

PALM HARTIG pH PROCESS WATER SYSTEM

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I. INTRODUCTION

A. POTENTIAL ENVIRONMENTAL PROBLEMS WITH GYPSUM STACKS & ACID WATER COOLING PONDS

Pond water is a weak acid mixture of phosphoric and fluosilicic acids and a host of other impurities, with a pH range from 1.5 to 2.0. The pond water contains several thousand ppm of fluorides and phosphates, and up to 80 pCi/l of radium-226.

Gypsum pond water is recirculated around large cooling ponds of several hundred acres for cooling, used to slurry gypsum, and is stored on gypsum stacks and in rainfall surge ponds. Cooling ponds and gypsum stack-rainfall surge ponds are usually contiguous and may be as large as 900 acres. These operations, in some instances, have contaminated ground water by seepage of the pond water into the underlying water aquifers. All installations emit gaseous fluorides to the air.

Ground water must meet Florida primary drinking water standards of 6.5 min. pH. 1.6 ppm F and 5 pCi/l [Ra-226 + Ra-228]. EPA revised its fluoride standards to 4.0 mg/l F (effective 10/2/89) as a primary standard and 2.0 mg/l F (effective 5/2/86) as a secondary standard.

Florida has ground water standards which require that primary drinking water standards be met at the property line. Some gypsum stacks, built on the property line, are not able to meet this requirement. The federal EPA is currently working on the adoption of ground water standards.

Some proposed fertilizer plants outside the U.S. have requested plant designs without gypsum pond water cooling ponds to eliminate their potential environmental problems with respect to ground water contamination and vegetation damage by gaseous fluorides. A number of existing phosphate fertilizer plants do not have cooling ponds but rely on cooling towers.

EPA RCRA regulations allow virtually no migration of leachate from land disposal facilities. Pond water meets two criteria for hazardous wastes - low pH and corrosivity. At present, it has not been declared a hazardous waste by EPA. Gypsum was recently classified by EPA as a non-hazardous waste.

Elimination of cooling ponds does not eliminate the potential for ground water contamination or gaseous fluoride emissions that could occur from gypsum stacks. However, if partially neutralized gypsum slurry is pumped to the gypsum stack, these problems could be minimized.

B. SOLUTION TO THE PROBLEMS

Integration of the PALM & HARTIG pH PROCESS into a phosphate complex's water circuit can be used to reduce ground water contamination levels of fluorides, phosphates, radium-226, and heavy metals to negligible amounts. Gaseous fluoride emissions from acid water cooling ponds

and gypsum stacks would be eliminated. Simultaneously, P_2O_5 recovery would be increased a few percent.

II. OVERVIEW

A. PALM & HARTIG pH PROCESS

The PALM & HARTIG pH PROCESS is a marriage of the patented Palm Process Waters Process with the patented Hartig Neutralization Process for the principal purpose of eliminating phosphate process acid (gypsum) pond waters and the ground water pollution caused by their use in water cooling ponds and gypsum stacks.

The Palm Process Waters Process, generates new acid process waters and partially or completely neutralized process waters, not previously used, to accomplish the above purpose. In addition, other advantages result. Acid pond (gypsum) water cooling ponds are eliminated. Thus, air pollution by fluoride emissions from pond water used in cooling ponds and gypsum stacks is eliminated. A further advantage is an increase in P_2O_5 recovery, which for many operations, will pay for the installation and operation of the new process equipment required.

The PALM & HARTIG pH PROCESS offers the following substantial economic and environmental advantages:

- Increased P_2O_5 Recovery
- No Acid Pond Water
- No Acid Water Cooling Ponds
- No Gaseous Fluoride Emissions from Gypsum Stacks & Ponds
- A Partially Neutralized Gypsum Stack
- Negligible Ground Water Contamination
- Lowered Gaseous Fluoride Emissions from the Complex Scrubbers
- Operating Savings up to \$1.30 per ton DAP

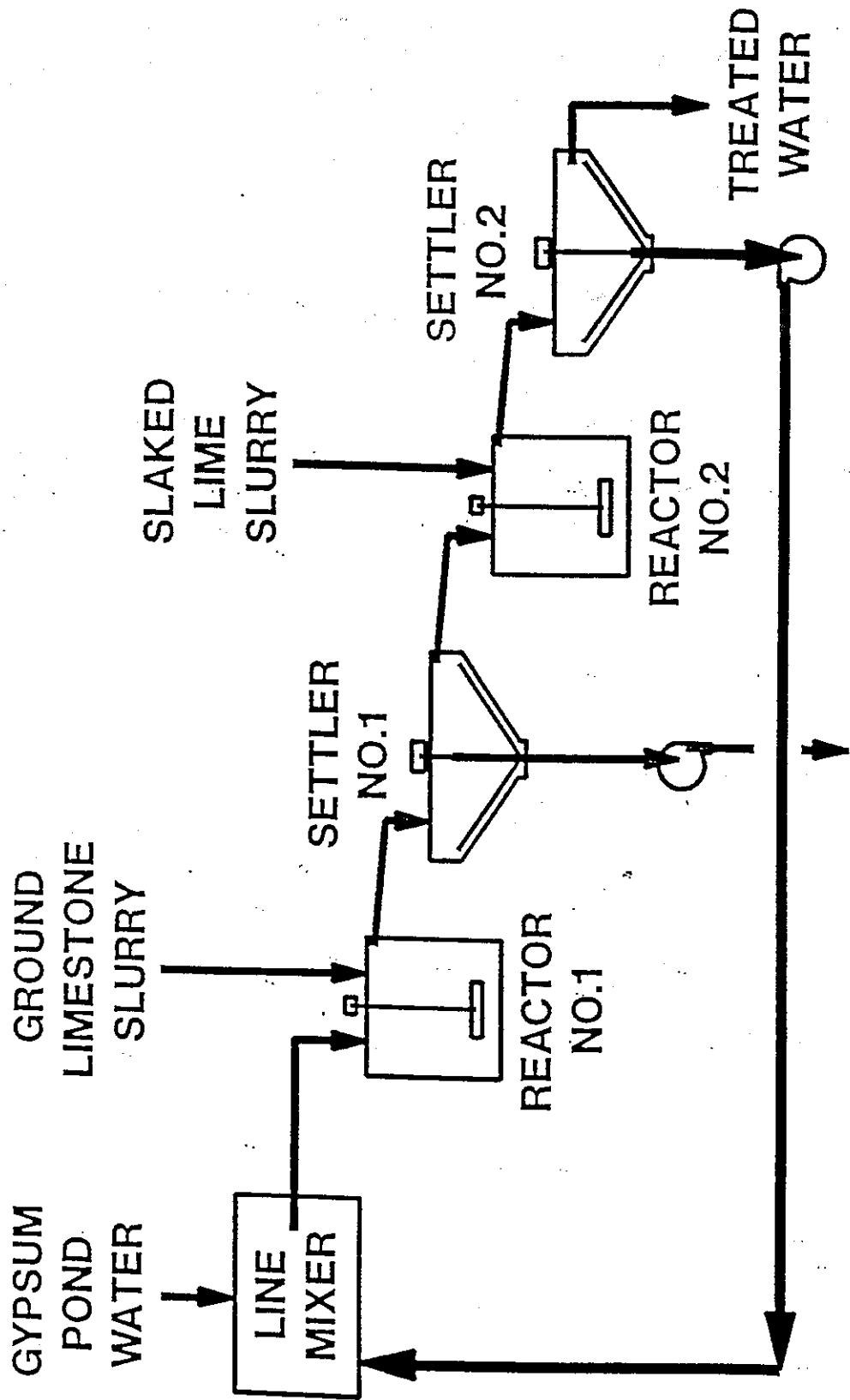
B. HARTIG NEUTRALIZATION PROCESS- FIG. 1

