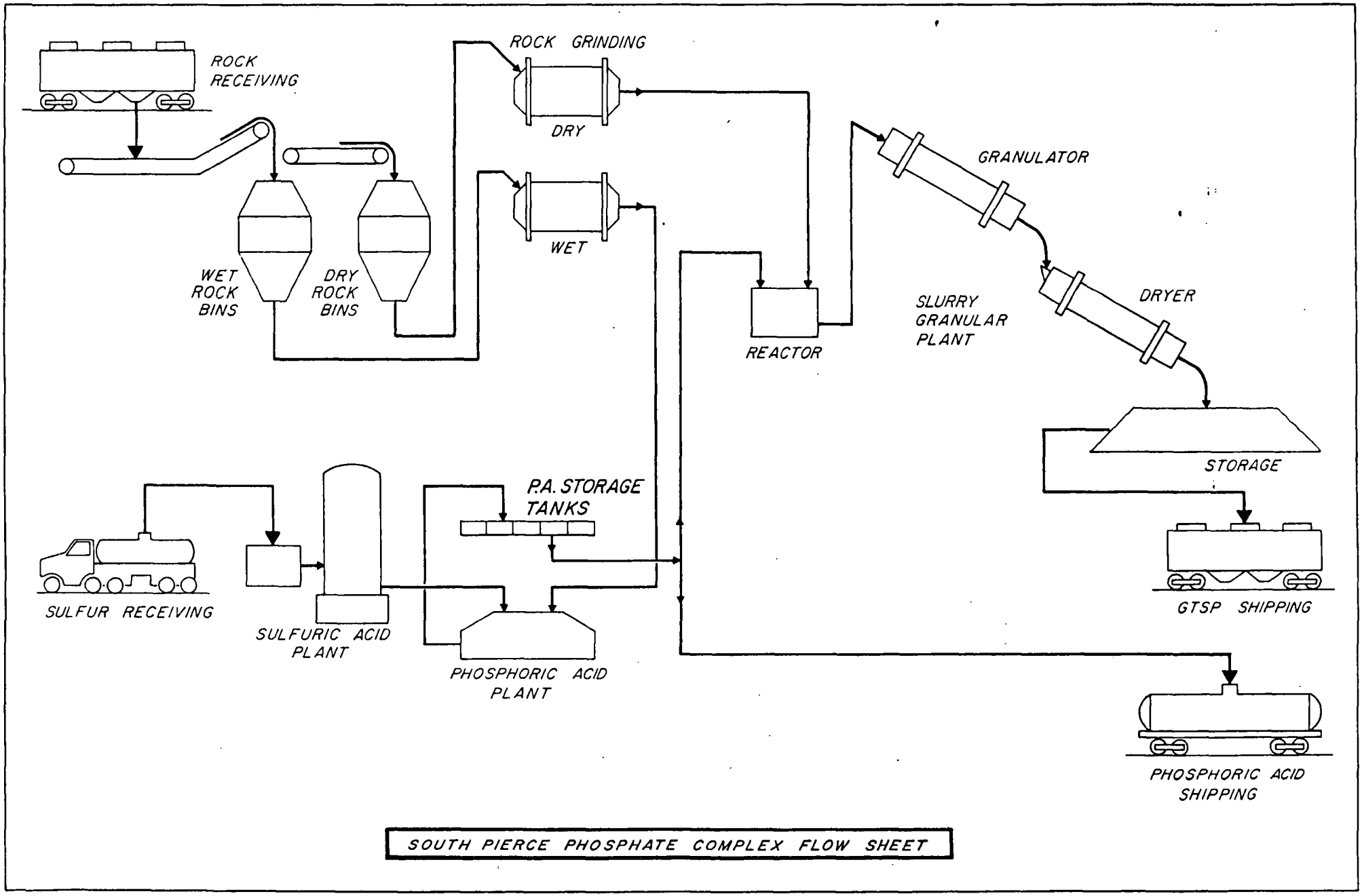
Agrico

South Pierce Chemical Works

PLANT OVERVIEW

Plans for the South Pierce Chemical Works were activated approximately two decades ago. The initial scheme called for two trains of Phosphoric Acid production at 325 TPD each, two trains of Sulfuric Acid production at 1,200 TPD each, a 1,200 TPD Granulated Triple Super Phosphate plant and a 1,400 TPD ROP plant. In 1987, the South Pierce Chemical Complex does not closely resemble the earlier facility. With two new 1,800 TPD Sulfuric Acid plants, upgrading of the Phosphoric Acid production facilities to 613 TPD each, three grinding mills, one of the world's largest GTSP plants, and a 9,200 KW Turbo-Generator, the facility reflects the New Age in phosphate production. In the following pages, we invite you to become familiar with the major operating units within the facility.

Revised: 5/87


ROCK RECEIVING
ROCK GRINDING
DRY
WET
WET ROCK BINS
DRY ROCK BINS
GRANULATOR
DRYER
SLURRY GRANULAR PLANT
REACTOR
STORAGE
GTSP SHIPPING
P.A. STORAGE TANKS
SULFUR RECEIVING
SULFURIC ACID PLANT
PHOSPHORIC ACID PLANT
PHOSPHORIC ACID SHIPPING
SOUTH PIERCE PHOSPHATE COMPLEX FLOW SHEET

SULFURIC ACID

Sulfuric acid is produced by combining elemental sulfur, air and water in successive steps. First, sulfur is burned with excess air to form the gas, sulfur dioxide, SO_2. This gas is then oxidized by passing it through beds of vanadium pentoxide (catalyst) producing sulfur trioxide, SO_3. Since SO_3 is only slightly soluble in water, it is absorbed in 98% sulfuric acid, or rather into the water present in 98% sulfuric acid. Additional water is added to dilute sulfuric acid to desirable strength. All reactions are exothermic, separate and independent. The excess heat is used in waste heat boilers to generate steam for the Complex.

