International Fertilizer Industry Association

ISMA* Technical Conference

Orlando, Florida, USA
23-27 October 1978

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

TA/78/15

A Zero Discharge Acid - Water Recycle System For Wet Process Phosphoric Acid Plants

Douglas G. Mercer

Texasgulf Inc.

U.S.A.

In the early 1960's, Texasgulf (Texas Gulf Sulphur Company) conducted extensive studies to evaluate the potential development of North Carolina (U.S.A.) phosphate deposits. These studies resulted in the development of the Lee Creek Phosphate Operation, a 700 acre facility located on the shores of the Pamlico River in North Carolina. The complex consisted of a mining operation, ore beneficiation facilities, two (2) sulfuric acid units, two (2) wet process phosphoric acid trains, a diammonium phosphate plant, a granular triple superphosphate plant, a run-of-pile triple superphosphate plant, and a superphosphoric acid plant.

The two (2) phosphoric acid units were identical Wellman-Lord designed Prayon trains with a capacity of 525 tons a day of P_2O_5 each. The annual design capacity was 170,000 tons of P_2O_5/year each.

The cooling water system associated with these plants consisted of a 120 acre reservoir with a pumping station and return water line. The pumping station consisted of three (3) pumps, each rated at 22,000 GPM and 150 feet TDH. The normal operation consists of two pumps in services with a third pump as a standby unit. During normal processing, all the plant waters are collected at a sump system and pumped to the reservoir for cooling. However, about 2500 GPM of the water was diverted to the gypsum slurry pump and used to transport gypsum slurry to the gypsum disposal area. The water was drained from the gypsum and returned to the reservoir.

This water is used in the plants for such services as barometric condensers, cooling, and gas scrubbing, and for the washing of equipment and pipelines. In these services the water becomes contaminated by acidic materials, primarily phosphoric and fluosilicic acid. Also, much of the heat generated in producing phosphoric acid and other fertilizer materials is removed in the condensing and scrubbing operations. Adequate retention volume and surface area is needed in the reservoir so that heated water returning from the plants can be cooled for reuse. The maximum temperature permitted for cooling water being pumped to the plant is 90°F.

Because of the acidic content, this water system is operated as a closed loop. After numerous cycles of operation, the fluoride content of the water increases to an equilibrium value which is determined by the solubility.

Sodium and potassium fluosicates precipitate in the cooling pond and settle to the bottom as relatively coarse crystals. The equilibrium content of the phosphate is not determined by solubilities, but by complex relationship between the amount of P_2O_5 being added and the amount of P_2O_5 being withdrawn in the water used to make phosphoric acid. In this sense, the reservoir can be considered as a stable inventory of very weak phosphoric acid in which addition and removal are approximately in balance. This initial cooling water reservoir had a nominal operating depth of 3 feet with the design surface elevation plus 10 feet msl. The peripheral dike had an elevation of plus 13 feet. A divider dike was used to channel the warm return waters and prevent short circuiting to the pumping station. The initial construction and operation of this 120 acre reservoir was governed by a permit issued by the State of North Carolina through its environmental regulatory agency. The maximum operating level in this pond was dictated by the permit and treating of excess water was required. The treating water was discharged by a canal system to the Pamlico River.

In the early 1970's, Texasgulf began an expansion program which resulted in the production capacity being increased in the phosphoric acid unit to an annual production rate of 680,000 tons of P_2O_5 annually. The additional capacity was acquired by the contruction of two (2) additional Prayon design wet phosphoric acid trains each with a design capacity of 525 tons a day of P_2O_5. The construction of these new phosphoric acid plants required additional water circulation and more surface area for cooling purposes. One way of satisfying this need would have been to increase the size of the existing reservoir and adding pumps to the present pumping station. Unfortunately, space for increasing the reservoir was available only in a southerly direction and this was a low swampy area. In addition, operation of the system had revealed certain limitations which Texasgulf felt could be corrected by making some modifications in the facilities. Therefore, the entire closed water circuits were reviewed and basic changes proposed. The following major objectives were reviewed:

1. Consumption of acidic pond water had to be increased. Water is a major ingredient in making phosphoric acid. For technical reasons, a good part of the water consumed in the existing facilities was fresh water. The new phosphoric acid plant design was modified so that all the process water is taken from the closed water system. This resulted in approximately 2200 tons/day of additional acidic waters being consumed in the process, an average flow of approximately 350 gallons per minute. This consumption offered several major benefits.