The Hartig Neutralization Process provides the proven technology for the partial or complete neutralization of the appropriate process waters where and when required. The Hartig Neutralization Process is a patented process originally developed for the neutralization of acid pond water generated by the phosphate fertilizer industry.

Acid pond water contains phosphoric acid (from 1.0 - 2.0% P_2O_5) and fluosilicic acid (from 1.0 - 2.0% F) and has a pH of 1.5 - 2.0. Neutralization is accomplished in two stages. In Stage 1, limestone or lime is added to a pH of 3.2-4.5 and precipitated solids are settled.

HARTIG NEUTRALIZATION PROCESS

FIG. 1



Decanted water is then treated with lime in Stage 2 up to a pH of 11.0 and the precipitated solids and excess lime settled. Stage 2 settled solids are removed, reacted, and dissolved in the acid pond water entering Stage 1. Thus, the excess lime to reach pH 11.0 is recovered and used for neutralization of incoming acid water to Stage 1. The reacted and dissolved Stage 2 solids are reprecipitated as calcium fluoride and dicalcium phosphate and other impurities along with the solids normally precipitated in Stage 1. All precipitated solids leave in the underflow from the Stage 1 clarifier.

The principal advantages for the Hartig Neutralization Process are substantial savings in raw materials costs. Operation is automatic and results in uniform treated water with stoichiometric use of limestone and lime. Rapidly settling waste solids are formed - in contrast to the usual flocculent waste solids. Demonstrated solids levels of 25+ % have been obtained in Stage 1 in contrast to usual levels of 15% or less for conventional two stage liming stations. Stage 2 solids in the latter are very flocculent and settle slowly. as discussed above, these second stage solids are eliminated in the Hartig Neutralization Process. Centrifuging the Stage 1 solids to 50% is a possibility, based on experience from similar operations. Analyses of treated pond waters are shown in Table 1.

TABLE 1
HARTIG PROCESS - NEUTRALIZED POND WATER ANALYSIS

Plant	pH	ppm	
		P_2O_5	F
X	11.4	8.6	2.5
Y	10.5	68	5
Z	9.4	6	4
Q	10.5	3	3

The Hartig Neutralization Process has been demonstrated on a commercial scale and evaluated in numerous batch and continuous laboratory units.

Table 2 shows the analysis of a Florida pond water treated to pH 12.0 and then settled in ponds. The impurity levels for the heavy metals are very low. At pH 11.0, the levels are probably about the same (data at pH 11.0 are not available).

TABLE 2
FLORIDA POND WATER TREATED TO pH 12.0

ANALYSIS	PPM	ANALYSIS	PPM
TDS	400	As	2 ppb
NH ₃	1.4	Pb	0.05
P	7-10	Hg	2.5 ppb
F	2-4	Ni	0.12
SO ₄	109	Cd	0
Fe	0.22	Cr	0
Al	4	Zn	0.11
Ca	97	Mn	0.01

III. PROCESS DESCRIPTION

Preliminary process design, capital costs, and operating costs, have been prepared for the integration of the PALM & HARTIG pH PROCESS into a fertilizer complex with the following capacities:

1,200 tpd Acid P₂O₅ = 375,000 tpy Acid P₂O₅
800,000 TPY DAP

A custom design can be made for each installation taking into account capacity and product slate. This preliminary design illustrates the process features and flexibility of the PALM & HARTIG pH PROCESS.

A. PALM & HARTIG pH PROCESS

The PALM & HARTIG pH PROCESS is integrated into the phosphate complex operations in order to realize substantial environmental and economic advantages. Gaseous fluoride emissions from cooling water ponds and gypsum stacks are virtually eliminated. Ground water contamination caused by seepage from gypsum stacks and acid water cooling ponds is reduced to a negligible level. P₂O₅ recovery is increased.

B. DESIGN CONCEPT

1. Elimination of Pond Water

The primary object of the PALM & HARTIG pH PROCESS is the elimination of phosphate process acid (gypsum) pond waters and the ground water pollution caused by their use in water cooling ponds and gypsum stacks (for slurring gypsum pond water which is deposited in the gypsum stack).

2. Elimination of Gaseous Fluoride Emissions from Ponds and Gypsum Stacks

Other objects of the PALM & HARTIG pH PROCESS are the elimination of the air pollution associated with phosphate process acid pond waters and reduction of P_2O_5 losses in the process of manufacturing wet-process phosphoric acid.

3. Acidic Process Waters

In general, the objects of the PALM & HARTIG pH PROCESS are attained by providing new acidic process waters--not previously so used--in place of conventional phosphate process acid pond water. Acid process water results from the aqueous collection of gaseous fluorides by circulating water through flash coolers and evaporators condensers and are combined with the collection of P_2O_5 process spills, leaks, and wash liquids.

Such combined acid process waters are contained in process tanks, pipelines, and like equipment. They are not in direct contact with external air, soil, and water; unless they have been modified by partial neutralization to a moderate pH of about

New combined acid process waters are used for washing the filter cake, thereby supplying process water to the phosphoric acid reactor, and simultaneously recovering substantially all of the miscellaneous water-soluble P_2O_5 normally lost in the conventional processing. Fluosilicic acid in the acid process water passing through the washed filter cake reacts with phosphate rock in the phosphoric acid reactor to produce phosphoric acid. This precipitates the fluorides, and to reduces the consumption of sulfuric acid.

Gaseous fluorides collected from the reactor and other process equipment are captured in the process scrubbers by the scrubber process acid water. This water is neutralized in Step 1 of the Hartig Neutralization Process to a pH of about 4.5 and then used for slurring phosphate rock in wet rock grinding.

