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89p.
diagrams
illus.

UNIDO FERTILIZER MANUAL

SECTION XIII PHOSPHORIC ACID

SECTION XIII PHOSPHORIC ACID

Introduction

In 1991 the UNIDO/FAO/World Bank Fertilizer Working Group (FWG) predicted a decline in fertilizer consumption in the year 1991/92 followed by a gradual revival in the years following. For P_2O_5 production capability there is a surplus over demand of 2.75 million tonnes, representing over 7% of global consumption of 36.3 million tonnes P_2O_5 per annum. This is mainly a result of the decline in P_2O_5 fertilizer consumption in Europe. However developing countries are using more.

Over the period 1990/91 to 1995/96 the FWG forecast that phosphate fertilizer consumption will rise from around 36.6 million tonnes per annum to just over 39.9 million tonnes. The phosphoric acid supply capability (for fertilizer use) is expected to rise from 26.75 million tonnes to 29.5 million tonnes per annum, over the same period.

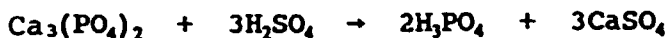
The vast majority of phosphoric acid for fertilizer use is produced by processes using phosphate rock and sulphuric acid. Although there are examples of alternatives, for instance a process using hydrochloric acid is employed in Israel, and there are small plants using the thermal process in China, generally these are not economic throughout the world.

Processes using nitric acid attack on phosphate rock are known as the nitrophosphate process and are described in Chapter XV.

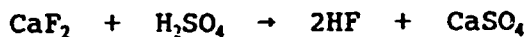
Phosphoric Acid Production using Sulphuric Acid

Chemistry of the Process

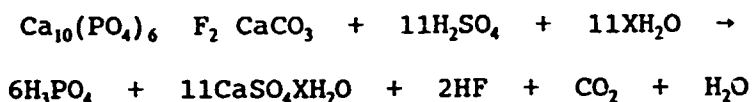
Phosphate rock is a complex material; the principle mineral constituent is fluorapatite which contains phosphate, fluoride, carbonate and other radicals bound together within a crystal lattice. When the rock is treated with a strong mineral acid, the apatite lattice is destroyed and the components pass into solution. In the wet phosphoric acid process the apatite is dissolved in a phosphoric acid solution and sulphuric acid is added to precipitate the calcium according to the following overall reaction:



Various side reactions occur concurrently: the most important being the action of sulphuric acid on calcium fluoride and calcium carbonate.



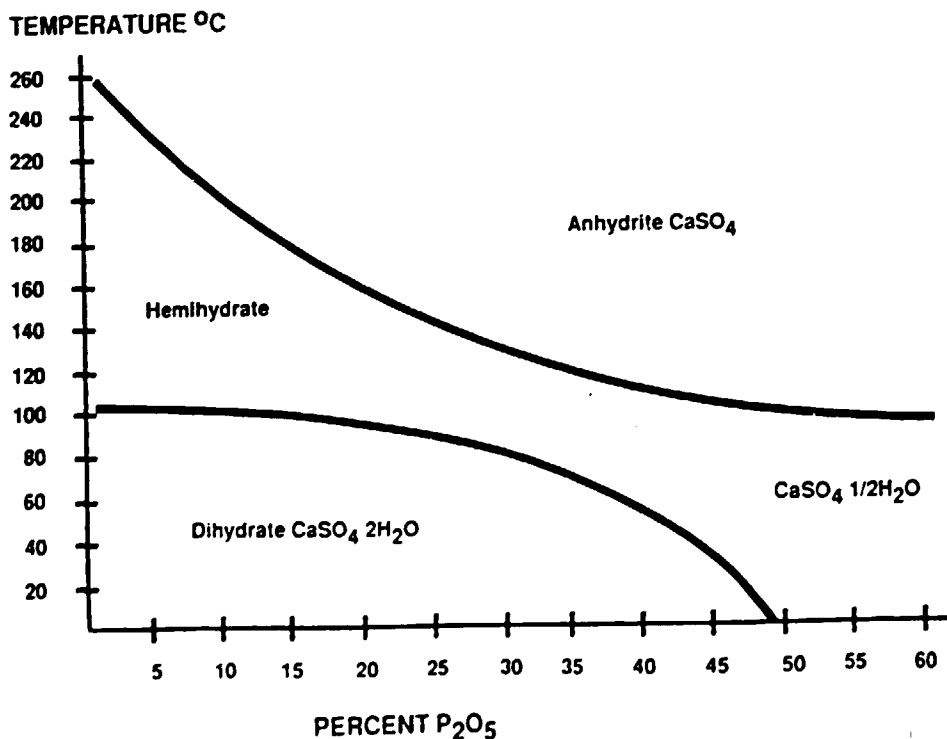
An overall reaction for the process may therefore be written as:



Depending on the reaction temperature and phosphoric acid concentration, the calcium sulphate formed in the reaction can be in three stages of hydration; anhydrite, hemihydrate or dihydrate (i.e. $\text{CaSO}_4 \cdot \text{XH}_2\text{O}$ where $X = 0, \frac{1}{2}$ or 2 respectively) (see Figure 1).

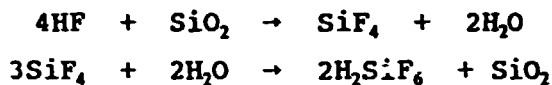
Figure 1

EFFECT OF REACTION CONDITIONS ON CALCIUM SULPHATE CRYSTALLISATION



For fluorine recovery, the hydrogen fluoride evolved in reaction may react with excess silica present in the rock to form silicon tetrafluoride which then hydrolyses to form fluosilicic acid.

These reactions can be expressed as:



Heat of Reaction and Dilution

The heat of reaction may be calculated by use of the following heats of formation of reactants and products:

Table 1

Compound	Heat of Formation at 25°C, kcal/g-mole	Reference
Ca ₁₀ F ₂ (PO ₄) ₆ (crystalline solid)	3,267.2	Farr and Elmore (1)
H ₂ SO ₄ (liquid)	193.91	National Bureau of Standards (2)
H ₂ O (liquid)	68.317	National Bureau of Standards (2)
CaSO ₄ .2H ₂ O (crystalline solid)	483.06	National Bureau of Standards (2)
H ₃ PO ₄ (aqueous, 30% P ₂ O ₅)	308.25	Egan and Luff (3)
HF (aqueous)	75.56	National Bureau of Standards (2)

The heat of reaction so calculated is 256.94 kcal/g-mole of apatite which is equivalent to 255 kcal/kg of apatite or about 600 kcal/kg of P₂O₅. The heat required to raise the temperature of the gypsum (C_p = 0.272) and phosphoric acid (30% P₂O₅; C_p = 0.703) from 25° to 82°C is calculated to be 197 kcal/kg of P₂O₅, (4, 5). Thus, about 403 kcal/kg of P₂O₅ remains to be dissipated, and most processes provide a means of removing the excess heat. In practice, some of the heat is lost by convection and conduction.

On the other hand, some heat may be brought in by use of heated wash water or, if the wash water is not heated, some of the heat in the gypsum is transferred to the recycled weak acid and thus returned to the reaction. Additional heat will be generated by reaction of additional sulphuric acid with impurities in the rock. Most phosphate rock contains 10-20% more calcium than that required to form pure fluorapatite with the phosphorus in the rock, which may result from substitution of carbonate for phosphate in the apatite or presence of calcite or both. Reaction of this amount of calcium with sulphuric acid to form gypsum would increase the net heat of reaction per kilogram of P_2O_5 by about 11-16%.