Reactions:

(1) $S + O_2 \longrightarrow SO_2 + \Delta$

(2) $SO_2 + 1/2O_2 \xrightarrow{\text{catalyst}} SO_3 + \Delta$

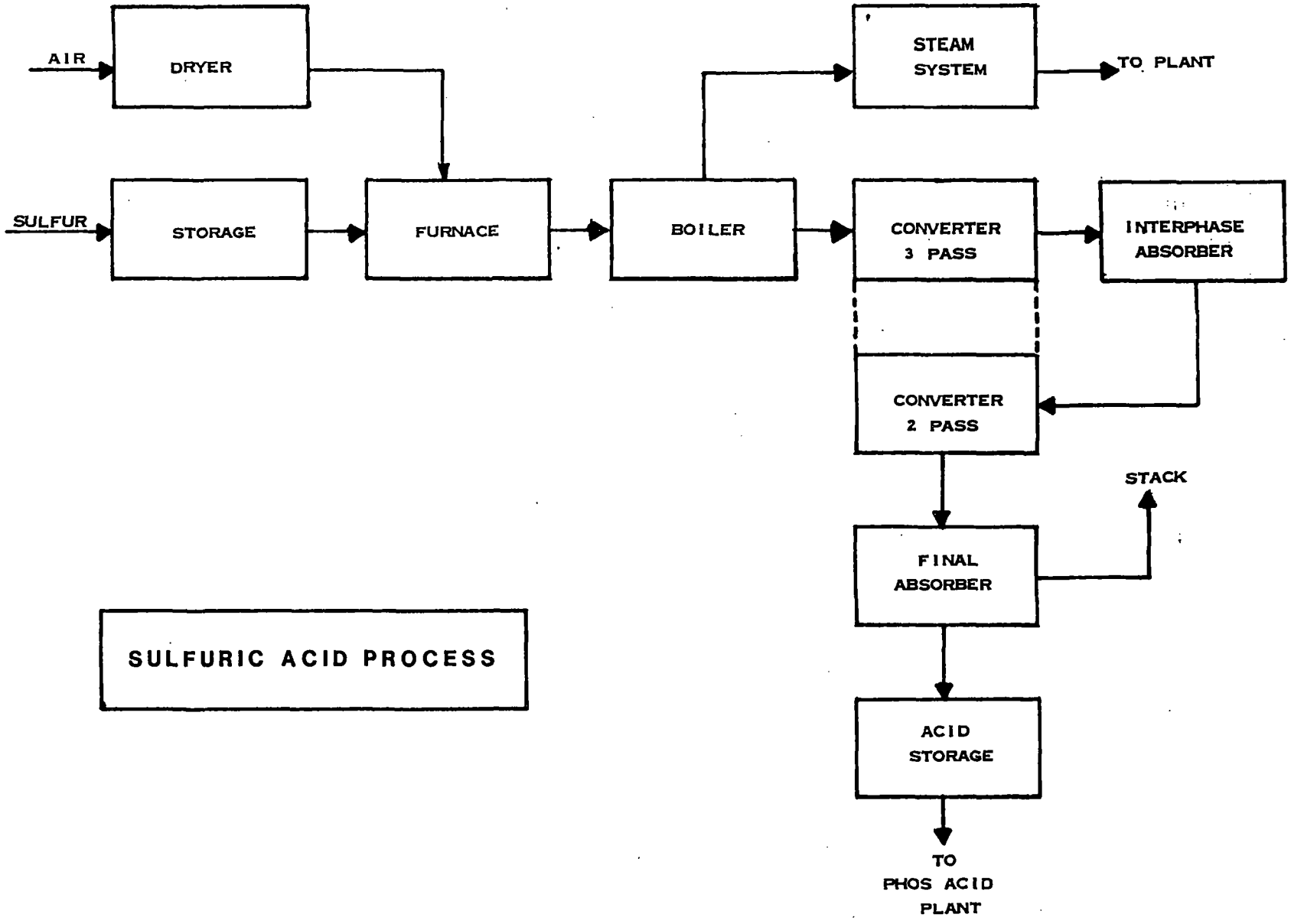
(3) $SO_3 + H_2O \longrightarrow H_2SO_4 + \Delta$

Process:

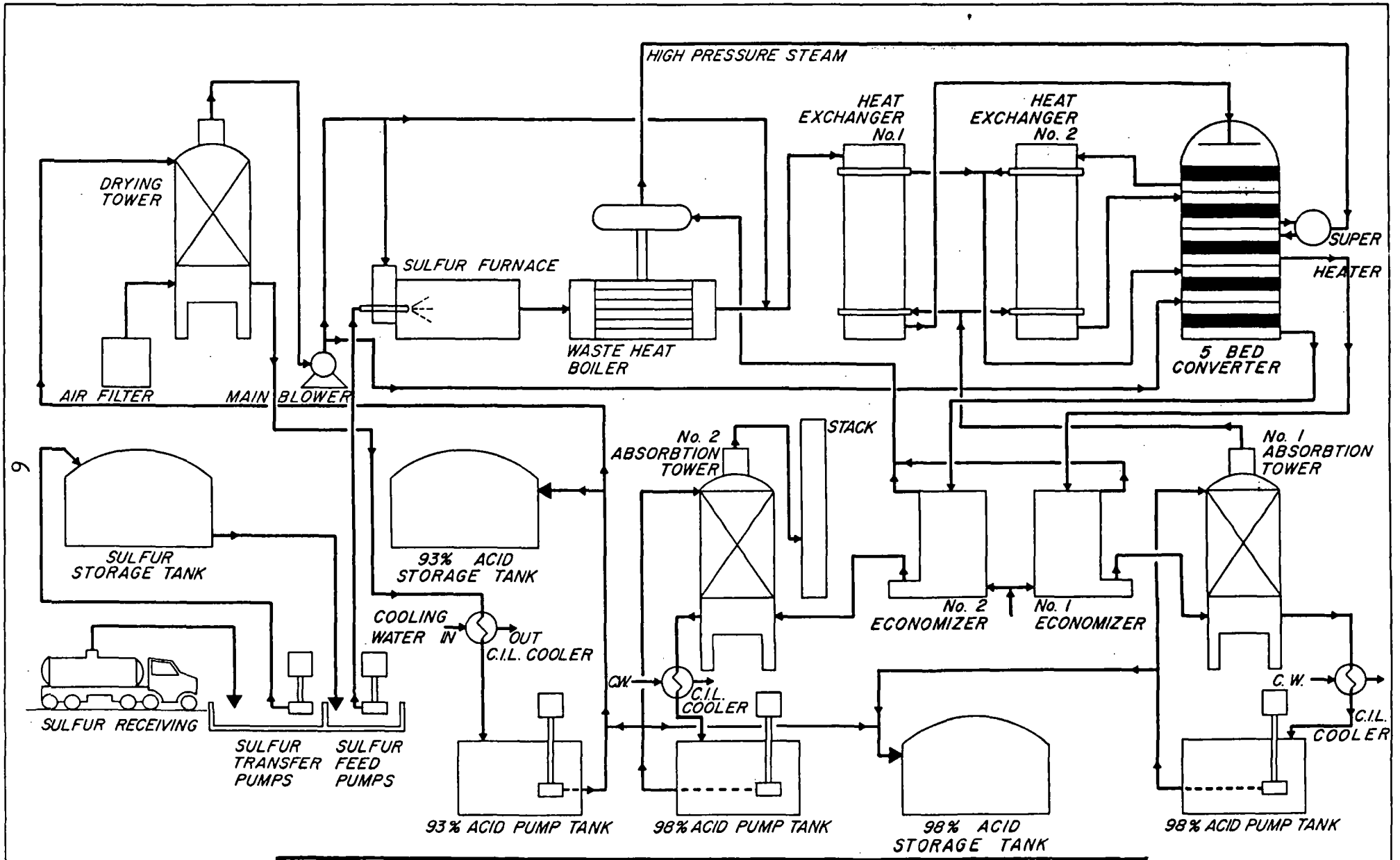
Our two Parsons double absorption sulfuric acid plants replaced the original Dorr-Titlestad plants in 1975. Molten sulfur received by trucks is stored in both a