Water draining from previously or newly formed gypsum stacks is also appropriately treated and utilized. Such gypsum stack water is freed of strong acid and soluble fluorides by partial neutralization to a pH of 4.5 by addition of limestone to a gypsum neutralization tank. Upon being

recirculated, a portion is treated with lime to a pH of 11.0 to remove silica, calcium, and to further reduce the level of heavy metals and radioactive compounds. Thus, a non-scaling, pH-adjusted process water (pH-AW), suitable for such purposes as filter wash, scrubber make-up, cooling tower make-up, acid process water make-up, limestone slurring, and lime slaking and slurring is produced.

C. ACID PROCESS WATER (APW) - FIG. 2

Acid process water (APW) is generated from pH-AW and totally used for its intended purpose, i.e., a once-through water for process make-up in the wet process phosphoric plant. Simultaneously, substantially all of the miscellaneous P_2O_5 losses that occur in conventional processing are recovered.

In the acid process water (APW) condenser-heat exchanger-cooling tower circuit, pH adjusted water (pH-AW) is added to a circulating flow of APW. Steam from flash coolers and evaporators of a wet-process phosphoric acid plant is condensed with circulating APW at 95°F, which warms to about 128°F. The warm water is cooled in plate type heat exchangers by a separate isolated circuit of cooling water recirculating from there to a cooling tower and back in a range of about 85°F to 109°F. Cooling tower make-up is pH-AW which is non-scaling and compatible with cooling towers designed for fresh water use.

D. ACID PROCESS WATER P205 RECOVERY-Fig. 3

The APW absorbs all gaseous fluorides evolved by the flash coolers and evaporators as well as collecting entrained phosphoric acid. concentrations are usually in the range of about 8 to 10,000 ppm of fluorides (F) and about 14,000 ppm P205. A purge stream of warm water from the APW sump tank precludes accumulation above such concentrations--and is sent to the P205 recovery tank. APW in the tank is circulated to plant areas to collect and recover P205 from spills & leaks and is used for washdowns. A purge stream from the P205 recovery tank is sent to the P205 recovery settler for removal of suspended solids to prevent blinding of the filter cake when washing with this water.

Solid free APW is used for the Step 1 filter cake wash to provide about 60% of the process make-up water to the process. In so doing, about 80-85% of the miscellaneous P205 loss is recovered to the process. This is normally collected by conventional acid pond water, used to slurry the gypsum, is present in the moisture in the deposited gypsum in the gypsum stack, and thereby lost to the process. The APW is acidic, pH 1.8-2.0, has not been partially treated with limestone or other neutralizing agents, and is generally non-scaling.

In addition to an increase in P205 recovery, the fluosilicic acid in the APW going into the phosphoric acid reactor will react with the phosphate rock to produce phosphoric acid, while saving on the use of sulfuric acid and removing the fluorides by precipitation.

ACID PROCESS WATER GENERATION

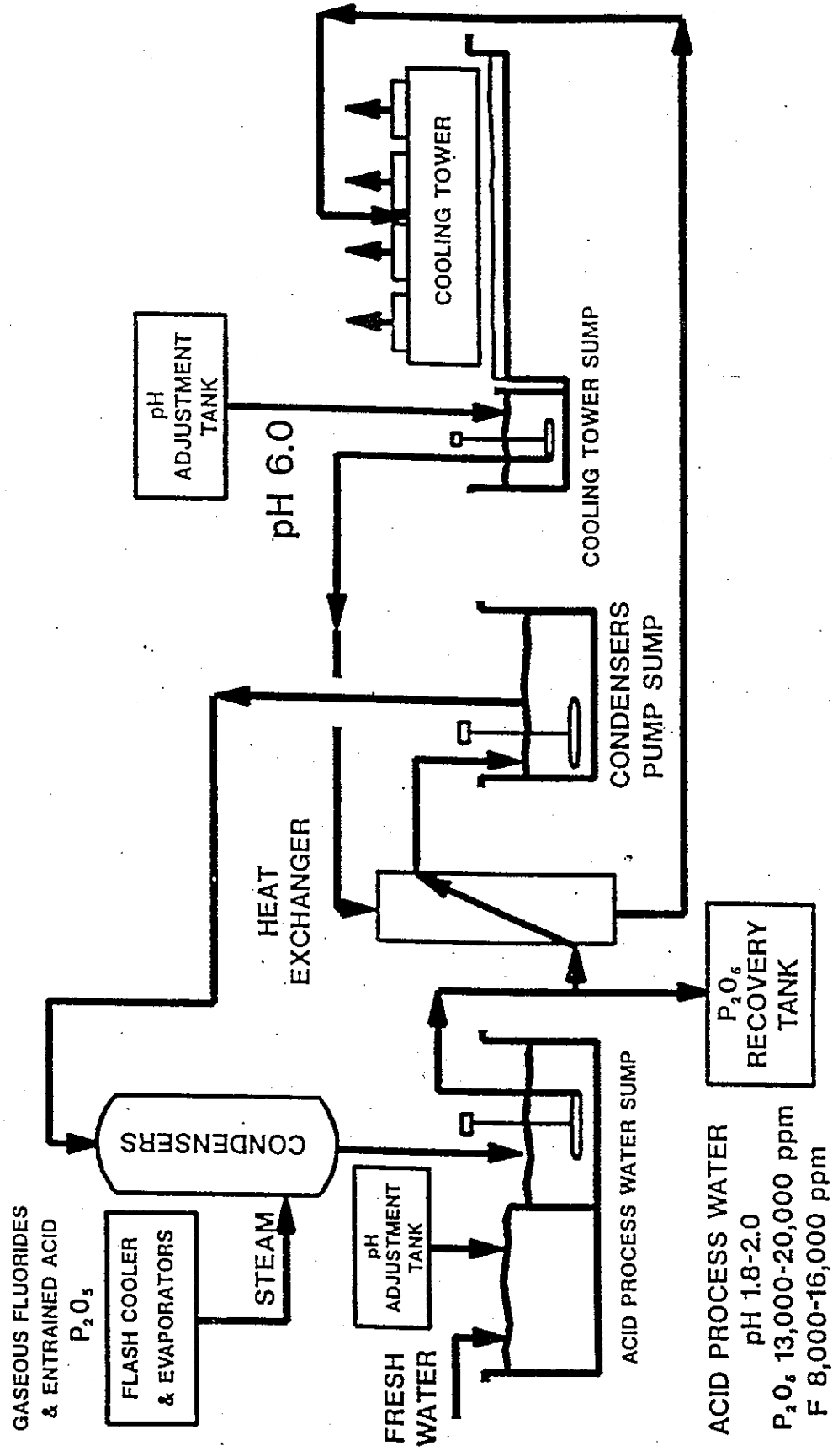
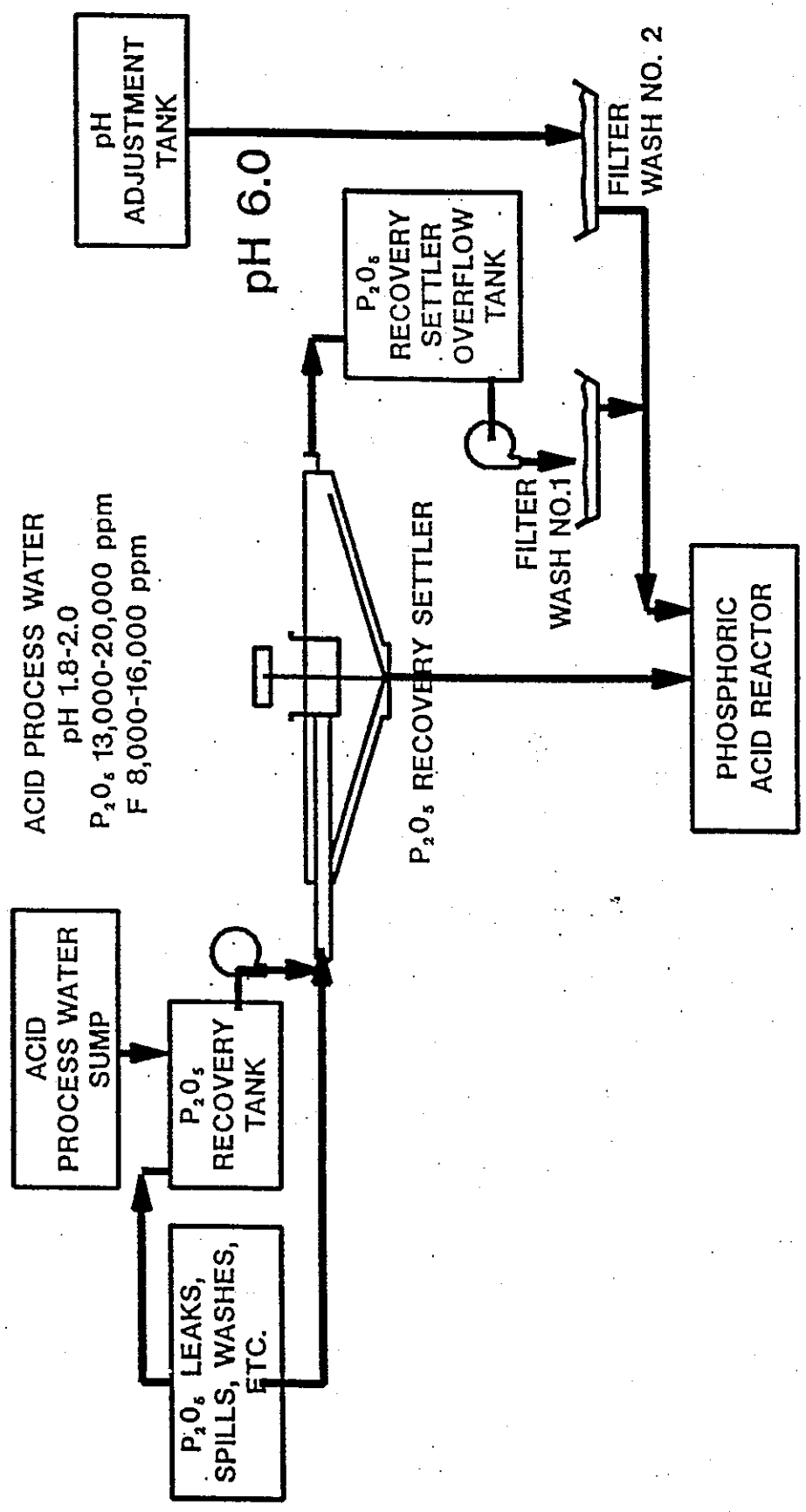