2. Because rainfall in the immediate area of the Lee Creek complex exceeds evaporation during certain seasons, the present reservoir level tends torise at times, during heavy rains, causes difficulty in complying with freeboard limitations imposed by the permit issued by the State of North Carolina. Increased consumption will greatly facilitate the management of the pond water level. Also, increased withdrawal of water will, over a period of time, shift the P_2O_5 concentrations in the reservoir downward. Corrosion problems with the pond water would be reduced and the water could be more effectively utilized when washing equipment and pipelines. Reserve storage capacity had to be provided for extraordinary rainfalls. During the hurricane season, it is possible to have very heavy rains which could cause the reservoir to rise above permitted levels. Because the gypsum drainage area was extensive, the effect of runoff area for the reservoir was approximately twice the actual water surface area. Thus, a six inch rain could cause the pond level to rise 1 foot or more. Engineering studies indicated that it would be difficult to raise the elevation of the existing dikes in order to add the freeboard necessary to satisfy the North Carolina regulatory agency.

3. The pond area must be adequate for the heat load and pumping capacities necessary to meet the demands. In general, cooling capacity of a cooling reservoir is a function of the water surface and as the heat load increases, the reservoir area must also increase.

4. All State and Company requirements safeguarding the environment had to be met. The Company designed a system which would result in no discharge from this weak acidic reservoir of phosphoric acid. The State desired a system in which there was minimum opportunity for release of contaminated waters to the surface waters of the State.

In order to achieve all these goals, Texasgulf devised a system in which the cooling water surfaces would be separated into two ponds. Two (2) main plant areas would be serviced by closed cooling water circuits. These are the phosphoric acid plant area and the superphosphoric acid plant area. The latter also includes the solid fertilizer plants. These areas are separated by pipeline distance of approximately ½ mile. Also, nearly all of the acidic contaminants which build up in the circulating waters are contributed by the phosphoric acid plants. Very little phosphoric acid is picked up in the superacid - fertilizer plants area and only modest amounts of fluoride.

The P_2O_5 and fluorides collected in this system are primarily from the gas cleaning apparatuses associated with the fertilizer production facilities. Scrubber operations in the superacid - fertilizer area had been penalized by having to use the same highly acidic pond water from the 120 acre reservoir as the phosphoric acid plants. If a separate water system was used, the superacid - fertilizer plants would benefit greatly by having improved water quality for cooling and gas cleaning apparatus. Plant availability should be better with the two systems and there should be some savings in pumping cost because the second pond was to be located immediately adjacent to the superacid - fertilizer production area.

The attached Figure 1 shows the pond system which is placed in operation during this expansion program. The existing 120 acre reservoir pumping station was expanded to include 5 pumps in order to provide the necessary water to the new phosphoric acid facilities and still have standby capacity. The dike was raised to 15'6" to provide additional storage capacity. The new 60 acre reservoir was located adjacent to the superacid - fertilizer production area. The 60 acre reservoir also had a pumping station which utilized 3 pumps each with a rated capacity of 11,000 GPM and 95 TDH. The reduction in pumping distance also resulted in energy savings.

The system provides a tie between the two (2) ponds which will allow a transfer of water between the reservoirs during periods of exceedingly high rainfall. The pond was designed to operate under a manner similar to the 120 acre reservoir with a normal operating level of approximately 11 feet. The crest of the peripheral dike was approximately 19 feet mls. This left a reserve storage capacity of approximately 150 acre feet for storm surge storage. This reserve capacity was required by the State of North Carolina and is designed so that dual pond system, under normal operating conditions, has the ability to retain 40 inches of rain occurring within a 60 day time period. This rainfall is the rainfall of record for the area in which the Lee Creek complex is operated and occurred when three (3) major hurricanes passed through the area in 1955.

After this rather lengthy discussion of the consideration given by Texasgulf, let us consider the modification made in the phosphoric acid facilities which resulted in the increased consumption of the acidic waters and make the entire closed loop system operate. As pointed out earlier, the conventional Prayon plant used fresh water for the dilution of sulfuric acid from 93 to 56%. The blending of water and sulfuric acid evolves a considerable amount of heat due to the heat of dilution of the sulfuric acid. It is necessary to remove this heat from the acid which is accomplished with a sulfuric acid dilution cooler.

