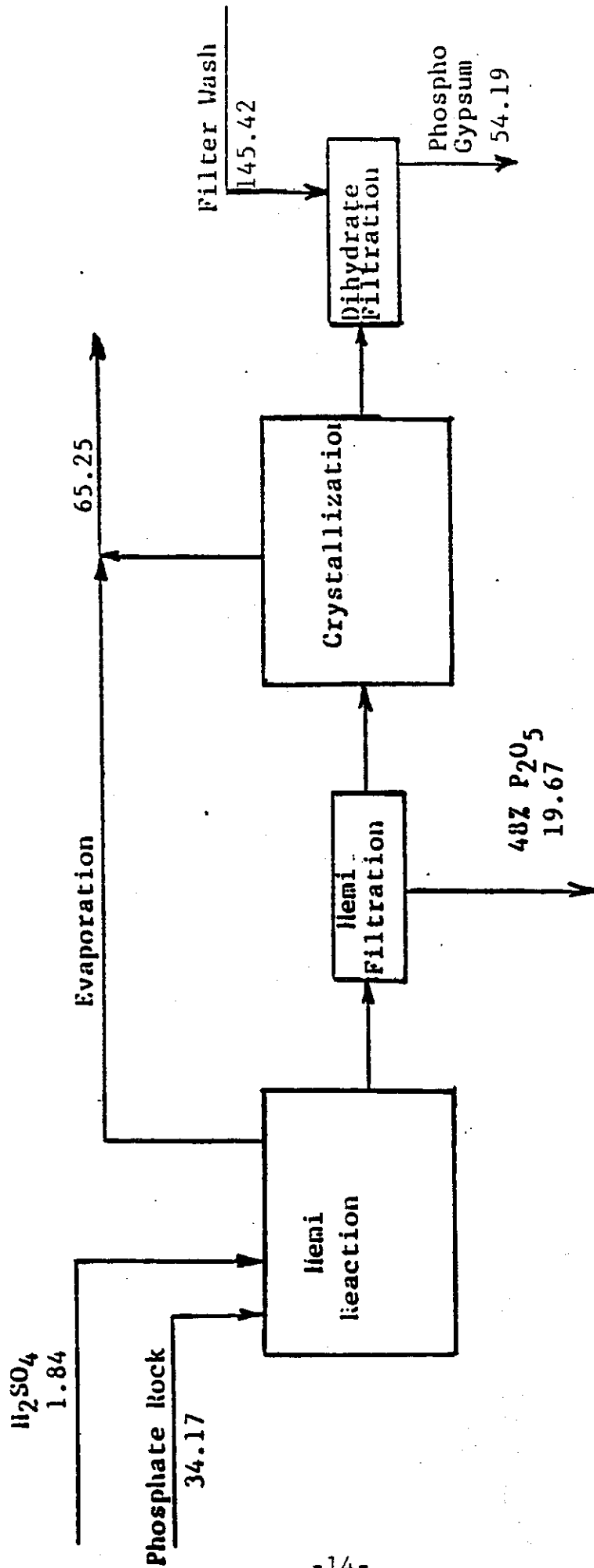
H₂O of Reaction = 150.52 - 112.26 = 38.26 T/H