The heat evolved in the reaction is influenced appreciably by the concentration of the sulphuric acid used, as shown by the following tabulation.

This contribution to the heat evolved is known as the heat of dilution (of sulphuric acid).

Table 2

Concentration of Sulphuric Acid, % H_2SO_4	Net Heat of Reaction, kcal/g-mole of Apatite	Excess Heat to be Dissipated, kcal/kg of P_2O_5
100	256.94	403
98	247.54	385
93	224.54	329
90	211.54	299
85	191.94	253
80	174.24	211
75	160.74	180

If the conditions are such that the calcium sulphate crystallises in the form of anhydrite or hemihydrate rather than gypsum, the excess heat to be dissipated is about 100 kcal/kg of P_2O_5 less than the values given above.

Types of Process

Commercial wet processes may be classified according to the hydrate form in which the calcium sulphate crystallises:

- Anhydrite - CaSO_4
- Hemihydrate - $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
- Dihydrate - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

The hydrate form is controlled mainly by temperature and acid concentration. At present there is no commercial use of the anhydrite process, mainly because the required reaction temperature is high enough to cause severe corrosion difficulties. Processes in commercial use follow:

Table 3

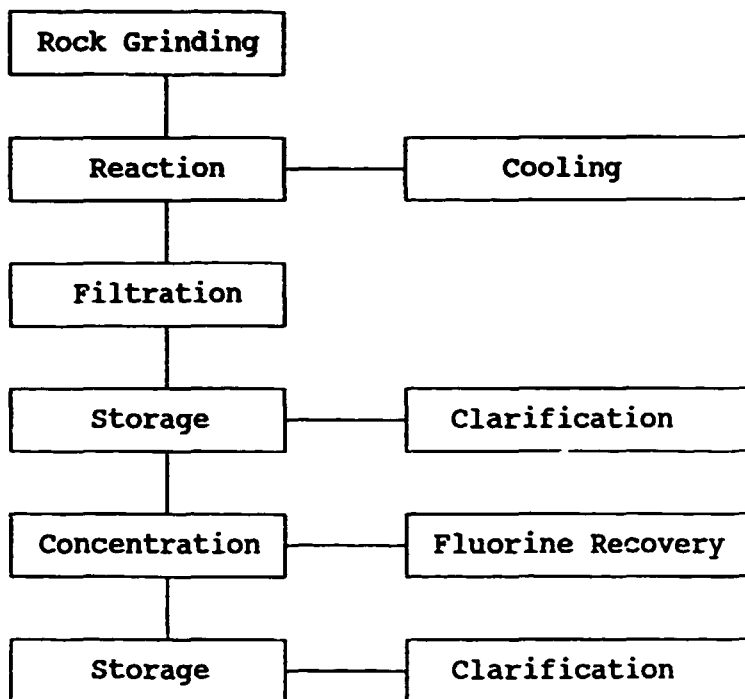
Crystal Form(s)	Number of Separation Steps *	Usual Conc. of Product Acid, % P_2O_5	Usual Temperature, °C	
			Reactor	Re-crystalliser
Dihydrate	1	26-32	78-85	-
Hemihydrate	1	40-50	90-100	-
Hemihydrate-dihydrate	1	26-30	90-100	50-60
Hemihydrate-dihydrate	2	40-50	90-100	50-65
Dihydrate-hemihydrate	2	35-38	65-70	90-100

* Filtration or centrifuging steps.

The most widely used processes today are the dihydrate (DH), hemihydrate (HH) and hemidihydrate (HDH) processes, and these will be described in a little more detail.

The DH process is the traditional route for producing phosphoric acid. As the phosphoric acid industry expanded dramatically between about 1950 to 1970, most of the plants built used one of the DH processes.

The unit operations in the DH process are typically:

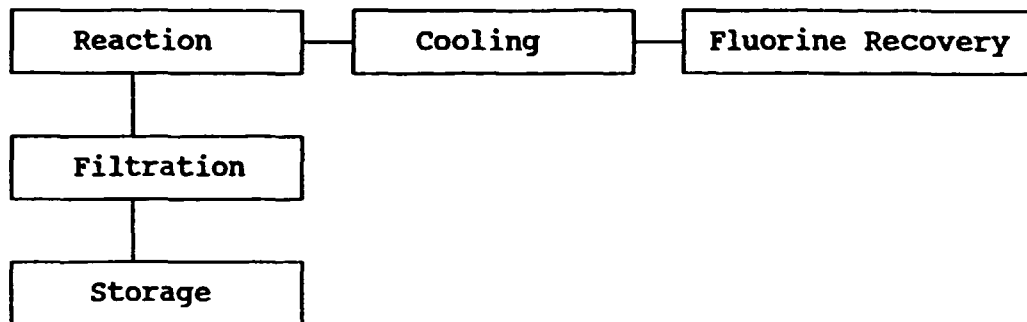


Since around 1970 the use of hemihydrate processes has become more popular.

Hemihydrate processes have the advantage of producing phosphoric acid of a relatively high concentration. This means that the concentration step can be eliminated if the concentration is high enough for the desired use, which will result in lower capital and operating costs. Since phosphoric acid plants often have on-site sulphuric acid production facilities that supply by-product steam and since little or no steam is required in the HH process, then a maximum amount of electricity can be generated from this by-product steam.

Hemihydrate processes also claim the advantage of a sludge-free acid product and some decrease in the amount of impurities (especially aluminium) extracted from the rock and appearing in the product acid.

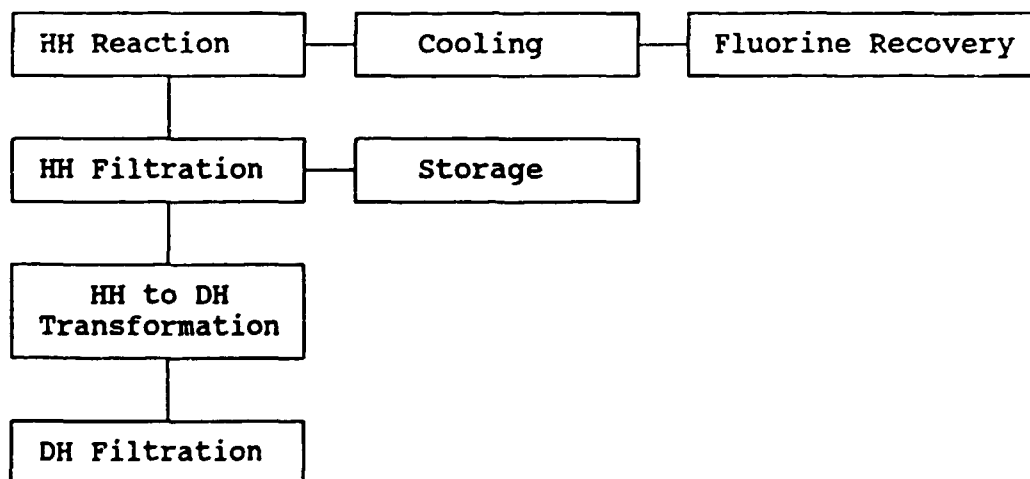
The unit operations in a HH process are:



The fewer unit operations than the DH process make it simpler to operate, as is testified by the operating staff of the several DH plants which have been converted to HH processes.

The HDH processes exhibit similar advantages to the HH process above and have the added benefit of a very high P_2O_5 recovery, at 98.5-99% is approximately 4% higher than a DH or HH process.