FIG. 2

ACID PROCESS WATER P₂O₅ RECOVERY

FIG. 3



E. SCRUBBER WATER (SW) GENERATION - FIG. 4

Scrubber water (SW) is generated from pH-AW and totally used for its intended purpose, i.e., a once-through water. The pH-AW is introduced into the last stage of the scrubbers and by circulating around the process scrubbers, substantially absorbs all the gaseous fluorides. P2O5 content would be negligible, especially in modern plants with wet rock grinding. A scrubber heat exchanger, using cooling tower water, cools the scrubber water from about 100 °F to 95°F for more efficient scrubbing. The recirculated water rate to the scrubber is on the order of 35 gallons per minute (GPM) per 1,000 actual cubic ft³ of gas per minute (ACFM). The fluoride content will range from about 8,000 ppm to 14,000 ppm depending on the phosphate rock used, the manner in which the filter recycle acid and sulfuric acid are fed to the reactor, and the process used, i.e., dihydrate or hemi-hydrate.

F. SCRUBBER WATER PARTIAL NEUTRALIZATION - FIG 5

A purge stream from the scrubbers feed sump is used to control fluoride concentration and is sent to the Stage 1 Reactor of the neutralization system for removal of fluorides.

Limestone slurry provided to the Stage 1 reactor raises the pH of the SW (usually in the range of about 1.5 - 2.0 pH to a range of about 3.0 to 4 pH at which essentially all the fluorides precipitate. The clarified overflow goes principally to wet rock grinding with any remainder going to the Stage 2 reactor. Underflow solids from the Stage 1 clarifier, primarily precipitated fluorides, are sent to a sludge disposal area outside the plant area.