steam heated pit and two adjacent storage tanks and then pumped to each plant furnace through steam traced lines. Combustion of the sulfur is supported by dried air supplied by an Allis-Chalmers centrifugal compressor driven by a 5000 horsepower axial flow Terry turbine. While the combusted sulfur leaves the burner as SO_2 enroute to the first of two heat exchangers, the waste heat of combustion is used to produce 200,000 pounds per hour of 600 psig, saturated steam at rated production. Final steam temperature after superheating is 600°F.

The SO_2 is alternately cooled and passed through VO_5 beds in the following sequence: #1 heat exchanger to "A" mass to #2 heat exchanger to "B" mass to superheater to "C" mass. After leaving "C" mass the gas passes through the #1 economizer and into the #1 absorbing tower where cascading 98% H_2SO_4 absorbs the majority of the available SO_3. Residual gases are redirected through both the #1 and #2 heat exchangers and "D" mass. Prior to entering "E" mass, quench air is added to the gas stream. From "E" mass the SO_3 passes through the #2 economizer and into the second absorbing tower. Any gases escaping absorption in the second tower are vented through a 150 foot stack. 93% acid produced is stored in one of seven 2500 ton storage tanks. An attachment pictures the process flow.



SULFURIC ACID PROCESS



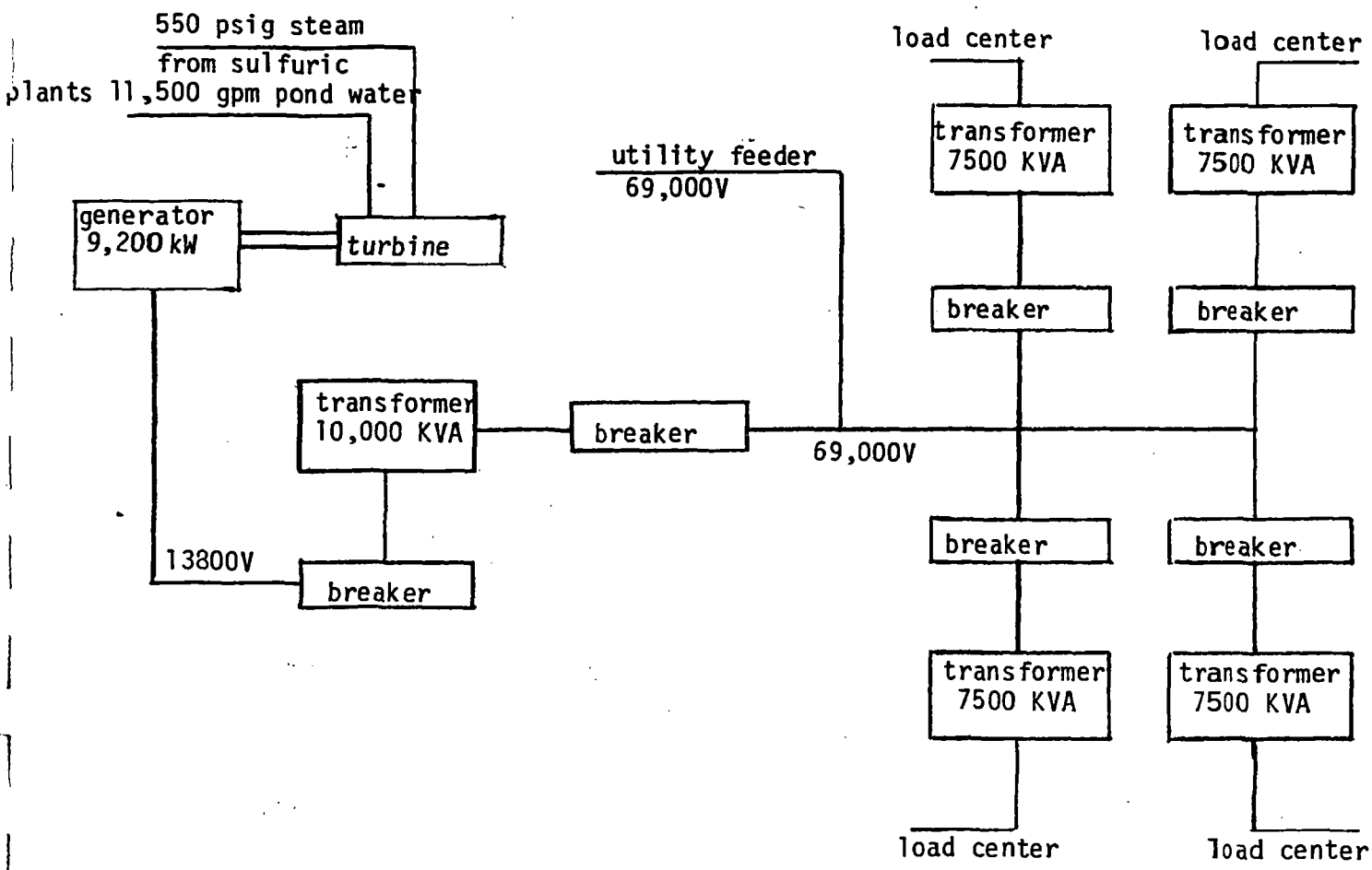
DOUBLE ABSORBTION CONTACT SULFURIC ACID PROCESS FLOW SHEET

POWER GENERATION

The Turbo-Generator was installed during 1977 and early 1978 to utilize by-product steam from the Sulfuric Acid Plants. It is a used Worthington Turbodyne unit which was rated at 7,500 KW, 80% power factor, 600 psig, 825°F steam and has been re-rated to use 550 psig, 575°F steam. It is a condensing unit with controlled extraction at 11 psig. Extraction steam is used to preheat boiler feedwater.

The Generator operates at 13,800 volts. Power is transformed to 69 kv and connected in parallel with the utility power.

An automatic power factor controller has been installed which makes it possible to operate at 9,200 KW and 95% power factor. Capacitors were added to handle the reactive current. The Power Generation unit has been in operation since May, 1978. Actual power production varies, depending on overall plant production, however, it has been as high as 50% of the total power requirements.