The unit operations in a HDH process are:



The discussion of the processes will be divided into the following steps:

1. Selecting phosphate rock.
2. Selecting source of sulphuric acid.
3. Receiving and storing raw materials.

4. Grinding and otherwise preparing of the rock.
5. Reacting the phosphate rock and sulphuric acid.
6. Filtering to separate phosphoric acid from gypsum and
7. Concentrating and clarifying the phosphoric acid.

Selection of Phosphate Rock

In the last ten years or so most phosphoric acid and phosphate fertilizer plants have been built close to a source of phosphate rock, except for India & Pakistan which continue to import phosphate rock and sulphur in order to produce a significant proportion of their fertilizer requirements.

Thus the procedure of selecting a phosphate rock does not apply to many new producers. Nevertheless it is useful for producers generally, to be aware of the effects of the various impurities in phosphate rocks on the performance of the rock in the phosphoric acid process, to assist with the design and operation of the plant as well as the selection of the rock.

The following factors are a useful guide:

1. Lower grade (% P_2O_5) means that more tonnage must be bought, transported, handled, and (sometimes) ground.
2. An increase in the $CaO:P_2O_5$ weight ratio increases the sulphuric acid requirement. (Any CaO present as $CaSO_4$ should be excluded in calculating this ratio.)
3. High MgO content is considered undesirable. When phosphoric acid is used to produce ammonium phosphates or poly-phosphates, water-insoluble (but citrate-soluble) magnesium ammonium phosphate compounds may be formed. These compounds form troublesome impurities in liquid fertilizers.
4. Increases in the $Fe_2O_3 + Al_2O_3$ content above 2-3% decrease the plant capacity, often decrease the P_2O_5 recovery, and cause post-precipitation problems (sludge). However, up to about 5% may be tolerable if the plant is designed accordingly.

5. It is desirable to have enough reactive silica (SiO_2) to form SiF_4 and/or fluosilicates so as to avoid formation of free HF, which is corrosive. Excessive silica or other acid-insoluble impurities may cause erosion of equipment and possible accumulations in digestion vessels depending on particle size, character, and plant design. Also, a high percentage of silica in the rock would increase the required filter area.

6. Chlorine contents above about 0.04% cause increased corrosion of stainless steel. More expensive alloys may tolerate a Cl content of 0.10% or perhaps higher.

Alternatively, rubber covered or plastic materials of construction can be used with high chloride rocks.

7. High organic matter may increase foaming problems (by stabilising the foam), increase viscosity, and hinder filtration. The effect depends on both the character and quantity of organic matter. Some rocks must be calcined to remove organic matter to make them usable.

8. Carbon dioxide (CO_2) contributes to foaming and increases consumption of anti-foam reagents.

9. All commercial phosphate rocks contain fluorine (F); no special effect has been noted due to variations in fluorine content within the range of experience. Effects of fluorine on scaling, corrosion, and post-precipitation are related to other elements that combine with fluorine, including Na, K, Al, Mg and Si.

10. Some rocks which contain sulphides release hydrogen sulphide (H_2S) upon acidulation. This gas is toxic. Also sulphides tend to increase corrosion.

11. Many other less common impurities may be present in sufficient quantity to require consideration (TiO_2 , SrO , BaO , Cd, etc.).

In Western Europe and Scandinavia there is increasing government legislation to restrict the cadmium content in plant effluents, and in fertilizer products.

12. Hardness is a factor in that harder rocks require more grinding capacity and electricity consumption. There is also more maintenance required in the grinding mill.
13. The particle size of the rock as received affects the amount of crushing and grinding required. Very fine particle size may lead to dust losses in handling.
14. Low reactivity of the rock may require finer grinding.
15. Filterability of the gypsum-acid slurry is one of the most important characteristics of a phosphate rock for use in phosphoric acid production. Factors influencing filterability are complex and not completely understood. However, if a plant is to be designed to use a specific rock, an acceptable filtrate rate can usually be attained through experimental means by adjusting operating conditions, addition of crystal modifiers, or pre-treatment of the rock.

Table 4 shows the range of composition and typical values of a group of phosphate rocks from commercial sources. Although the group is representative, compositions outside this range have also been used.

Table 4

Typical Analysis of Commercial Phosphate Rocks

Constituent	% by Weight	
	Range	Typical
P ₂ O ₅	28-38	31
CaO	46-54	51
SiO ₂	0.2-8.7	2
Al ₂ O ₃ + Fe ₂ O ₃	0.4-3.4	1.4
MgO	0.1-0.8	0.2
Na ₂ O	0.1-0.8	0.5
CO ₂	0.2-7.5	4.5
F	2.2-4.0	3.7
Cl	0.0-0.5	<0.02
SO ₃	0.0-2.9	1.0
CaO:P ₂ O ₅ weight ratio	1.35-1.70	1.5

Assuming 94% overall P₂O₅ recovery, the number of tonnes of phosphate rock required per tonnes of P₂O₅ recovered as phosphoric acid is:

Table 5

	Grade of Rock, % P ₂ O ₅	Rock Requirement, t/t of P ₂ O ₅ in Acid
Low	28	3.80
Median	31	3.43
High	34	3.13

Calculation of Sulphuric Acid Requirement

Although the sulphuric acid requirement for production of phosphoric acid from any given rock is best obtained experimentally, it is sometimes necessary to calculate it from the chemical analysis of the rock. For a first approximation the sulphuric acid requirement may be equated to that required to combine with the calcium in the rock to form calcium sulphate. This calculated value is often close enough for planning purposes. The requirement per tonne of P_2O_5 recovered should be adjusted according to the expected recovery. The overall recovery is seldom more than 94% if mechanical and sludge losses are included.

If a complete analysis of the rock is available, a more exact calculation may be made. The method is illustrated in Table 6 and is explained below.

1. Assuming 94% overall P_2O_5 recovery, 1064 kg of rock P_2O_5 is required per ton of P_2O_5 recovered.
2. If the rock contains 31% P_2O_5 , 3432 kg of rock is required.
3. The CaO content of the rock is calculated. If the rock contains any other cation that forms an insoluble sulphate (such as barium), its CaO equivalent should be added.
4. The CaO equivalent of the SO_3 content (not total S) should be taken into account.
5. Typical filter cake contains about 3.3% of the input P_2O_5 in insoluble forms of which 1% may be unreacted rock and 2.3% $CaHPO_4$ co-crystallised with gypsum. The aggregate weight ratio of CaO combined with P_2O_5 is about 1.0.
6. The empirical assumption is that 15% of the fluorine combines with CaO to form CaF_2 . Actual reactions are much more complex; $Ca_4SO_4SiF_6AlF_6(OH) \cdot 12H_2O$ is an example of a complex insoluble compound found in filter cake.

7. Items 4, 5 and 6 are totalled.
8. Item 7 is subtracted from 3 to give net CaO for reaction with H_2SO_4 .
9. The H_2SO_4 equivalent of the CaO is calculated.