G. pH ADJUSTED WATER (pH-AW) - FIG. 6

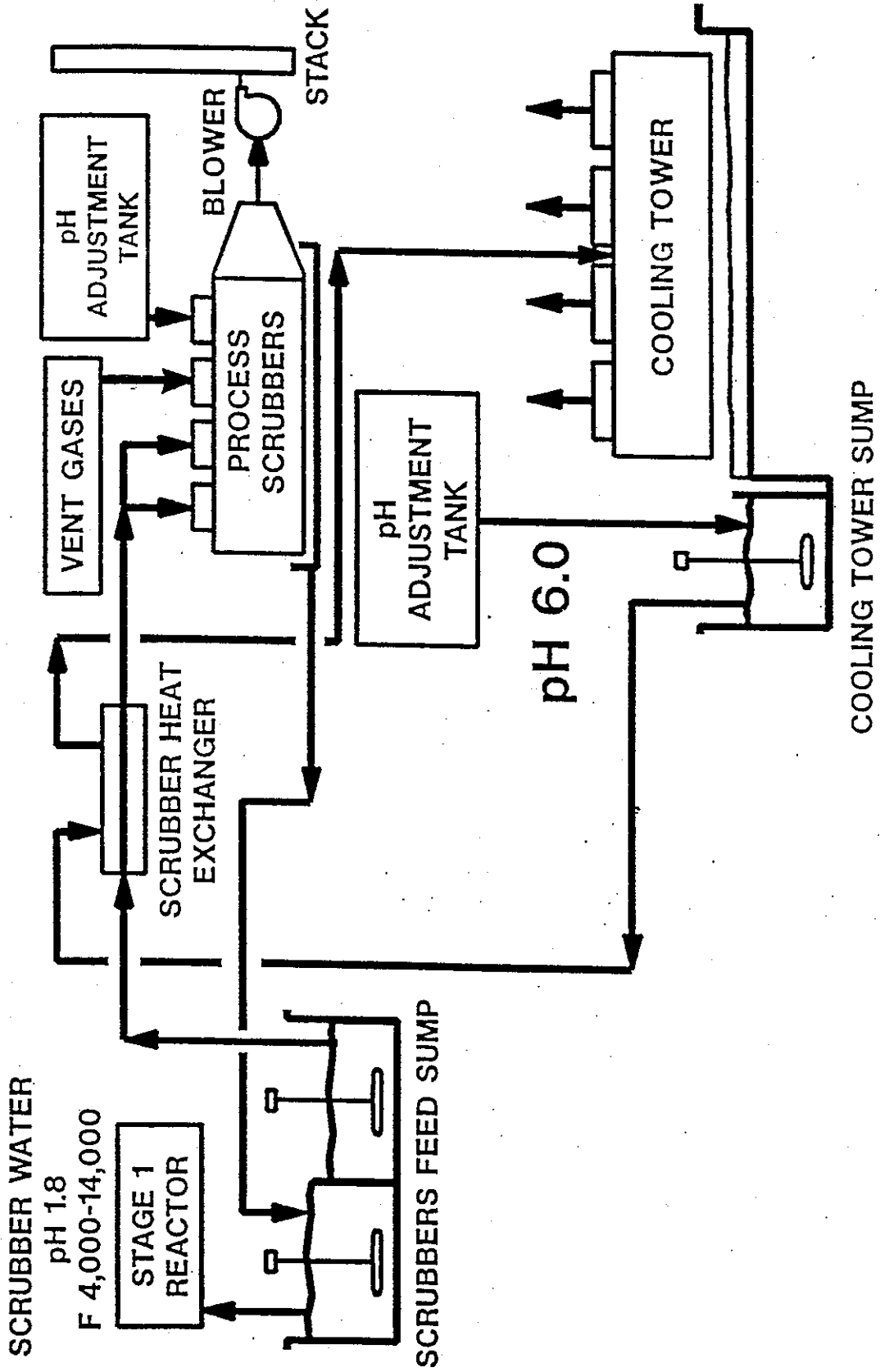
Partially neutralized gypsum stack return water, at pH 4.5, is the principal feed to the stage 2 reactor, wherein lime slurry is added to raise the pH to about 11.0 and the reacted mixture overflows to the second-stage settler. Limestone slurry and lime slaking-slurrying water use pH adjusted water for more efficient slaking and to conserve on fresh water use.

The clarified, clear, overflow water goes from the stage 2 settler to the pH adjustment tank (Fig.2B) where sulfuric acid is added to lower the pH to about 6 to produce pH adjusted water (pH-AW). Underflow slurry, containing flocculent solids, from the stage 2 clarifier, is sent to a static line mixer above the top of the Stage I reactor where it is mixed with and dissolved by the scrubber water entering the top of the mixer, thus eliminating the flocculent solids.

In the PALM & HARTIG pH PROCESS gypsum filter cakes from phosphoric acid plant operations undergo a Step 1 filter cake wash with warm APW as previously discussed. The Step 1 filter wash volume approaches about 1.4 displacements of the filter cake water. The Step 2 filter cake wash (Fig. 3) is performed with clear, non-scaling, pH adjusted water (pH-AW) using about one displacement wash volume of the filter cake water to substantially remove APW in the filter cake, thereby improving P2O5 recovery. Approximately one percent of water-soluble P2O5, normally lost in the filter cake in conventional operations, is not recovered regardless of the steps