The dilution cooler is a shell and tube karbate heat exchanger. The diluted acid flows through the karbate tube while cool pond water flows in the shell constructed of rubber line steel. The dilution cooler cools the sulfuric acid to approximately 135°F before the acid is fed to the attack tank.

The diluted sulfuric acid with its accompanying water permits hydration of the calcium sulfate exactly where it is produced by the reaction of rock with sulfuric acid in the digestion tank. The cooling of the sulfuric acid is needed to reduce the danger of localized overheating at the point of reaction where the gyp crystals form. The local overheating would result in poor reaction of the rock and considerably affects the regularity of the gyp crystals and consequently the filtration of the acid slurry.

The cool sulfuric acid flows from the dilution cooler through a valve mechanism which splits the sulfuric acid into the first three compartments of the attack tank. The quantity to each tank can be controlled in order to insure proper digestion of the rock in the attack vessels.

In the digestion compartments, the phosphate rock and sulfuric acid react, releasing heat of reaction. As the slurry flows into Compartment No. 7, the slurry is pumped into a flash cooler where the slurry is cooled approximately 9°F. The cooled slurry is returned to the attack system and a major part of the cooled slurry is recycled to the front part of the attack digestion system and the remainder is pumped to the filter circuit for removal of the product acid from the by-product calcium sulfate.

In the modified phosphoric acid facilities the dilution cooler is no longer employed. The dilution of the 93% sulfuric acid is accomplished by mixing the acid with recycled acid pond water. The mixing tee is shown in Figure No. 4. The mixing tees are mounted directly on the top of Compartments 1, 2 and 3 of the rock digestion system. The amount of pond water used for the dilution is regulated so that the resulting mix approaches 56% sulfuric acid without creating a boiling solution in the mixing tee. The temperature of the resulting diluted sulfuric acid is dependent upon the initial concentration of the sulfuric acid, its temperature, and the temperature of the pond water being used for dilution. The rate of dilution is adjusted in order to maintain an acceptable sulfate level in the attack slurry tank.

Because there is no dilution cooler, the heat of dilution is added into the attack system and this is increased by the normal heat of reaction in the attack vessels. These combined heat loads must be removed from the digestion system in order for proper reactions to be completed. This is accomplished by significantly increasing the size of the flash cooler which is used in the process for cooling of the acid slurry. In our modified Prayon plant the slurry feed to the flash cooler is increased to 14,000 gallons/minute of slurry from Compartment 7 to the flask cooler. Slurry from the flash cooler discharges by gravity back into Compartment No. 9. From this compartment the slurry is distributed as follows:

1. Approximately 970 GPM of slurry flows back into Compartment No. 8 for aging and pumping to the filter where the product acid is removed from by-product calcium sulfate.

2. The remaining slurry (over 13,000 GPM) is returned to the 1st and 3rd compartments of the digestion system, flow being regulated by adjustable gate systems. In the first four compartments most of the reaction occurs. The next three compartments are for improving crystal growth.

The design temperature change across the flash cooler circuit is $9^{o}F$, to maintain reactor temperature control.

By comparison, the physical dimensions of the flash cooler in the original Prayon plants were an overall diameter of 18'7" and was 32' high. The cooler in the new facilities has a diameter 23'8" and are 46' high. The cooling capacity of the flash coolers in the original facilities was 27.6×10^{6} BTU/hr. The capacity of the unit in the modified facilities is 4.83×10^{7} BTU/hr.

The removal of the fresh water and increased consumption of pond water shifted the water balance in the entire cooling system as shown in attached Table 1. A consumption of the water normally occurs in the 120 acre reservoir. With the cross ties between the smaller 60 acre reservoir we are normally able to transfer water from this pond, where there is a normal input, to the larger reservoir. We are then able to consume these waters in the phosphoric acid facilities. An additional advantage is the continual dilution of the concentrated material in the 160 acre reservoir by the input of waters of the 60 acre reservoir containing lower concentrations of P_2O_5 and fluorine.