Table 6

Calculation of H_2SO_4 Required Per Ton of P_2O_5 Recovered as Phosphoric Acid Using Median Rock

Item	Kg per Tonne of P_2O_5 Recovered
1. P_2O_5 required in rock at 94% recovery, $\frac{1,000}{0.94}$	1,064
2. Kg of rock required per ton of P_2O_5 recovered, $\frac{1,064}{0.31}$	3,432
3. CaO in rock, $3,432 \times 0.51$	1,750
4. CaO equivalent to SO_3 , $3,432 \times 0.01 \times \frac{56}{80}$	24.02
5. CaO combined with P_2O_5 in filter cake, $.031 \times 1,064$	32.98
6. CaO combined with fluorine, $0.15 \times 0.037 \times 3,432 \times \frac{56}{19 \times 2}$	28.07
7. Total CaO not combined with sulphate	84.1
8. Net CaO for reaction with H_2SO_4 , $1750 - 84.1$	1,665.9
9. H_2SO_4 required for $CaSO_4$, $1,666 \times \frac{98}{56}$	2,915.5
10. Excess H_2SO_4 , $\frac{1.5}{30} \times 1,000$	50.0
11. Total H_2SO_4 required	2,965.5
Short Calculation	
12. H_2SO_4 required based on CaO only, $1750 \times \frac{98}{56}$	3,062.5

10. The amount of excess H_2SO_4 is calculated by assuming that the filter acid contains 1.5% free H_2SO_4 .
11. Total H_2SO_4 requirement is item 9 plus item 10.
12. A simplified calculation based on H_2SO_4 equivalent to total CaO is shown in Table 6.

In the following tabulation the sulphuric acid requirement for median grade rock is taken from Table 6 (2.97 t of H_2SO_4 per t of P_2O_5), and requirements for rocks of other Ca: P_2O_5 ratios are estimated in proportion to that ratio.

	High	Median	Low
Grade of rock, % P_2O_5	34	31	28
Rock requirement, t/t of P_2O_5	3.13	3.43	3.80
CaO: P_2O_5 ratio in rock	1.50	1.55	1.60
H_2SO_4 requirement, t/t of P_2O_5	2.87	2.97	3.07

Source of Sulphuric Acid

Although sulphuric acid production is discussed in Chapter XII, some aspects of the source of the acid will affect plans for phosphoric acid production. Most, but not all, phosphoric acid plants have on-site facilities for producing sulphuric acid from sulphur or pyrites. In this case, heat is recovered from the sulphuric acid plants in the form of steam which is available for concentrating phosphoric acid and electricity generation.

Double-absorption processes are now used in sulphuric acid plants to control emission of SO_2 .

Sulphuric acid from pyrites, smelter operations, or other by-product sources may contain impurities that may or may not be deleterious for phosphoric acid production.

In at least one case, zinc in smelter acid proved useful since the fertilizer produced from phosphoric acid contained enough zinc, mainly derived from the smelter acid, to improve crop yields in zinc-deficient areas.

Receiving and Storing Raw Materials

An efficient system for bulk handling and storing phosphate rock and other raw materials is necessary for a modern phosphoric acid plant. (Other raw materials are discussed elsewhere.) The criteria to be met are:

1. Rapid unloading of ships or other delivery units.
2. Negligible loss of rock.
3. Easy storage with ability to separate shipments or to blend shipments as desired.
4. Efficient retrieval from storage.
5. Protection against wind, rain, snow and freezing weather.
6. Protection from contamination with other raw materials, windblown dust, soil, etc.
7. Provision for expansion if future needs warrant.

When phosphate rock is received dry, it is usually desirable to keep it dry by covered storage, especially if it is to be used in a dry grinding system in order to avoid the expense of re-drying. If open storage is used, wind or heavy rains can cause losses of rock that may amount to several percent if it contains much fines. However, relatively coarse rock can be stored in open piles, particularly if it is to be wet ground. The storage capacity should be at least $1\frac{1}{2}$ times the largest shipment to allow for delays. Even larger storage capacity may be advantageous for blending shipments.

Rock Grinding and Preparation

The required particle size analysis of a phosphate rock used to make phosphoric acid will depend on the reactivity of the rock and the type of process used. Typical rock size requirements for the HH, HDH and DH processes are given below:

BSS Sieve Size (Mesh)	Aperture (Microns)	Particle Size Requirement % Through	
		HH/HDH Plant	DH Plant
10	1700	100	-
30	500	75	100
60	250	25	95
100	150	-	60
200	75	-	30

This means that some phosphates such as Bu Craa, Khouribga (Morocco), Shidiya (Jordan), Togo and Taiba are provided fine enough to be processed in the HH and HDH processes without further grinding. But it is still necessary to grind these rocks if the DH process is used.

Some igneous rocks such as Phalaborwa (South Africa) require a finer particle size to overcome low reactivity.

If grinding is required then the choice is between the dry and wet methods.

For dry grinding either ring-roller or ball mills are often used with air classification. The power requirement depends on the initial size of the particles, the hardness, and the final particle size required. For Florida rock the electricity consumption required for grinding is between 35-40 kWh per tonne P_2O_5 .

Wet grinding is done in a ball mill; a slurry containing 62-70% solids is produced and fed to the digester via a surge tank. Advantages of wet grinding are 30-40% reduction in power requirement and elimination of dust losses, atmospheric pollution by dust, and the necessity of drying the rock. The main disadvantages are somewhat faster wear of the balls and mill lining and a decrease in the amount of recycled water that can be used elsewhere in the plant.

It is also necessary maintain reasonably close control of the water : solids ratio in grinding.

Furthermore the water which is fed in with the rock slurry detracts from that which is available for filter cake washing this leading to higher P_2O_5 losses and a lower P_2O_5 recovery.

Beneficiation of the rock removes some impurities and generally enhances product acid quality.

The declining quality of phosphate rocks raises the impurity levels in phosphoric acid. When low grade phosphate rock is used it is necessary to reduce the quantity of impurity in the product acid, to obtain a "Merchant-grade" acid. There are two ways to obtain that; reduce or remove the impurities prior to acid manufacture, or to treat the acid. The second way will be treated later in this chapter. The rock beneficiation can be obtained by different techniques, in some cases simple washing and screening is sufficient because the phosphate material accumulates in a specific size fraction (0.2 - 1 mm) of the rock. In other instance with rocks containing Calcite ($CaCO_3$) or Dolomite ($CaMg (CO_3)_2$), froth flocculation is necessary (6).

Calcining of phosphate rock usually is considered part of beneficiation. However, some phosphoric acid producers who purchase rock also calcine it to eliminate organic matter or to decrease carbonate content or both. One purpose in calcining is to improve the colour of products such as liquid fertilizer or non-fertilizer products such as sodium tripolyphosphate.

Reaction System

The objective in designing the reaction system is to carry out the reaction between phosphate rock and sulphuric acid in such a way as to recover a maximum percentage of the P_2O_5 originally in the rock as product phosphoric acid in the simplest and least expensive manner. Since the filtration step is the most critical in the process, a primary objective in the reaction step is to form gypsum crystals of such size and shape that the filtration and washing can be carried out rapidly and efficiently.

Maximising recovery means minimising losses. Three types of P_2O_5 losses are recognized: (a) unreacted phosphate rock, (b) P_2O_5 co-crystallised with gypsum through isomorphic substitution of HPO_4 for SO_4 , and (c) phosphoric acid lost in the gypsum due to incomplete washing. Perhaps a fourth source of loss should be mentioned - mechanical losses due to spillage; leakage; washing of filter cloth, piping, and equipment for scale removal; and losses as sludge.

Although the objectives of the reaction step are clear, the means for attaining them may seem complicated. To the uninitiated, it might seem that the best way to carry out a chemical reaction would be to mix the two reactants directly. In practice, however, reaction systems are designed to prevent direct contact between the two reactants, phosphate rock and sulphuric acid. One purpose of this arrangement is to ensure slow growth of gypsum crystals to a relatively large size rather than formation of many small ones. Also, a high concentration of free sulphuric acid will result in coating the phosphate rock with calcium sulphate reaction product, thus inhibiting the progress of the reaction.