Hemihydrate in
 1000 T/D of P₂O₅ as 48% P₂O₅
 Water Balance
 Tons/Hr



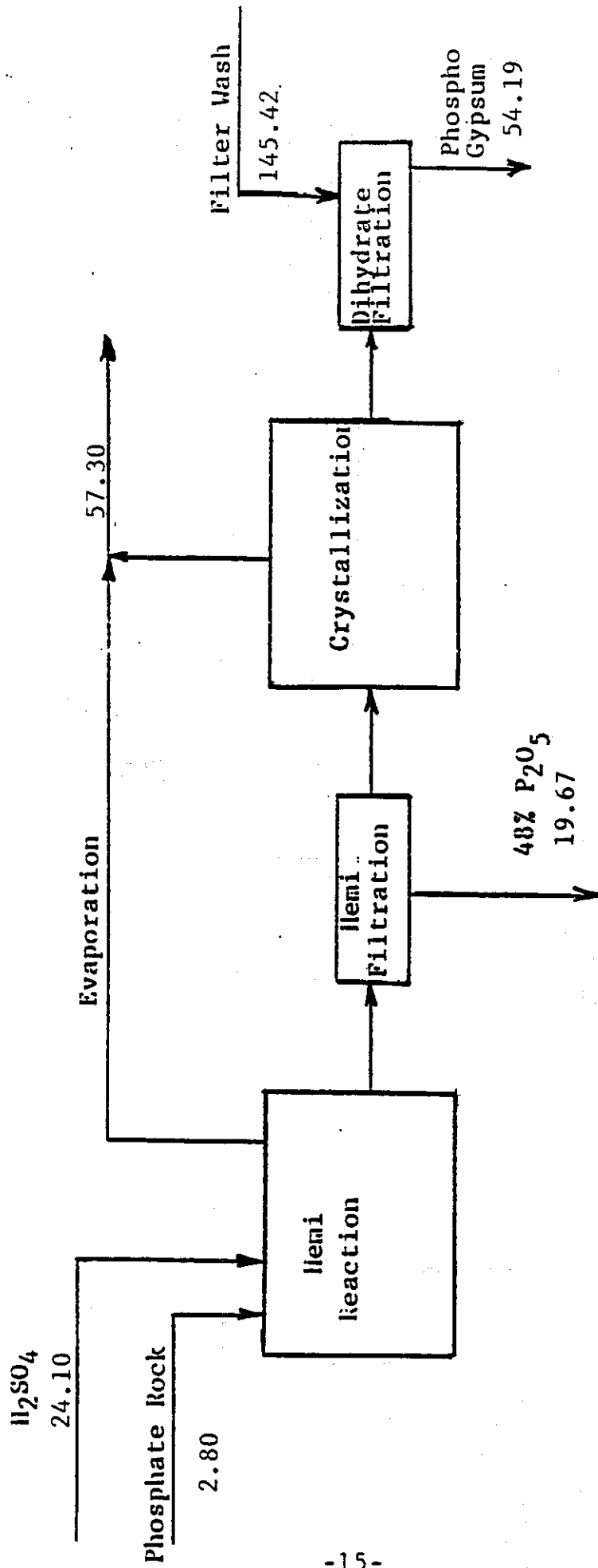
H₂O of Reaction = 220.27 - 172.78 = 47.49 T/H

Hemi-hydrate
 1000 T/D of P₂O₅ - 48% P₂O₅
 Water Balance
 Tons/hr



H₂O of Reaction = 181.43 - 139.11 = 42.32 T/H

Hemihydrate
 1000 T/D of P₂O₅ as 48% P₂O₅
 Water Balance
 Tons/Hr



H₂O of Reaction = 172.32 - 131.11 = 41.21 T/H

United States Patent (19)
Goers

(11) Patent Number: 4,501,724
(45) Date of Patent: Feb. 26, 1985

**[54] METHOD FOR THE WET PROCESS
MANUFACTURE OF PHOSPHORIC ACID**

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[21] Appl No.: 875,903

[22] Filed: Feb. 1, 1984

[51] Int. Cl. CO1B 25/16

[52] U.S. Cl. 423/320; 423/167

**[58] Field of Search 423/320, 321 R, 321 S,
423/522, 166, 167**

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Primary Examiner—Gregory A. Heller
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[57] ABSTRACT

An improved method for the wet process manufacture of concentrated phosphoric acid is disclosed herein. A mixture of gaseous sulfur trioxide and sulfuric acid now replaces concentrated sulfuric acid as a process reactant which results in a higher heat of reaction and the ability to evaporate out of the reaction slurry increased inputs of water. With this method the increased inputs of water, either from undried phosphate rock, wet grinding of phosphate rock, use of dilute sulfuric acid, or from other sources will not interfere with associated high P₂O₅ yields, lower concentrations of filtrate phosphoric acid and/or unbalance the zero steam requirements.

13 Claims, 4 Drawing Figures