This system was constructed and placed in operation in 1974. At this time we have had nearly 4 years of operation of the system and it has performed above expectations. At all times during the operation we have had control of the water inventories in the dual pond system. In fact, in 1976 and 1977 when we had periods of unusally low rainfall, we had to add water into the pond system in order to maintain adequate operating levels.

In 1976, the U. S. Environmental Protection Agency adopted effluent regulations for phosphate fertilizer processing facilities which require all new sources to adopt a closed water recycle system. It is also the goal for existing facilities to achieve. However, the Environmental Protection Agency regulations do allow for the discharges of treated acidic process wastewaters following treatment during periods when the rainfall excdeds certain establish criteria. Our system is designed so that there should be no discharge of treated wastewater. We feel this system will allow us to consume the waters at rates that are adequate to insure the integrity of the dike systems surrounding the pond and return to normal operating levels even if the design conditions are slightly exceeded. The concept of no discharge is of major importance to the environment of our area in which there is a major river system used for recreational and economic uses. The river already has a high level of phosphorus in the water.

In addition, the ability to return water from the fertilizer gas scrubbing systems to the phosphoric acid production facilities allows us to reclaim P_2O_5 which might otherwise be lost if the waters were treated and released. Because we have been forced to add fresh water to the operating system on several occasions, it is difficult for us to estimate at this time the effect that the return of this P_2O_5 into the acid production facilities has had on the overall yield for the complex.

Several important items should be considered by any plant before installing this operating system. They are as follows:

1. The rainfall and the evaporation rates in the area of the plant.

2. The surface acreage needed for cooling purposes.

3. The acreage dedicated to gypsum disposal from which rainwaters will return to the cooling water system.

The consideration of these factors is necessary because the ability of the plant to consume water is limited by the production capacity. If the volume of water being returned to the cooling system is greater than the consumptive capacity of the facility, the system will not work. However, if these considerations can be met, this system will provide a totally closed acid water system for the manufacture of phosphoric acid. If additional processing facilities are located on the same complex, there is the additional advantage of being able to reclaim P_2O_5 which is being recovered from gas cleaning devices associated with the other production facilities.

WATER BALANCE*

Phosphoric Acid Plants

Texasgulf Inc.

Water Consumption (Acid Pond Water)	Original Plants 1050 TPD P_2O_5 Tons H_2O/Day	Expansion Plants 2100 TPD P_2O_5 Tons H_2O/Day
Water of Hydration of P_2O_5 $P_2O_5 + 3H_2O \rightarrow 2\ H_3PO_4$	760	1520
Water of Hydration for Gypsum $CaO + H_2SO_4 \quad CaSO_4 \cdot 2H_2O$	1110	2220
Free Water Retained In Gypsum Storage (15%)	850	1700
Acid Pond Water Used In H_2SO_4 Dilution	106	2260
Losses From Acid Pond By Evaporative Cooling	2980	5960
Total Water Removed From Acid Pond System	5806	13660
Water Input To System (Fresh H_2O)		
Dilution Of H_2SO_4 From 93% to 58%	2150	2150
Water Of Hydration of H_2SO_4	570	1140
Total Water Added To System	2720	3290
Net Consumption of Water From Acid Pond System	3086	10370 (2.763×10^6 GPD)

*This balance does not consider input or loss of water by rainfall or solar evaporation.