A serious case of reaction inhibition in a phosphoric acid plant can take several hours or even days to correct. The aim of designers and operators of reactions systems is to maintain a uniform composition of the slurry, avoiding pockets of high sulphate (or calcium) concentration. The liquid phase usually consists of phosphoric acid with about 1.5-2.0% free sulphuric acid; the optimum concentration of free sulphuric acid varies with rock composition and process used. The solid phase is mainly gypsum. The proportion of solids in the slurry is about 30-35%. Phosphate rock particles introduced into this slurry dissolve rapidly in the phosphoric acid in the liquid phase causing supersaturation with calcium sulphate, which results in the growth of gypsum crystals.

To approach this ideal situation, the incoming streams of sulphuric acid and phosphate rock are mixed with the slurry (directly or indirectly) as rapidly and completely as possible, and the slurry in the reaction system is agitated to ensure homogeneity. The agitation is also used for foam breaking.

Many processes offered by different engineering companies are available in market. Examples of reaction systems offered by Hydro Agri are described with the help of flow-sheets. There is no intention to imply that processes offered by Hydro Agri, mentioned by name, are superior to those offered by other companies.

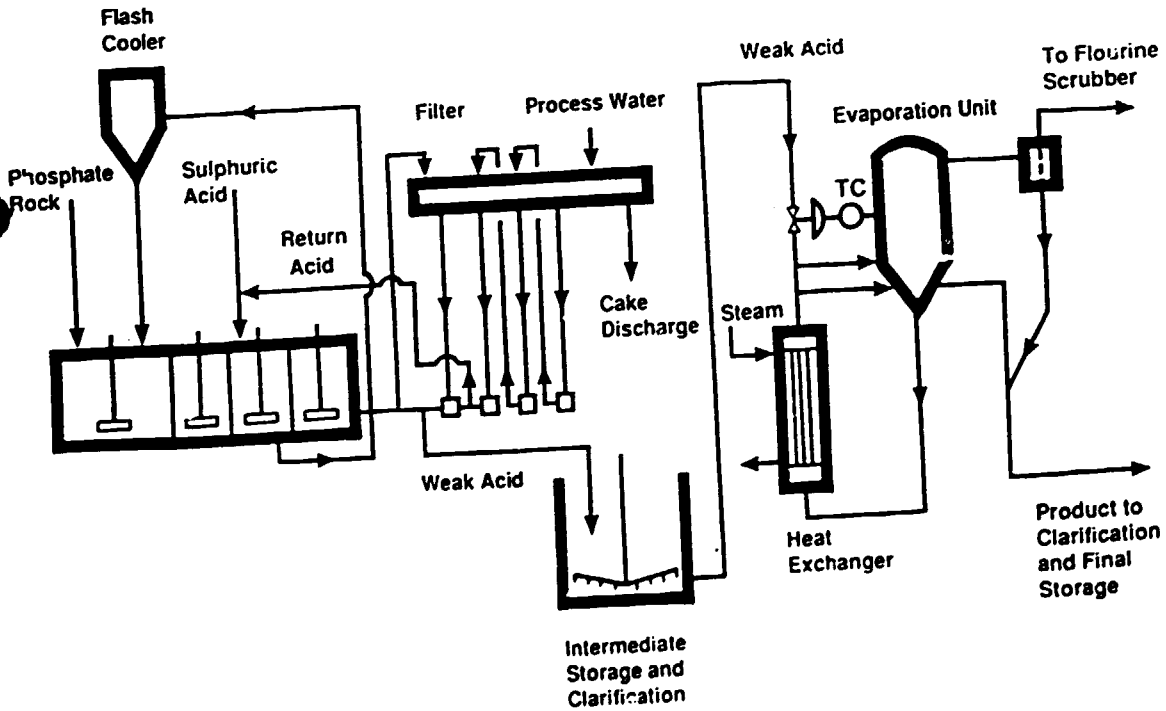
DH Processes

A simple flowsheet of the Hydro DH process is given in Figure 2.

- The reaction section consists of agitated compartments usually contained in a single vessel which is internally divided.
- Phosphate rock is fed to reactor 1, sulphuric acid and dilute phosphoric acid ("return acid" from the filter) are fed to reactor 3. Slurry from reactor 3 is recycled to reactor 1.
- Most of the reaction takes place in reactor 1 and is completed in reactor 2. Reactor 4 is a filter feed tank where the slurry matures before being pumped to the filter. Heat is removed from the reaction slurry to control the temperature between 78-80°C.
- The reactor acid is separated from the dihydrate gypsum by a horizontal vacuum filter with a three-stage counter-current wash system.

Figure 2

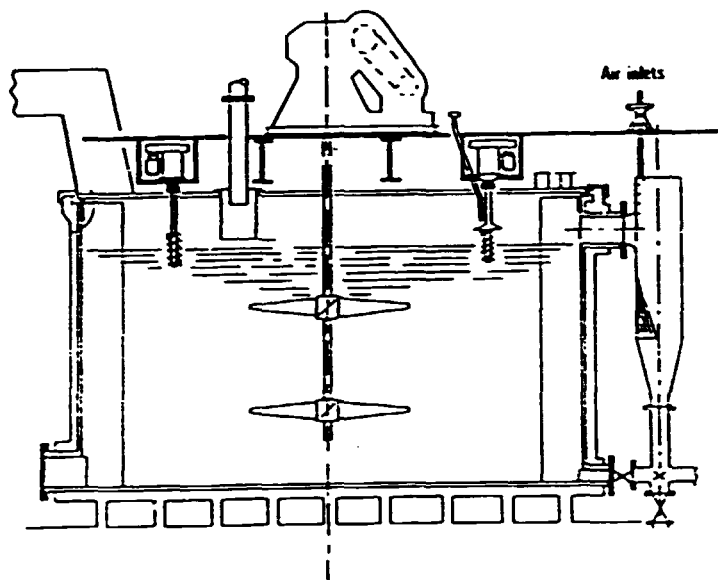
Dihydrate Process



The ex-filter acid is pumped to intermediate storage where it is clarified prior to being fed to the concentration plant.

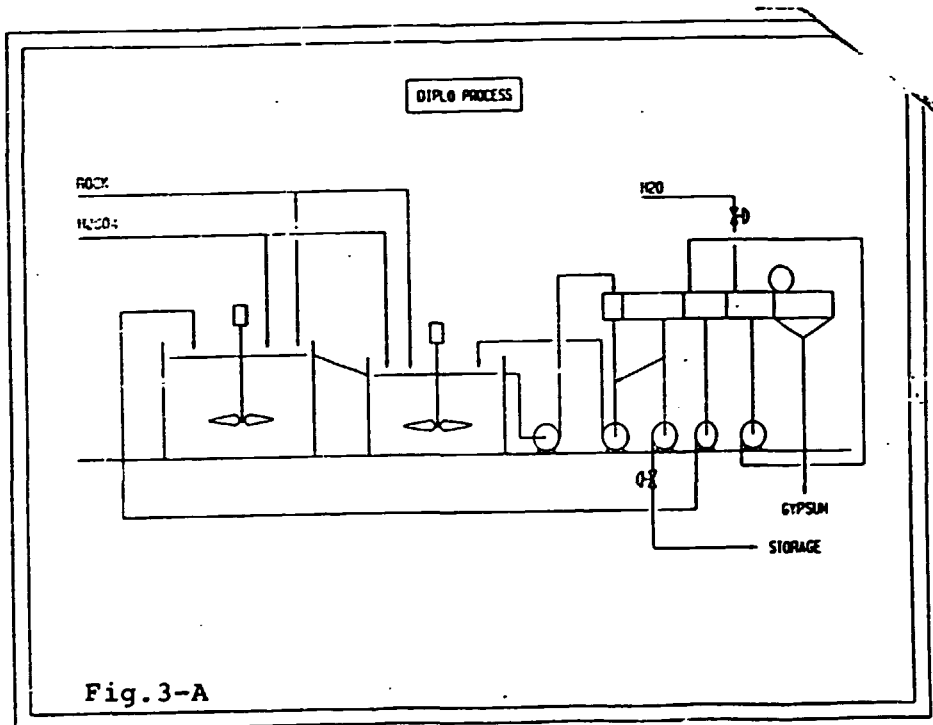
A process employing a single tank reactor is the Rhone-Poulenc process, illustrated in Figure 3.