TURBINE

Manufacturer	Worthington Corp.
Stages	1 Curtis - 14 Rateau
Condenser	10,000 sq/ft. surface
Speed	3600 RPM
Steam	575°F @ 550 psig.
Exhaust	2 to 3.5" Hg. Abs.
Extraction	11 psig.

GENERATOR

Manufacturer	Electric Machinery Co.
Rating	9375 KVA, 7500 kW
Volts	13,800
Exciter	40 kW, 125 volts

TRANSFORMER

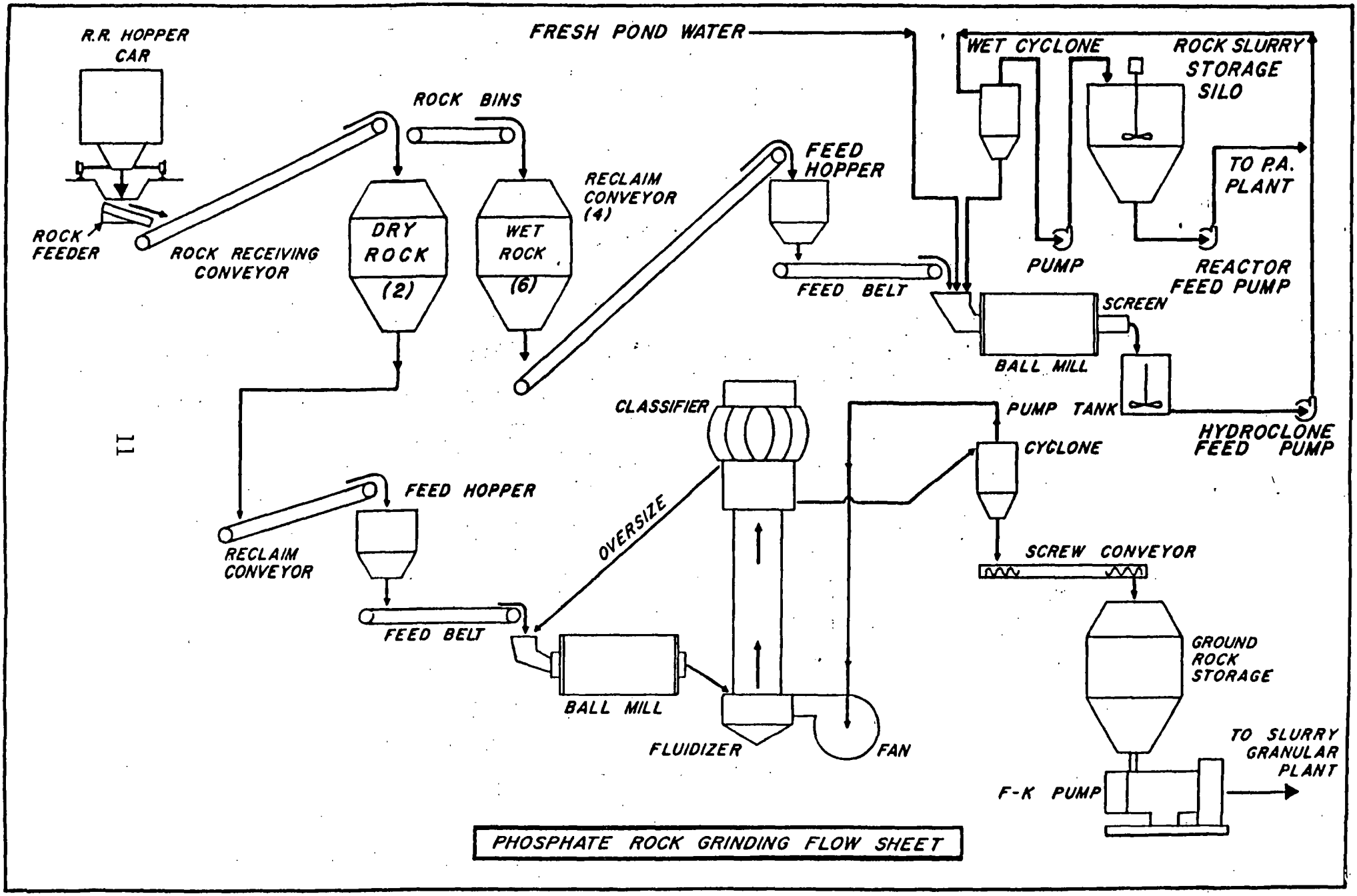
Manufacturer	Hevi-Duty Electric
Rating	10,000 KVA
Voltage	69,000 Delta, 13,800 Y

ROCK GRINDING

Both dry high grade rock and wet low grade rock are received by rail at a common terminal. The dry rock, which is used for GTSP production, is retained in one of two 1,670 ton storage bins prior to being conveyed to the weigh belt servicing a 40 TPH, 11'-6" Ø x 17' KVS ball mill. After being ground to 82-87% -200 mesh, the dry high grade rock is stored in a 2,400 ton silo. Upon call, a Fuller-Kenyon dust pump moves the ground rock to a 40 ton storage bin at the Granular Plant.

The wet rock, which is used to manufacture phosphoric acid, is retained in one of six 1,670 ton storage bins until conveyor belts take it to weigh belt feeders, servicing either an 11'-6" Ø x 24' KVS mill or a 12'-6" Ø x 23' KVS mill. Both mills carry Skega rubber-liners and are operated on closed-circuit. After grinding and passing through a trommel screen at the discharge of the mills, the resulting rock slurry is pumped directly to a set of Krebs wet cyclones which separates the coarse and fine fractions. The coarse fraction is returned to the grinding mills while the fine fraction (product) is pumped to a 1,470 ton storage tank. This rock slurry (68% solids and 98-99% -28 mesh) is then

fed to either of two phosphoric acid plant reactors for further processing. An attachment shows the flow chart for both the wet and dry rock processing.



PHOSPHATE ROCK GRINDING FLOW SHEET

PHOSPHORIC ACID

Phosphate rock is a complex material; the principal mineral constituent, fluorapatite, contains calcium, phosphate, fluoride, carbonate, and other elements or groups bound together in the crystal lattice. When a rock is treated with a strong mineral acid, the apatite lattice is destroyed and the phosphate constituent is solubilized as phosphoric acid.

MAIN REACTION:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

OTHER REACTIONS:

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4$$

$$CaCO_3 + H_2SO_4 \longrightarrow CO_2 + CaSO_4 + H_2O$$

ENTIRE REACTION:

$$Ca_{10}(PO_4)_6F_2 \cdot CaCO_3 + 11H_2SO_4 \longrightarrow$$

$$6H_3PO_4 + 11CaSO_4 + 2HF + H_2O + CO_2$$

Inasmuch as most of us are familiar with the phosphoric acid production process, the story we need to tell in this area involves first, the revisions that permitted

us to run 430 TPD on our 325 TPD design plants, then secondly, how we went to 613 TPD per plant. The first plant configuration featured a single tank reactor, Bird pan filter, and Struthers evaporators. One train was installed with air cooling for the reactor with minimal slurry recirculation while the second train had vacuum cooling, also with limited slurry circulation capability.