Figure I

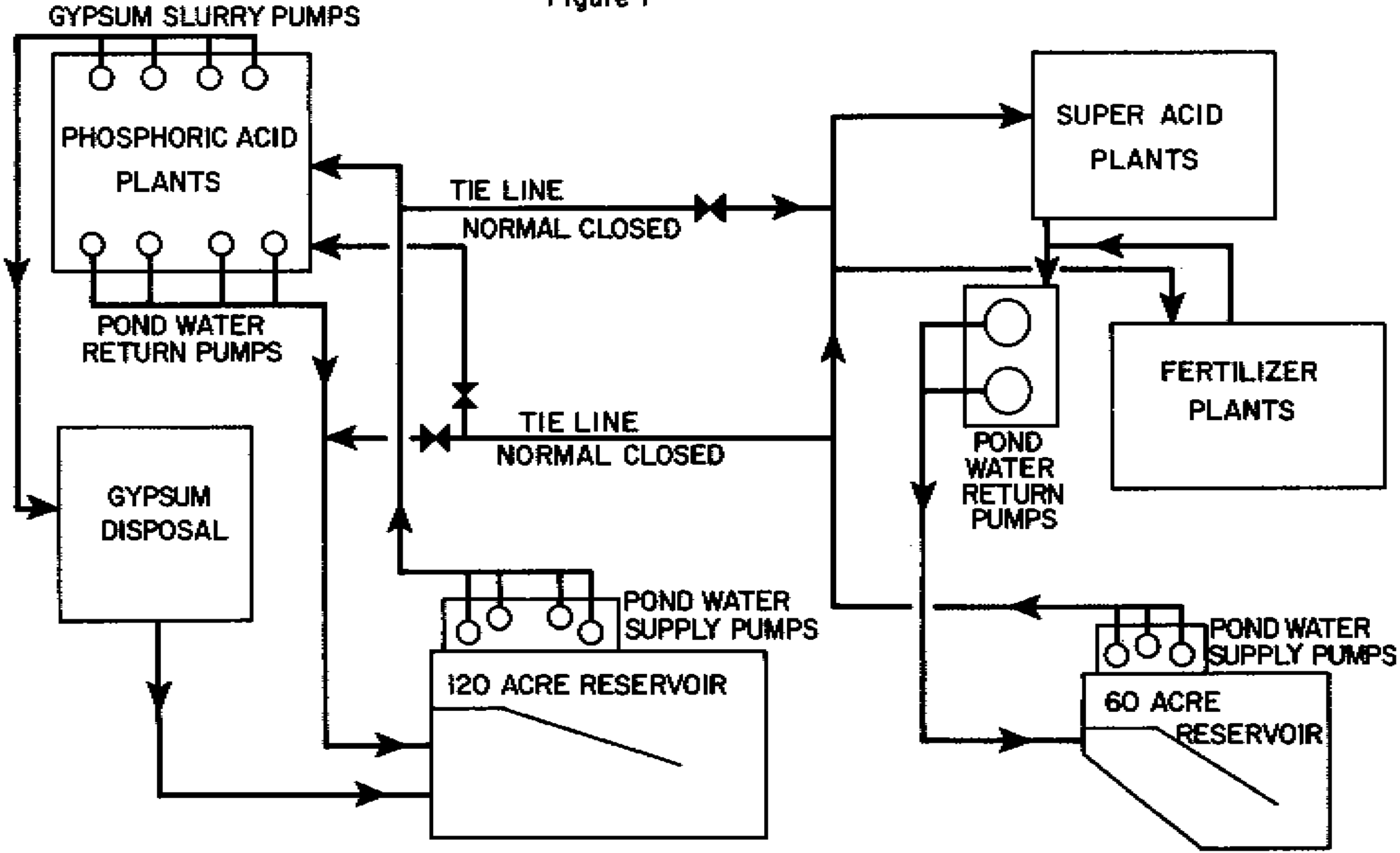