Figure 3
Rhone-Poulenc Phosphoric Acid Reaction System



One feature of this process is that the temperature in the reactor is controlled by a flow of air over the surface of the slurry in the reactor. To assist in evaporative cooling, special spray-like devices pick up some of the slurry from the surface and shower it in droplets through the air-swept space in the reactor above the slurry level. Sulphuric acid is also added as a spray at the top of the reactor. One of the problems of this system is the high level of entrainment of P_2O_5 and H_2SO_4 droplets in the airstream above the slurry surface, which requires an elaborate and expensive gas scrubbing system to remove it. Phosphate rock is introduced through a centre well to a zone of maximum agitation.

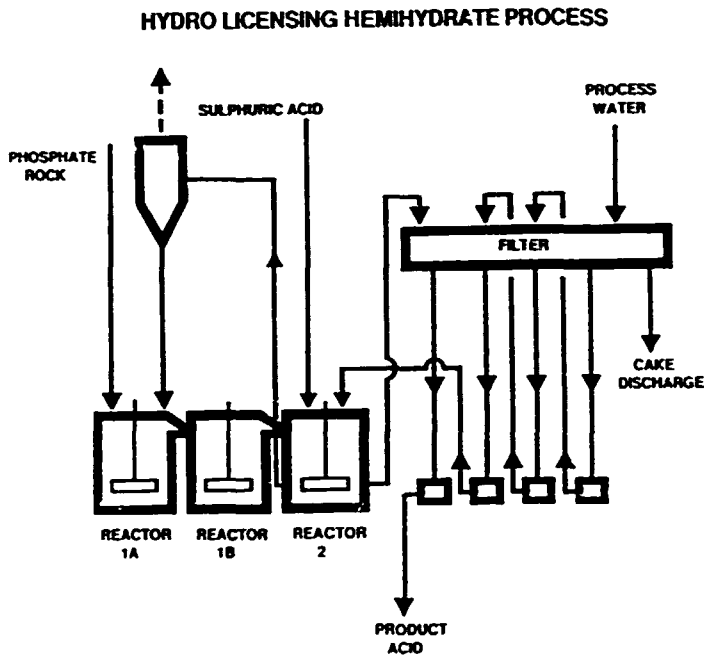
Rhone-Poulenc have introduced a variation of single tank process called Diplo process. In this process attack on rock is carried out in two tanks in series both fed with phosphate rock and sulfuric acid (Fig-3-A). In the first tank, where most of the phosphate is introduced a low concentration of P_2O_5 (24-28%) and highest possible concentration of free sulfate compatible with the phosphate is maintained. In the second tank the remaining phosphate and sulfuric acid is added. This variation is reported to have improved the yield due to less co-crystallized P_2O_5 losses, less unattacked P_2O_5 losses (better residence time distribution) less water soluble losses at the filtration stage (good crystallization) and also good filtration rate (7).



HH Process

A simplified flowsheet of the Hydro HH process is given in Figure 4.

Figure 4



The hemihydrate reaction proceeds in two distinct zones. It is therefore necessary to have at least two vessels or compartments. The preferred volumetric ratio is 2:1. The first zone is often divided into two identical compartments or vessels, 1A and 1B.

Phosphate rock is fed to reactor 1A, sulphuric acid and dilute phosphoric acid ("return acid" from the filter) are fed to reactor 2. Slurry from reactor 2 is recycled to reactor 1A, thus exposing the phosphate rock to sulphate ions under controlled chemical conditions. Slurry overflows from compartment 1A to 1B. Heat is removed by air or vacuum cooling to maintain the reaction slurry temperature at 98-100°C.

Acid can be produced at between 40-50% P_2O_5 , depending on downstream requirements.

The product acid and hemihydrate gypsum are separated by a horizontal vacuum filter with three counter-current wash stages. The product acid from the filter passes directly to storage. It does not require clarification or solids removal.

HDH Process

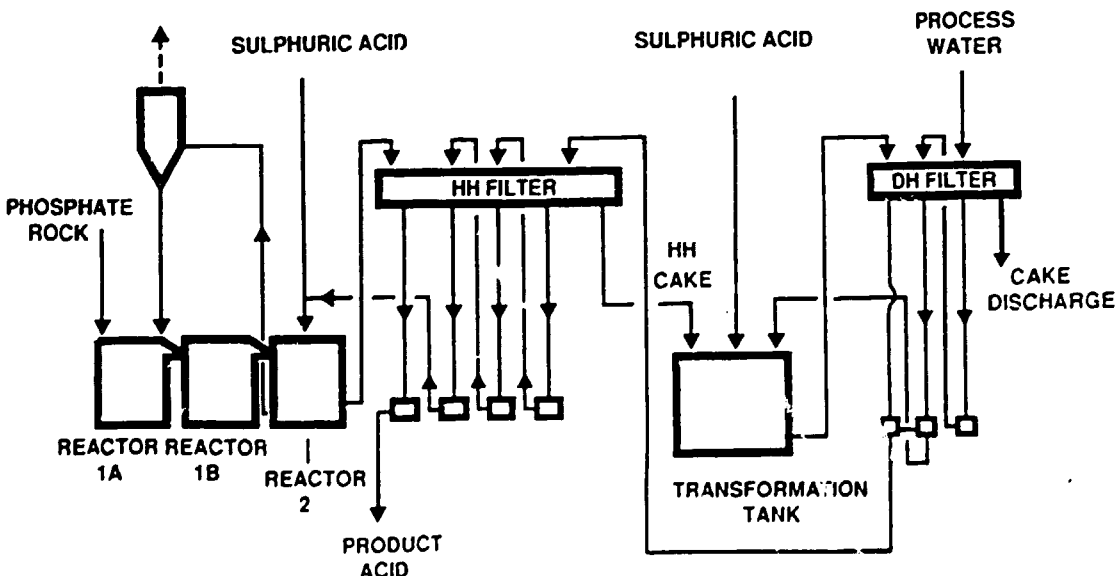
A simplified flow diagram of the Hydro HDH process is shown in Figure 5.

The first stage of the process is almost identical to the HH process already described.

In the transformation stage the hemihydrate cake is discharged from the filter stage filter into an agitated vessel. The operating conditions are controlled to ensure complete transformation of hemihydrate gypsum to dihydrate and to allow sufficient time for the dihydrate crystals to grow. The rate of transformation is increased by the addition of a small feed of sulphuric acid. Nearly all the lattice P_2O_5 co-precipitated with the hemihydrate is released into the liquid phase. The dihydrate gypsum is then filtered and the cake washed with process or pond water. The filtrate containing the released P_2O_5 is returned to the hemihydrate reaction stage as the last wash on the hemihydrate filter.