To go from 325 TPD to 430 TPD, both trains were eventually modified to have increased agitation in the reactors, vacuum coolers, and substantial slurry recirculation. The two trains then became identical with the exception of the size of the vacuum cooler. The originally installed experimental vacuum cooler was so successful that a new larger vacuum cooler soon replaced the original air cooling system in the first plant. Seven evaporators provided sufficient capacity to match the filter output.

In early 1981, we completed a major expansion that takes each plant to 613 TPD. Major revisions/additions included:

1. Install closed-circuit grinding on the ball mills
2. Install new larger reactor vacuum cooler (both reactor systems now identical)
3. Install new Ucego No. 10 table filter

4. Install new fluorine scrubber
5. Install two new evaporators
6. Expand acid shipping capability

The phosphoric acid tank farm provides storage and settling volume sufficient to provide 42% acid for GTSP production, 54% acid for MAP production and 54% acid for centrifuging to merchant grade acid.

A written overview of the production process is provided for your convenience. This description is followed by a flow chart of the plant process.

PROCESS:

Reactor:

In the reactor phosphate rock, sulfuric acid, and water react to produce a slurry of solid gypsum in a phosphoric acid solution. Rock digestion is carried out in a Dorr-Oliver single tank reactor. Heat generated during the reaction is removed by vacuum cooling.

Filter Feed Tank:

The phosphoric acid-gypsum slurry product from the reactor overflows to a filter feed tank. The filter feed tank is an agitated vessel which serves as a surge tank between the reactor and filter sections.

Filter:

From the filter feed tank, the phosphoric acid-gypsum slurry is pumped to one of three filters. The two Bird filters are continuous horizontal tilting pan type that utilize vacuum to effect the liquid-solid separation. On the filter the gypsum is separated from the phosphoric acid and the resulting cake is subjected to countercurrent washings to dilute acid and hot water. Washing is required to displace the last traces of liquid phosphoric acid contained within the gypsum cake. The acid-free gypsum cake is dumped into a hopper and reslurried with water. From the hopper, the water-gypsum slurry flows by gravity in a launder to the gyp pumps and is pumped to the gypsum pond.

The third filter, a new Ucego filter, differs from the two Bird filters in that it utilizes a screw conveyor to remove the gypsum cake from the filter. The cake is then reslurried with water and pumped out to the gypsum pond. The filter also has a continuous table with rubber partitions instead of separate pans for segregating wash sections. The process flow is basically the same for both type filters.

The product phosphoric acid, No. 1 filtrate, is pumped to a 30% surge tank that is equipped with a thickener

mechanism for clarifying prior to evaporation. A part of the No. 1 filtrate is mixed with the No. 2 filtrate from the acid wash section to make a return acid. This return acid mixture is pumped to the reactor from the filtrate seal tank. No. 3 filtrate from the water wash section is returned to the filter as dilute acid for the acid cake wash.

30% Surge Tank:

In the 30% surge tank, high solids acid from the gypsum settler underflow combines with product acid from the filter to form evaporator feed. In addition to providing surge capacity between the filter and evaporator sections, the 30% surge tank concentrates solids which settle out prior to evaporation. The solids are removed in an underflow stream which is pumped to the reactor.

Evaporators:

Evaporator feed from the 30% surge tank is pumped to the first stage of a multi-stage vacuum evaporator system. In the evaporators, water and fluorides are removed from the acid solution to produce a phosphoric acid product of desired strength. Low pressure steam provides the heat for evaporation. The fluorides are recovered as hydrofluosilicic acid by-product.

Gypsum Settler Tank:

Evaporator product is pumped to a thickener called the gypsum settler. In this tank, gypsum that precipitates out during the evaporation process is collected. The gypsum is removed in a high solids underflow stream which is pumped to the 30% surge tank. Product acid from the gypsum settler tank is then pumped to the tank farm for further clarification.

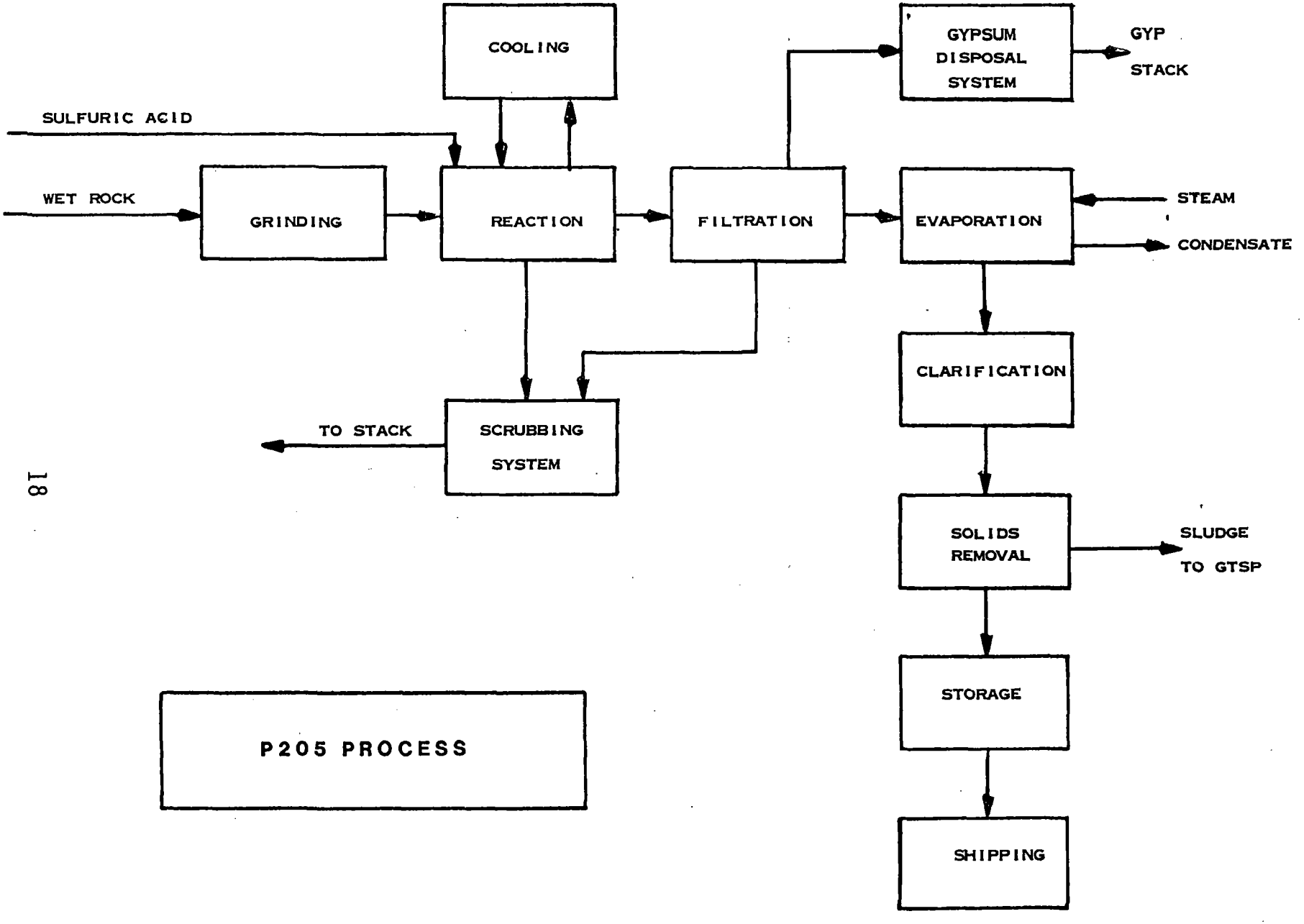
Tank Farm Clarification System:

A characteristic of concentrated phosphoric acid is to "post-precipitate" or drop-out solids containing phosphate values. The tank farm, or clarification system provides time and space for these solids to settle and collect. The solids are removed from the clarification system and used in the manufacture of granulated triple superphosphate. Clarified acid, containing low solids is transferred to the acid shipping area.

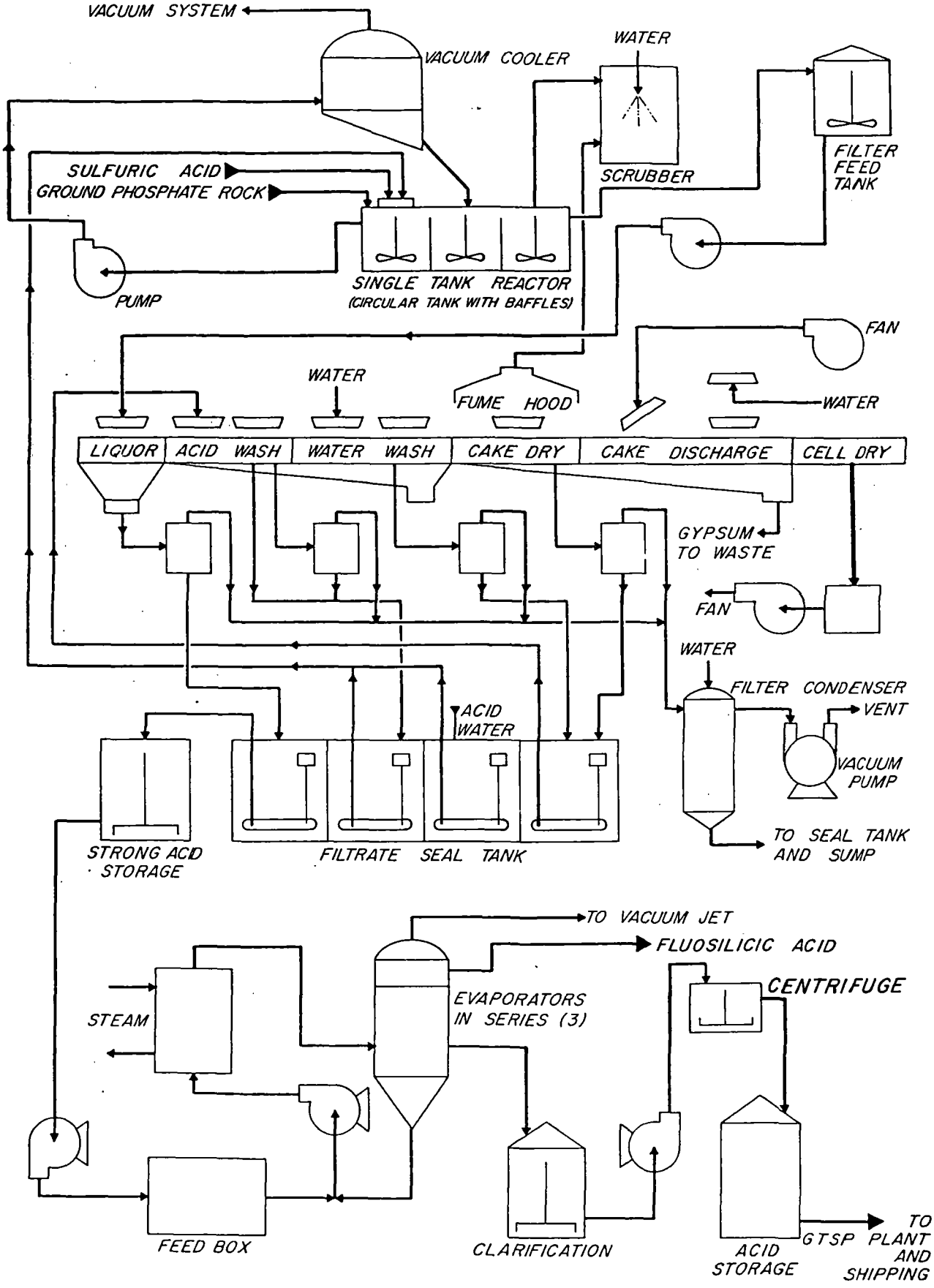
Acid Shipping:

In the acid shipping section, the acid is centrifuged to meet solids specifications. The centrifuge underflows are returned to use in GTSP manufacture.

The clarified acid is shipped in tank cars and tank trucks.



P205 PROCESS



WET PROCESS PHOSPHORIC ACID FLOW SHEET

G.T.S.P.

Granular Triple Superphosphate is produced by reacting phosphate rock with phosphoric acid to form monocalcium phosphate monohydrate.

Main Reaction:

$$2Ca_5(PO_4)_3F + 12H_3PO_4 + 9H_2O \longrightarrow 9Ca(H_2PO_4)_2H_2O + CaF_2$$

In practice, this theoretical relationship is not fully achieved. The presence of calcium, phosphate, fluoride, carbonate, iron aluminum and silica in the rock and acid allow several side reactions to take place.