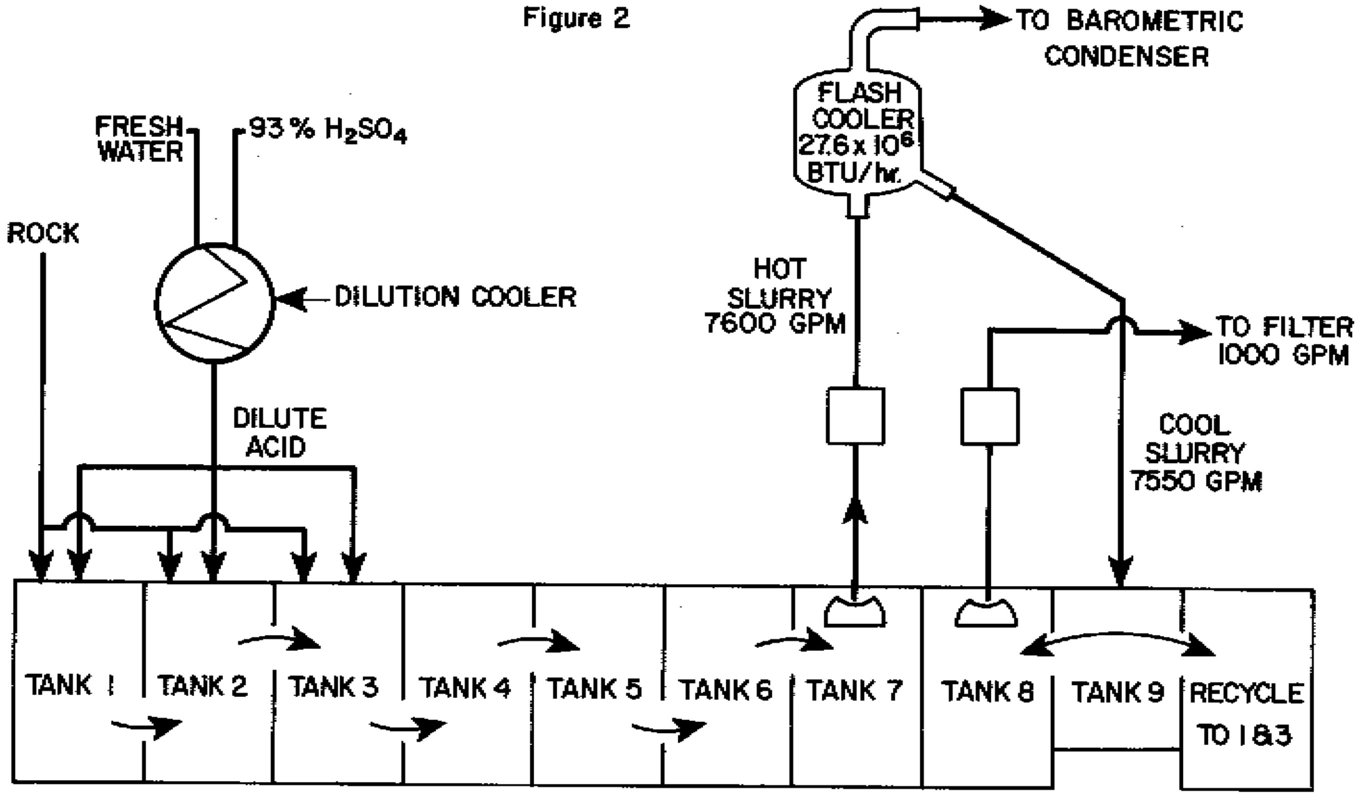
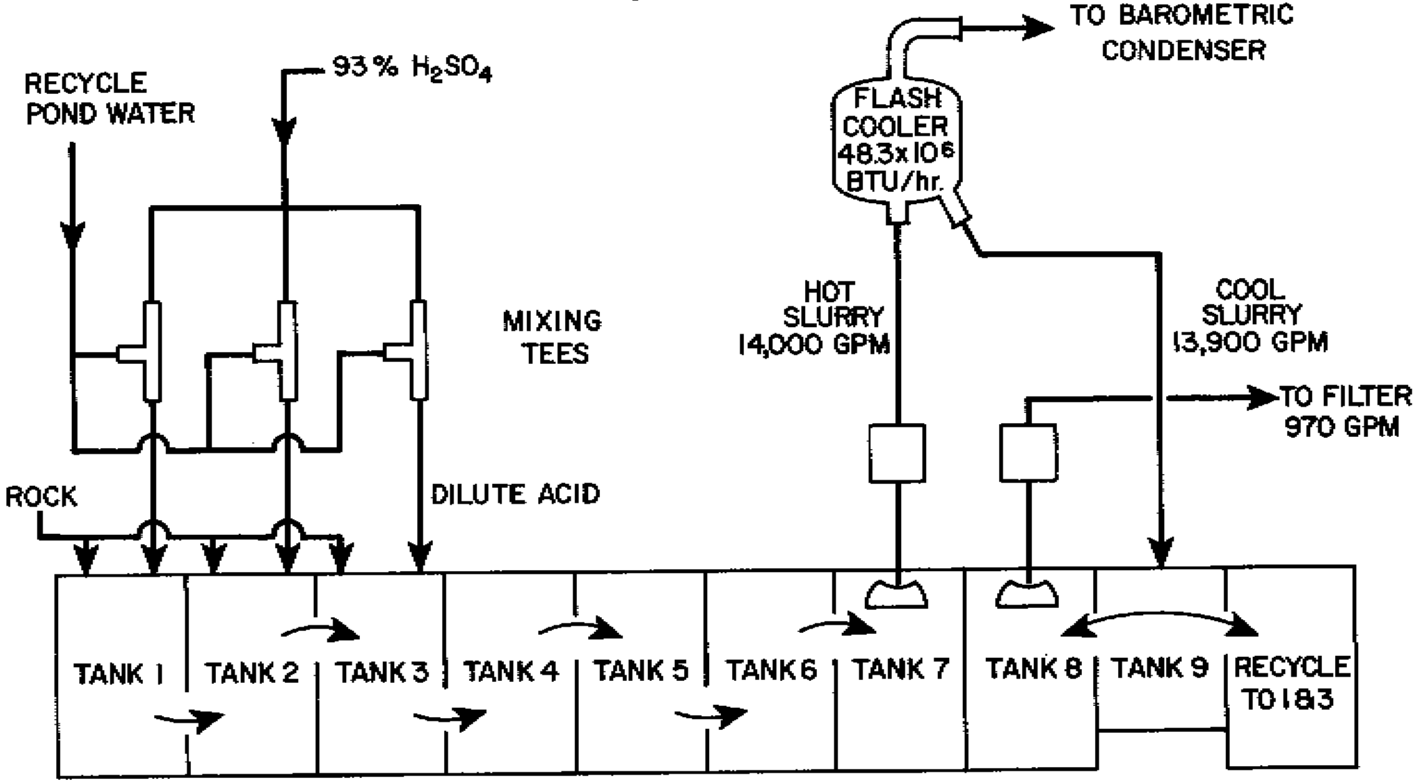