Figure 5

HYDRO LICENSING HEMIDIHYDRATE PROCESS



Filtration

There are three different types of filters used in the separation of hemihydrate or dihydrate gypsum from phosphoric acid. These are:-

- The Belt Filter
- The Tilting Pan Filter
- The Table Filter

All three types of filter have been used successfully in both DH, HH and HDH processes.

Traditionally, the industry has generally used tilting pan filters but belt filters and table filters are gaining more acceptance.

Belt Filters

Suppliers of belt filters include:

Delkor, Eimco, Filtres Philippe (Aoustin), Pannevis, Filtres Gaudfrin and the earlier Nordengren Landskrona filter.

Belt filters do not come in standard sizes but the standard belt width currently used is 3.2 m.

Most suppliers will also be able to offer belt widths of 2.6 m and 4.0 m.

The majority of belt filters employ an air slide system to support the belt but Pannevis provides a water slide system using a ribbed plate to distribute the water.

The largest size of belt filter used on phosphoric acid plants is 110 m² effective area although 120 m² units have been installed on other plants. The manufacturers have quoted for 135 m² units but these have not been constructed. This should be considered as the maximum size available for the time being.

Filter size range can be related to belt width as follows:

<u>Belt Width</u>	<u>Effective Filter Area</u>
2.6 m	15-45 m ₂
3.2 m	26-88 m ²
4.0 m	75-135 m ²

Tilting Pan Filters

Tilting pan filters have been used for many years in the phosphoric acid industry but there are only a few main suppliers of this type of filter;

Bird-Prayon, Eimco and Mechim (Prayon).

Other less known manufacturers include:

Walther (German) and ATFER (M Barloy).

In recent years there have been several improvements made such as improved cycle time, steeper sloped pans and "Chamberlain" pans to be more competitive with belt and table filters.

Bird-Prayon models and sizes are as follows:-

Model No.	Filter Diameter (m)	Effective Filter Area (m ²)
12 - B	7.74	15.5
12 - C	9.81	26.3
18 - B	11.52	38.7
21 - B	13.20	46.6
24 - B	14.63	60.4
24 - C	16.00	88.3
24 - D	17.58	108.7
30 - C	20.11	139.4
30 - D	21.64	165.9
30 - E	24.38	216.5

Table Filters

Table filters were developed in France and the UCEGO filter is supplied by Aoustin, France and a similar design is supplied by UCB, Belgium.

As with tilting pan filters, the UCEGO filter has adopted a low level installation and has even eliminated the single, compartmented separator.

UCEGO models and sizes are as follows:

Model No.	Table Diameter (m)	Effective Filter Area (m ²)
1	4.2	8.8
2	5.3	14.7
3	6.4	23
4	7.6	34
5	8.2	40
6	9.9	52
7	10.8	63
8	12.3	85
9	14.2	109
10	15.4	132
11	17.1	153
11A	18.3	186
12	19.4	205

Filtration rates of both hemihydrate and dihydrate gypsum are broadly similar when produced from the same phosphate rock. However the filtration rates of gypsums from different phosphate rocks can vary significantly.

A typical filtration rate for hemihydrate gypsum when producing 42% P₂O₅ acid is 7 tonnes P₂O₅/m²/day.

To save heat in subsequent evaporation to a 54% phosphoric acid solution, HDH and HH processes are preferred which yield higher strength acids. With concentration viscosity also increases e.g. phosphoric acid at 31% P_2O_5 and 150°F is 1.91 cp., as compared to 1.05 cp at 20%. The higher strength and more viscous acid slows down filtration and has the adverse effect of decreasing crystal size (which makes filtration more difficult) in question. Still the savings in evaporation heat, plus smaller amount of liquor to be drawn through the filter, have caused industry to raise the P_2O_5 concentration in past years. Evaporation steps has now been totally eliminated for many product applications.

An excess of Ca^{++} and SO_4^{--} ions contribute to nucleation and provide a driving force for growth of gypsum crystals. Various types of crystals appear; rhombic, clusters, needles, and plates. The kind formed depends on the rock source, operating conditions and quite probably on reactor design. The first two crystal types are easy to filter, but the last two are very difficult (8). Most important in growing good crystals (rhombic, clusters) is control of acid and the kind of rock fed. Operation at 1 to 4% SO_4^{--} gives best results but the concentration range actually held is narrower (2 to 3%). In general, high sulfate ion concentration leads to needle-like crystals that are difficult to wash, thereby reducing P_2O_5 recovery. Intermediate sulfate ion concentration gives rhombic and cluster types of crystals. These are the best since they can be grown as large as 150 microns, while they filter well and wash easily. Lower sulfate ion concentrations produce small plate-type crystals that are impossible to filter and wash at a satisfactory rate as they pack together leaving little room for liquid to pass. Low concentration also causes co-precipitation of some forms of phosphate with gypsum. Insoluble impurities in the rock, such as clay, may also affect filtration rates adversely. The filtration rate is also affected by the temperature, concentration viscosity of the acid and the desired recovery while many plants strive for maximum recovery, in specific plants there is often an economic optimum operation rate at which increased production is attained at some sacrifice of recovery.

Uniform good-filtering crystals of moderate size are better than large crystals of even 400 microns, since these may also be associated with fines. Fines will fill in voids between large crystals and filtering will be slower than with uniform smaller crystals.

Two more reasons why very high sulfate ions concentration should be avoided are that it can lead to rapid corrosion of stainless steel filter parts; it also causes a coating to form on rock particles thus preventing reaction of coated rock. (8).

Acid Concentration

The concentration (% P_2O_5) of phosphoric acid required to produce different fertilizers varies as follows:

Use	Acid Concentration % P_2O_5
Triple superphosphate - den process	50-54
Triple superphosphate - slurry process	38-40
Diammonium phosphate	40-48
Mono-ammonium phosphate (depending on process)	40-54
Shipment (merchant grade)	54*
Superphosphate acid for shipment or liquid fertilizer production	69-72

* Although 54% P_2O_5 is the usual standard for merchant grade acid, variations are in the range of 50-60%.

The above concentrations are merely guides to standard practice; it is quite possible to use other concentrations in most cases. For instance, 30% P_2O_5 acid has been used for TSP production in Tunisia by a process requiring extensive drying of the product. However, energy is usually more efficiently used by concentrating the acid than by drying the product with high rates of recycle. This is especially true when energy is available in the form of steam from an adjacent sulphuric acid plant.

In the HH and HDH processes, phosphoric acid can be produced at between 40-52% P_2O_5 , so can often be used in downstream plants without further treatment.

However in a DH process the filter acid is normally 28% P_2O_5 , so needs to be concentrated before it can be used elsewhere.

Most phosphoric acid concentration processes rely on heating the acid with steam in a heat exchanger. However there have been recent developments in heat recovery from sulphuric acid plants where hot water can be used as the heating medium when concentrating the acid from 28% to 35% P_2O_5 . Further concentration usually takes place with the use of steam.

The most common process is based on evaporation of water from the acid, under vacuum. The main variation between the processes is the type of heat exchanger used. Most popular is probably the shell and tube type and the tubes can be made from graphite or stainless steel. The graphite tubes are cheaper but are fragile and can crack if care is not taken in operation. The stainless steel tubes are more resilient but more expensive. Most users estimate that over a period of a few years the capital plus replacement cost for both systems is about the same.

Another type of heat exchanger is the carbon block but this suffers from frequent blockages as the diameter of the holes is smaller than that for a standard tube in a shell and tube type.