Side Reactions:

$$2CaF_2 + SiO_2 + 4H_3PO_4 \longrightarrow SiF_4 + 2H_2O + 2Ca(H_2PO_4)_2$$

$$CaSiF_6 + 2H_3PO_4 \longrightarrow H_2SiF_6 + Ca(H_2PO_4)_2$$

$$CaCO_3 + 2H_3PO_4 \longrightarrow Ca(H_2PO_4)_2 + H_2O + CO_2$$

$$Fe_2O_3 + 2H_3PO_4 \longrightarrow 2FePO_4 \cdot H_2O + H_2O$$

The Granular Triple Superphosphate (GTSP) Plant was designed and constructed by Davy McKee and commissioned in late 1974. The plant is designed primarily to produce GTSP but also has the capability to make ammoniated phosphates such as 11-52-0 and 16-20-0.

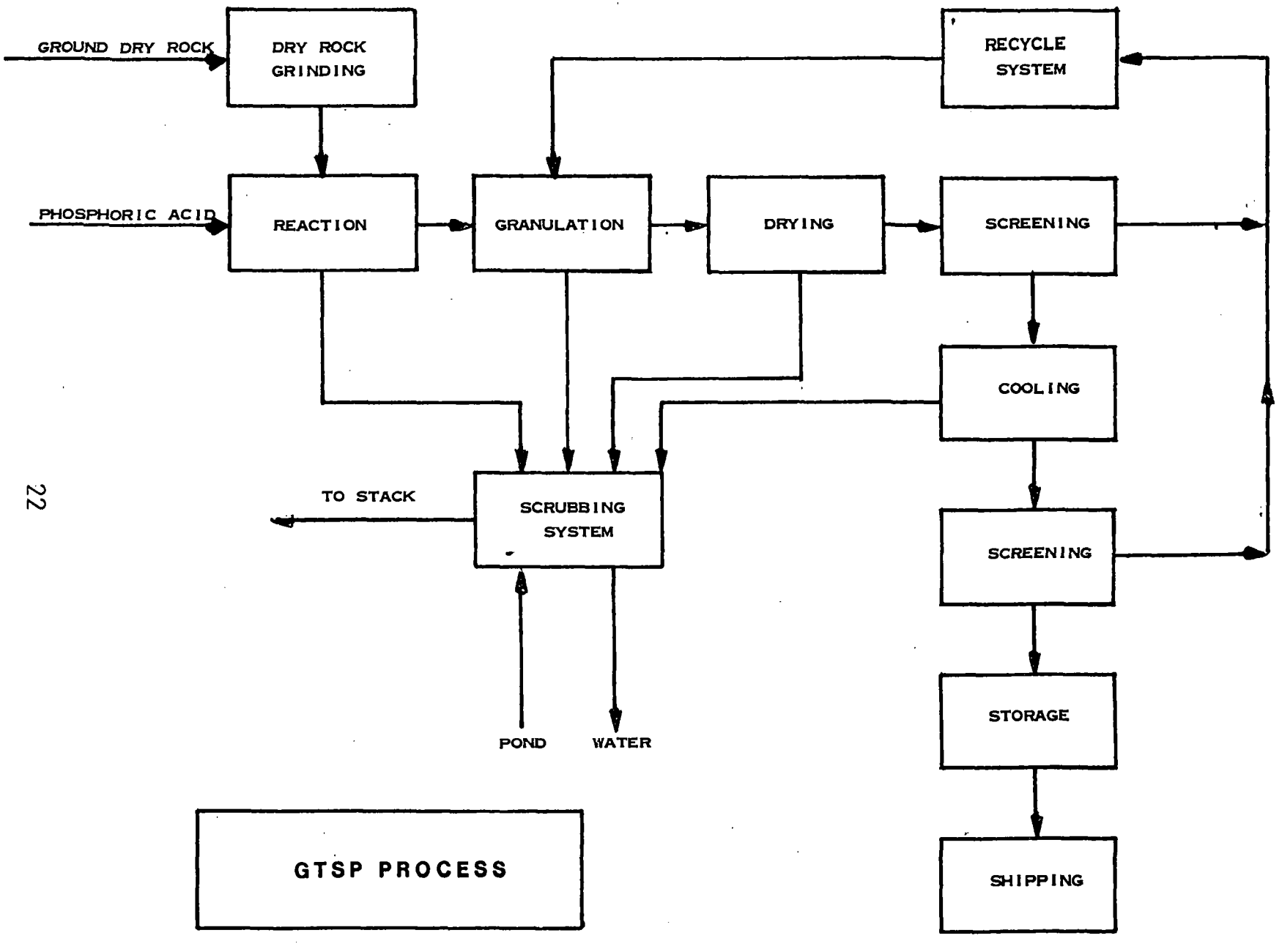
During GTSP production, high grade rock and 42% phosphoric acid are mixed in two agitated 14' Ø x 17' reactors operating in series. The resulting slurry is pumped to a 13'-6" Ø x 29' granulator where it spray coats recycled granular material. The granulator product then travels concurrently through a 15'-6" Ø x 95' oil-fired rotary dryer.

Dried material is conveyed to two elevators which discharge into a belt conveyor feeding a single deck screen, and onto a dragflight conveyor feeding four double deck screens.