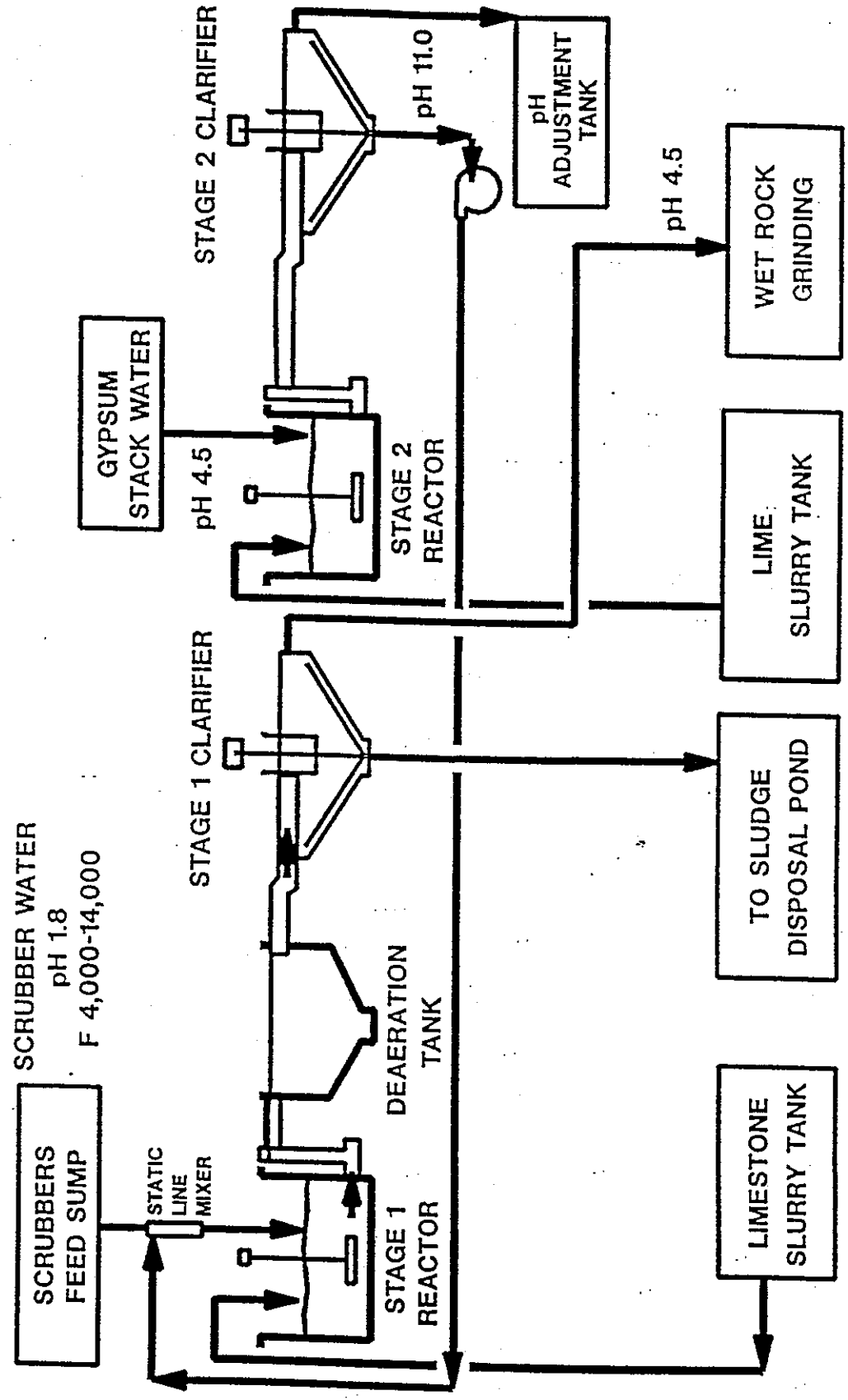
FIG. 4

SCRUBBER WATER GENERATION



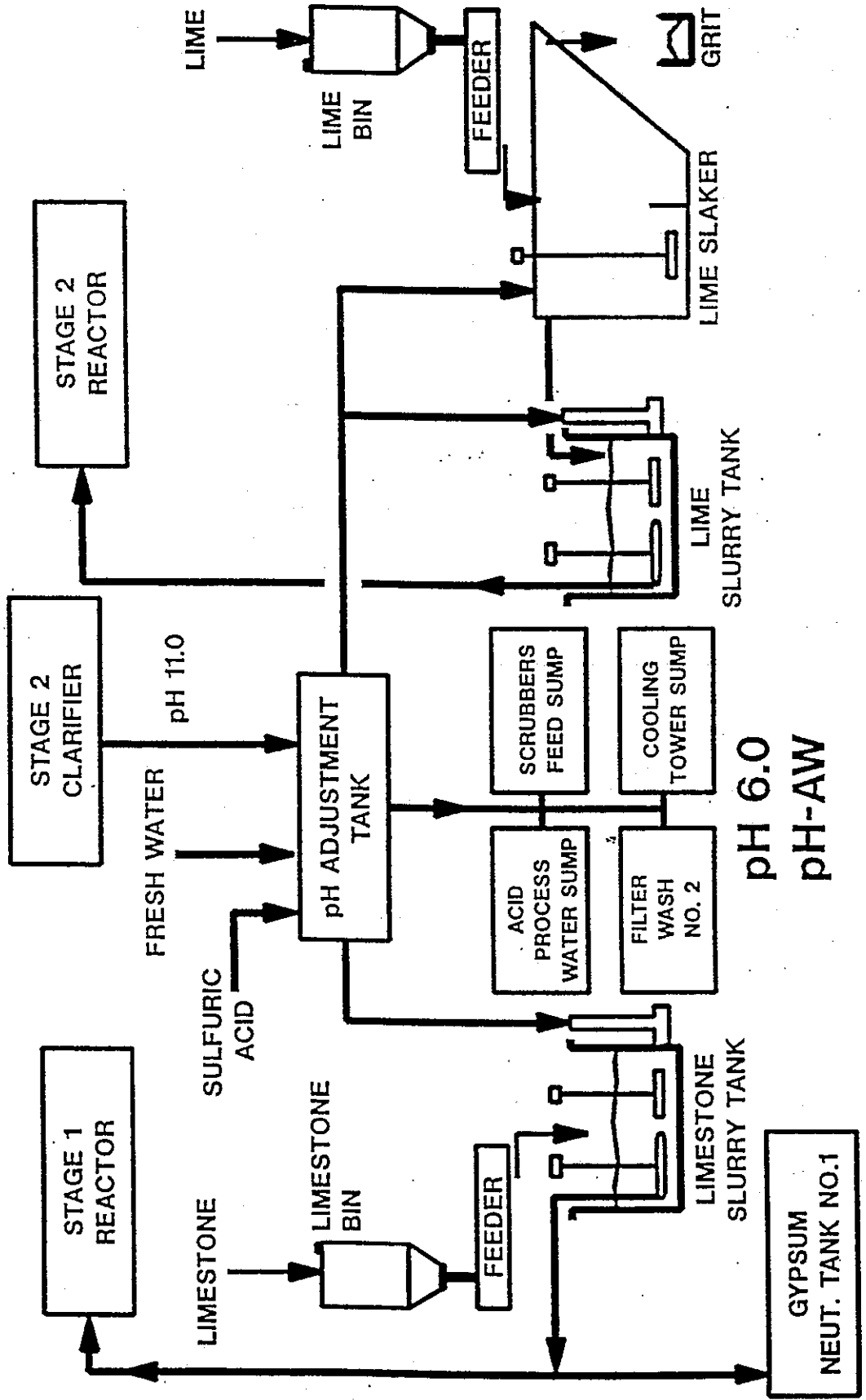
SCRUBBER WATER PARTIAL NEUTRALIZATION

FIG. 5



pH ADJUSTED WATER (pH-AW) GENERATION

FIG. 6



taken. The water from both washes is returned to the plant phosphoric acid reactor for P2O5 recovery and the washed filter cake goes into the gypsum slurry tank.