GYPSUM SLURRY PUMPS
PHOSPHORIC ACID PLANTS
POND WATER RETURN PUMPS
TIE LINE
NORMAL CLOSED
TIE LINE
NORMAL CLOSED
SUPER ACID PLANTS
FERTILIZER PLANTS
POND WATER RETURN PUMPS
GYPSUM DISPOSAL
POND WATER SUPPLY PUMPS
120 ACRE RESERVOIR
POND WATER SUPPLY PUMPS
60 ACRE RESERVOIR

Figure 2



FLOW - PHOSPHORIC ACID PLANT

Figure 3



MODIFIED FLOW - PHOSPHORIC ACID PLANT

Figure 5

WATER FLOWS - 120 ACRE COOLING POND and PHOSPHORIC ACID

(ALL POSSIBLE SOURCES)

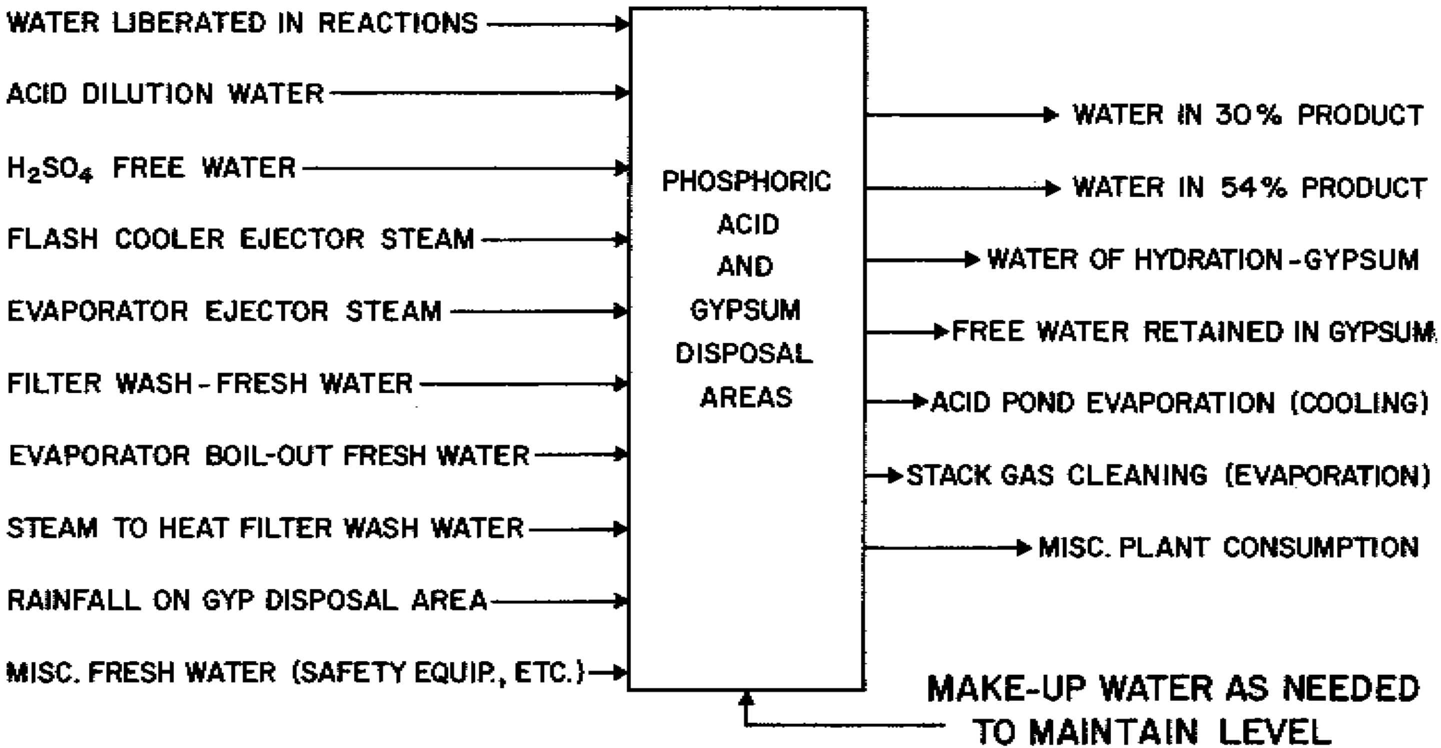
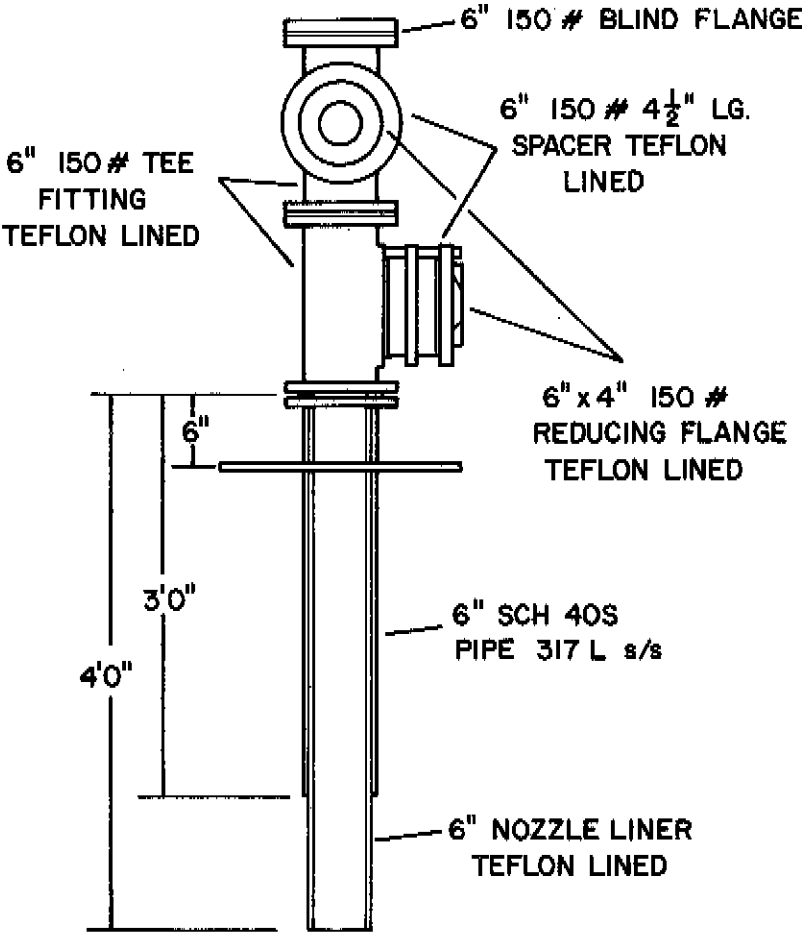


Figure 4



H_2SO_4 MIXING TEE - DIP TUBE

ACID IN UPPER TEE

POND WATER IN LOWER TEE