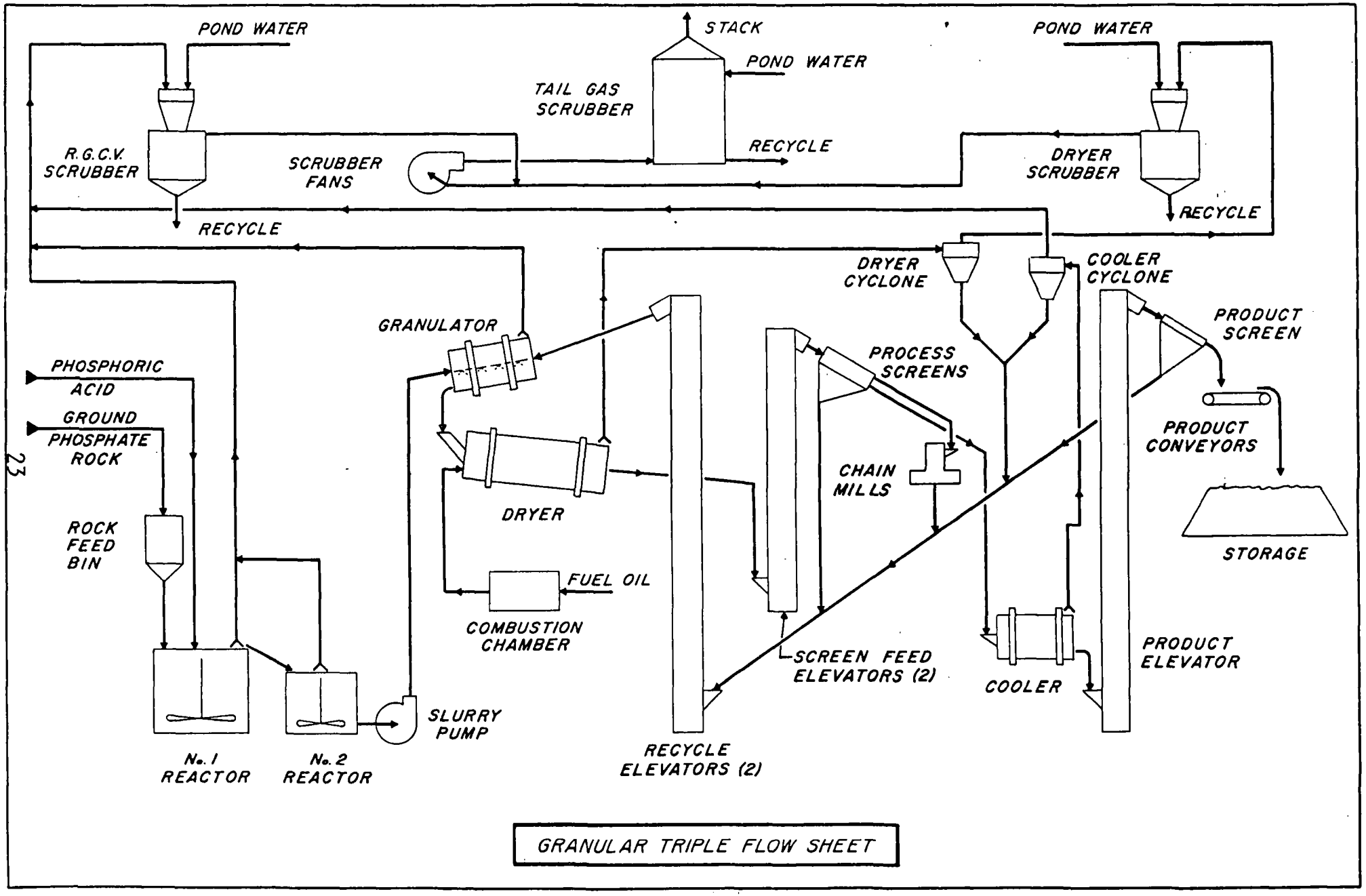
All oversized materials which are rejected by the screens then pass through double chain mills on their way into the recycle dragflight conveyor. Undersized materials (fines) go directly to the recycle dragflight conveyor. All recycle material is returned to the granulator.

On size product travels through a 13'-6" Ø x 40' rotary cooler and undergoes a final oversize screening prior to being conveyed to the storage building.

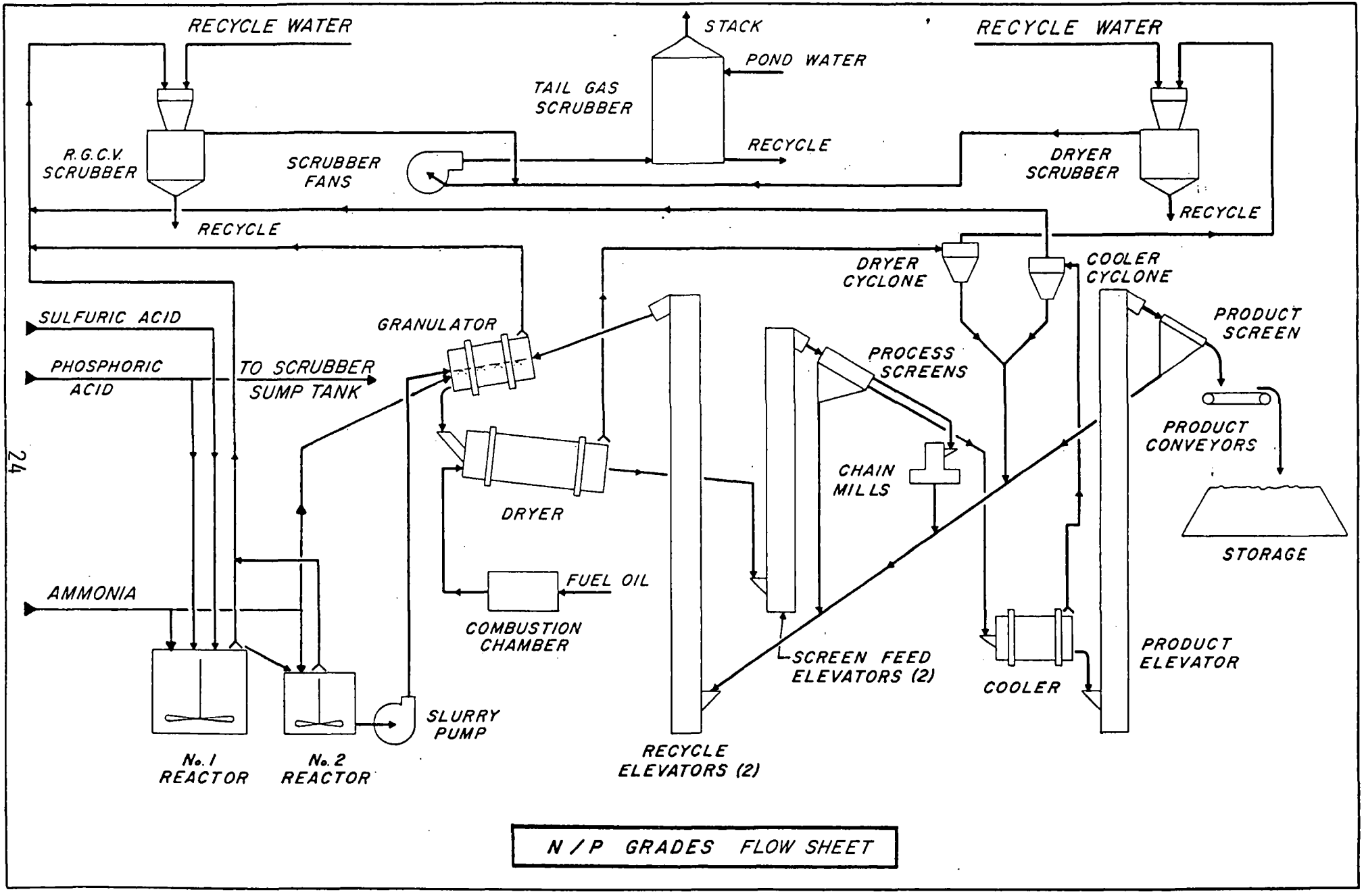
The granular plant was designed for 80 TPH with a recycle rate of 720 TPH. Process improvements over the years have resulted in rates as high as 100 TPH. The attachment following shows the process flow for the plant.



GTSP PROCESS



GRANULAR TRIPLE FLOW SHEET



N / P GRADES FLOW SHEET