H. GYPSUM STACK WATER - FIG.7

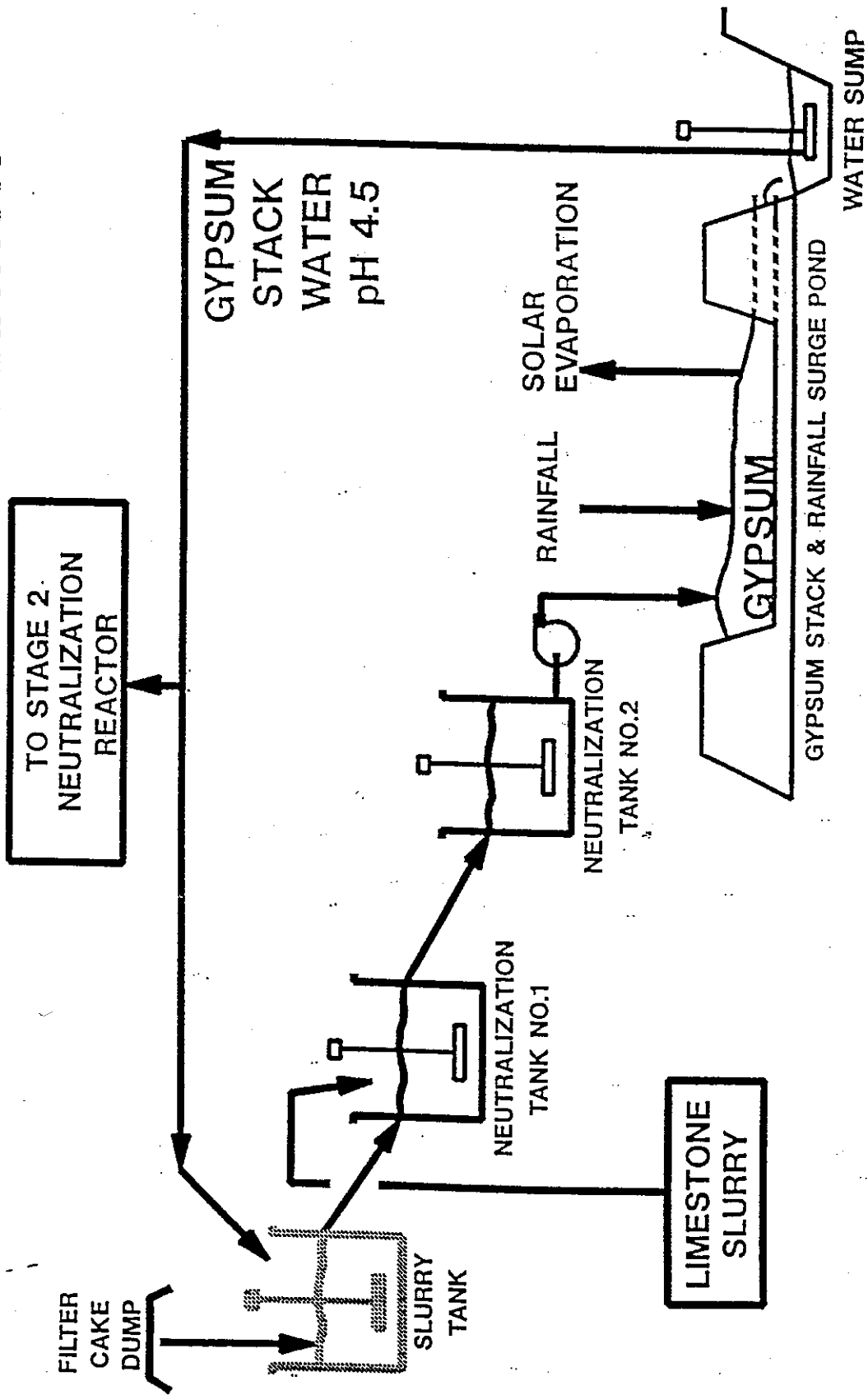
Gypsum stack water is fed to the gypsum slurry tank for slurring the cake and washing the cake from the filter. The slurry from the gypsum slurry tank is thoroughly agitated and then overflows to the first gypsum neutralization tank. Limestone slurry from the limestone slurry tank raises the pH to about 4.5, thereby precipitating fluorides, and about 80% of the phosphates, heavy metals, and radium-226. The dilute acids in the gypsum slurry are neutralized. The slurry then overflows into a second gypsum neutralization tank for stabilization time to complete the reaction and to minimize build-up in the gypsum pipelines.

The partially neutralized gypsum slurry is dewatered on the gypsum stack. Water drains from the gypsum stack into an adjoining rainfall surge pond, whose level increases from rainfall. The surge pond also loses water by evaporation. The gypsum stack water return sump receives the partially neutralized gypsum stack water (and rainfall) from the rainfall surge pond. The water is pumped to the gypsum slurry tank and to the Stage 2 reactor for neutralization to prepare the pH-AW water.

The partially neutralized gypsum stack water is distinguished from the usual gypsum stack pond water by its higher pH and substantial lack of phosphoric acid (and other acids) and of dissolved fluorides, as already noted. Extensive (i.e., several hundred acres) acid pond water cooling ponds, as now used, with acid pond water in direct contact with the ground, are no longer environmentally acceptable. Use of the PALM & HARTIG pH PROCESS eliminates the pond water ponds. Some of this area will be required for a rainfall surge pond, but it would contain partially neutralized gypsum stack water at a pH of 4.5 in contact with the ground in the rainfall surge pond instead of low pH pond water as now used in conventional processing.

GYPSUM STACK WATER GENERATION

FIG. 7



IV. CHARACTERISTICS OF MAIN STREAMS

A. PROJECTED ANALYSES OF PROCESS STREAMS

The estimated analysis of the various process waters, based on material balances and data developed from the neutralization of pond water. are shown in Table 3.

TABLE 3
ph PROCESS - PROCESS WATERS ANALYSIS

		ppm	
WATER:	pH	P ₂ O ₅	F
ACID PROCESS	1.8	14,000	10,000
SCRUBBER	1.8	3-9	11,000
GYPSUM STACK	4.5	1,600	22
WET ROCK GRINDING	4.5	6	22
pH ADJUSTED	6.0	6	3
PONDWATER	1.2	1,800	900
	TO	TO	TO
	1.8	22,200	14,300

B. SOLIDS PRECIPITATED FROM NEUTRALIZING GYPSUM SLURRY

The amount of solids precipitated when neutralizing gypsum slurry, as a percentage of the gypsum solids present are shown in Table 4. These values are important since they can affect the bulk density and stacking properties of the gypsum. The tests by Ardaman when neutralizing gypsum slurry to pH 3.5, that had been slurried with pond water, showed that the precipitated solids were 21.6% by weight of the gypsum in the slurry. Gypsum bulk density was lowered and stacking slope was less - each would result in larger gypsum stacks. Calculated solids that would precipitate with the pH Process would only be 1.2% and should not have any noticeable effect on gypsum stacking.

TABLE 4
SOLIDS PRECIPITATED - NEUTRALIZATION OF GYPSUM SLURRY

	<u>SOLIDS - % of GYPSUM</u>
ARDAMAN TESTS @ pH 3.5	21.5
pH PROCESS @ PH 4.5	1.2
RATIO	18.5

C. VOLUME OF NEUTRALIZATION SOLIDS

The volume of neutralization solids that must be stored in a separate pond were calculated by Ardaman, for Badger's 1,000 tpd Model P plant, when neutralizing all pond water to a pH of 3.5. The required volume for 15 years was 5,533 acre-feet based on 15% solids. For a 1,200 tpd P plant, using the PALM & HARTIG pH PROCESS, the volume of stored solids, at 25% solids, is 46.2 acre-feet/yr or 690 acre-feet for 15 years. This is 12.5% of the conventional system.

TABLE 5
PRECIPITATED SOLIDS STORAGE POND - ACRE-FEET - 15 YRS.

ARDAMAN ANALYSIS	@ 15% SOLIDS	5,533
pH PROCESS	@ 25% SOLIDS	690
	RATIO	8.0 X
pH PROCESS	@ 50% SOLIDS	296
	RATIO	18.8 X

V. ECONOMICS

A. NEUTRALIZATION RAW MATERIALS & COSTS

The annual use of limestone and lime for the pH Process is shown in Table 6 . Limestone is 15,800 tons and pebble lime rock is 5,400 tons of reactive CaO. Reactivity of each is about 90%.

TABLE 6
RAW MATERIALS - ANNUAL

	<u>TONS REACTIVE CaO</u>
LIMESTONE	15,800
LIME	5,400
TOTAL	21,200

B. PROCESS ECONOMICS AND EQUIPMENT

Capital cost for the Palm & Hart pH Process in the 1,200 TPD P based DAP Design Example would be \$11,000,000 (Table 7 including the process fee and a 25% contingency. Net operating savings with recovered P at \$250.00/ton, would be \$1.30/ton DAP for a plant with 5% miscellaneous P losses. This is based on no return on capital.

TABLE 7
PH PROCESS ECONOMICS

CAPITAL COST	\$11,000,000
RAW MATERIALS COST	\$862,900
P SAVINGS	\$2.4 - \$4.2 MILLION
OPERATING HORSE POWER	1,100
OPERATORS	TWO
DEPRECIATION	12 YRS
NET OPERATING SAVINGS	TO \$1.30/ T. DAP
	(\$2.70/ T. P ₂ O ₅)

Major process equipment requirements are shown in Table 8. Conventional equipment is used and has been proven in the applied service, with the exception of the plate heat exchangers. With the use of large in-line strainers and the proper materials of construction, these should function properly.

TABLE 8

<u>MAJOR PROCESS EQUIPMENT</u>	<u>SIZE</u>
Plate Heat Exchangers	200 MM BTU/HR
Cooling Tower 4 Cell	200 MM BTU/HR
Hartig Neutralization System	1,500 GPM
Pumps - 12 Operating & 12 Spare	15 - 600 HP
Six Tanks With Agitators	100 - 700,000 GALS
Clarifier	26 Ft. Diameter

VI. CHANGE-OVER EXISTING TO PALM & HARTIG pH PROCESS

The existing gypsum stacks and cooling ponds can be changed over to the PALM & HARTIG pH PROCESS if desired. This involves a number of operating steps and includes a separate Change-Over Neutralization Process Station (using the Hartig process) for treatment of the pond water in the gypsum stack and pond water ponds. The required change-over plan would be site specific and different for each operating facility, although the principles would be the same.

PALM & HARTIG pH PROCESS ADVANTAGES

INCREASED P₂O₅ RECOVERY

NO POND WATER

NO POND WATER COOLING PONDS

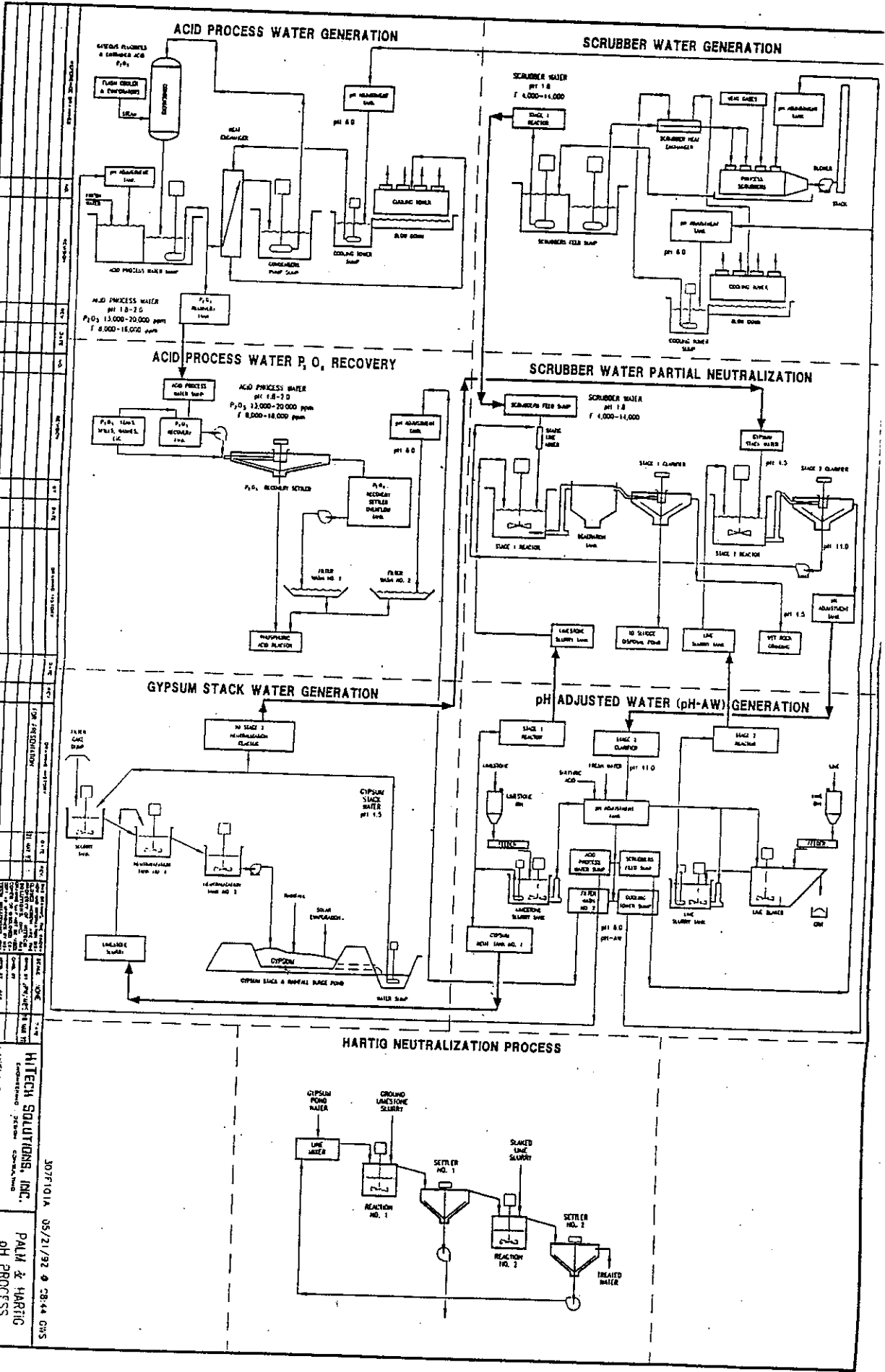
NO GASEOUS FLUORIDE-EMISSIONS - PONDS & GYPSUM STACK

PARTIALLY NEUTRALIZED GYPSUM STACK

NEGLIGIBLE GROUND WATER CONTAMINATION

LOWER GASEOUS FLUORIDE EMISSIONS- COMPLEX

OPERATING SAVINGS TO \$1.30 PER TON DAP



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