Because most phosphoric acids contain impurities such as sodium, potassium, fluorine, silica and dissolved calcium sulphate, then these elements can precipitate during the concentration process because of temperature and % P_2O_5 changes alter their solubilities. The solids precipitated are normally sodium and/or potassium fluosilicate, calcium sulphate, and if there is barium present in the rock, strontium sulphate.

The most common place for these deposits to occur is inside the heat exchanger tubes. It is normal practice to shut down the concentration plant once per week to wash the equipment, particularly the heat exchanger, to remove these solids.

The frequency of washing can vary depending on the level of impurities in the phosphate rock. A description of a typical concentration plant is given below.

For all but the very small plants, the concentration unit normally consists of two identical lines operating in parallel. This leads to easier operation and reduced downtime for washing and maintenance.

The concentration unit operates in three principle ways:-

- a) Acid circulation and heating.
- b) Acid boiling and removal of entrained acid from the released vapours.
- c) Vapour defluorination, condensation and vacuum control.

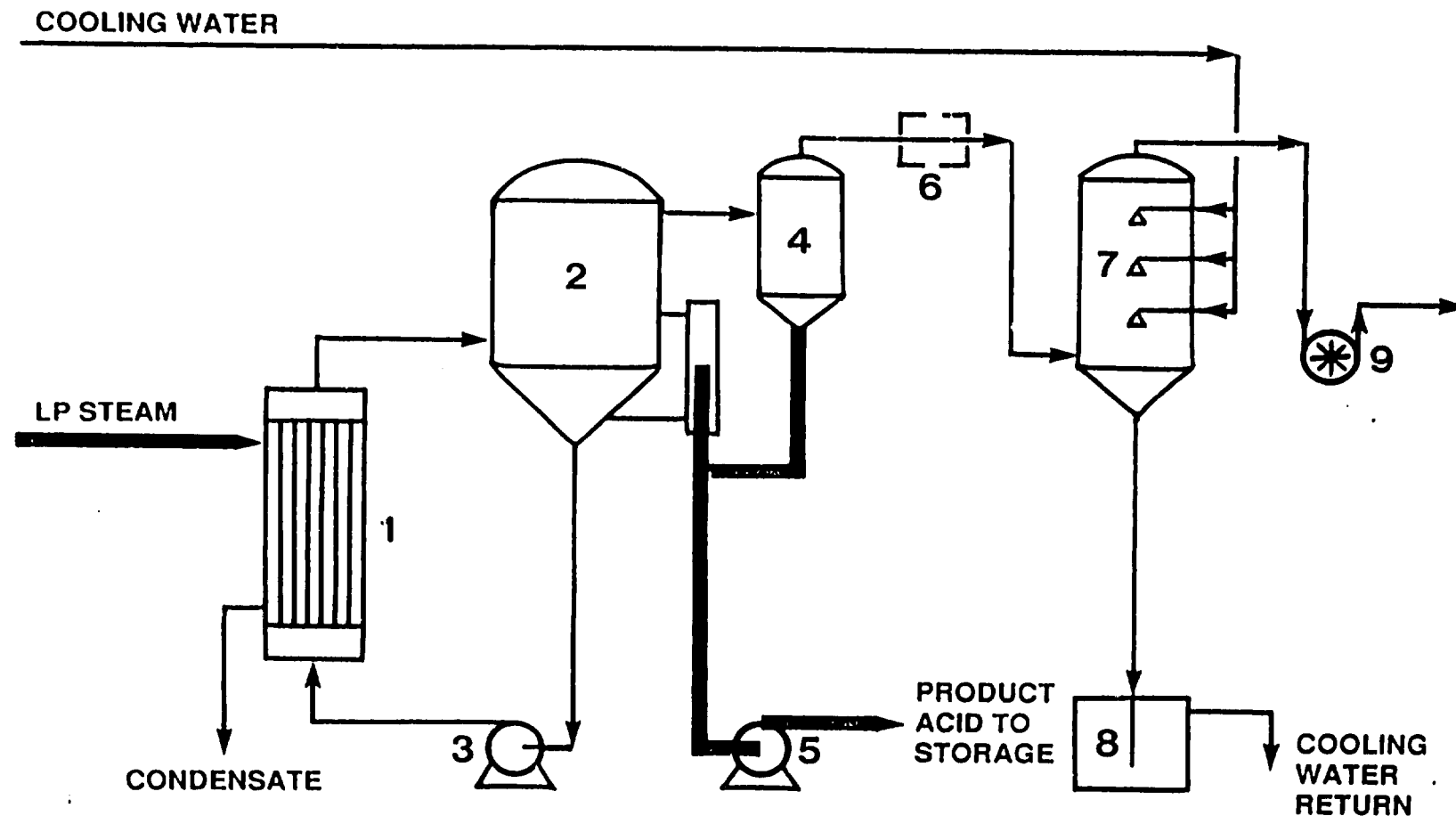
A simplified flowsheet of the Hydro concentration process is given in Figure 6.

28-29% P_2O_5 phosphoric acid ex-storage is fed to the flash chamber of the evaporation unit by the evaporator feed pumps. The feed rate to the flash chamber is automatically controlled as a function of the amount of water removed by evaporation. Acid is circulated continuously by axial flow pump through the flash chamber and heat exchanger where it is heated by about 3-5°C by means of low pressure steam. The exchanger is arranged vertically at an elevation considerably below that of the flash chamber such that boiling on the heating surface is eliminated and hence, scale formation is minimised. Reduction of the tendency to form deposits in the exchanger is also achieved by operation with low temperature gradients both along and across the tubes by the use of a high acid circulation rate.

The material of construction of the exchanger tubes is impregnated carbon. Concentrated product acid is withdrawn from the flash vessel by means of the strong acid pumps; boiling point temperature control ensures that only phosphoric acid of the desired concentration is obtained. Vapours from the boiling phosphoric acid pass through an entrainment separator to remove small acid droplets, and then to the fluorine recovery unit. From here the vapours pass into the condenser, where they are condensed by direct contact with water.

Non-condensable gases are removed from the system by means of a two-stage steam ejector set. The condensate, mixed with cooling water, is collected in the condenser seal tank and is then pumped to the condensate return system. The pressure in the evaporator flash chamber is controlled by regulation of the cooling water flow to the condenser.

TYPICAL PHOSPHORIC ACID CONCENTRATION UNIT



PLANT ITEMS :-

- | | | |
|--------------------|-------------------------|-----------------------|
| 1 HEAT EXCHANGER | 4 ENTRAINMENT SEPARATOR | 7 CONDENSER |
| 2 FLASH CHAMBER | 5 PRODUCT PUMP | 8 CONDENSER SEAL TANK |
| 3 CIRCULATION PUMP | 6 FLUORINE RECOVERY | 9 VACUUM PUMP |

Concentration of acid from 28% to 54% P_2O_5 , requires about 2 tonnes steam per tonne P_2O_5 .

If there is a sulphuric acid plant on site then it can provide the required steam but this will reduce the quantity available for electricity generation or other uses.

In the case of a HH or HDH process when the acid can be used directly from the filter without concentration, then this steam consumption is saved.

This steam saving can lead to a significant effect on a factory energy balance as can be seen from Figures 7 and 8.

In a factory producing DAP which has a sulphuric acid plant and a HH or HDH phosphoric acid plant, then a surplus of electricity can be generated. Whereas a similar factory using a DH phosphoric acid plant would have a electricity deficit of 130 kWh per tonne acid P_2O_5 , and have to import power.

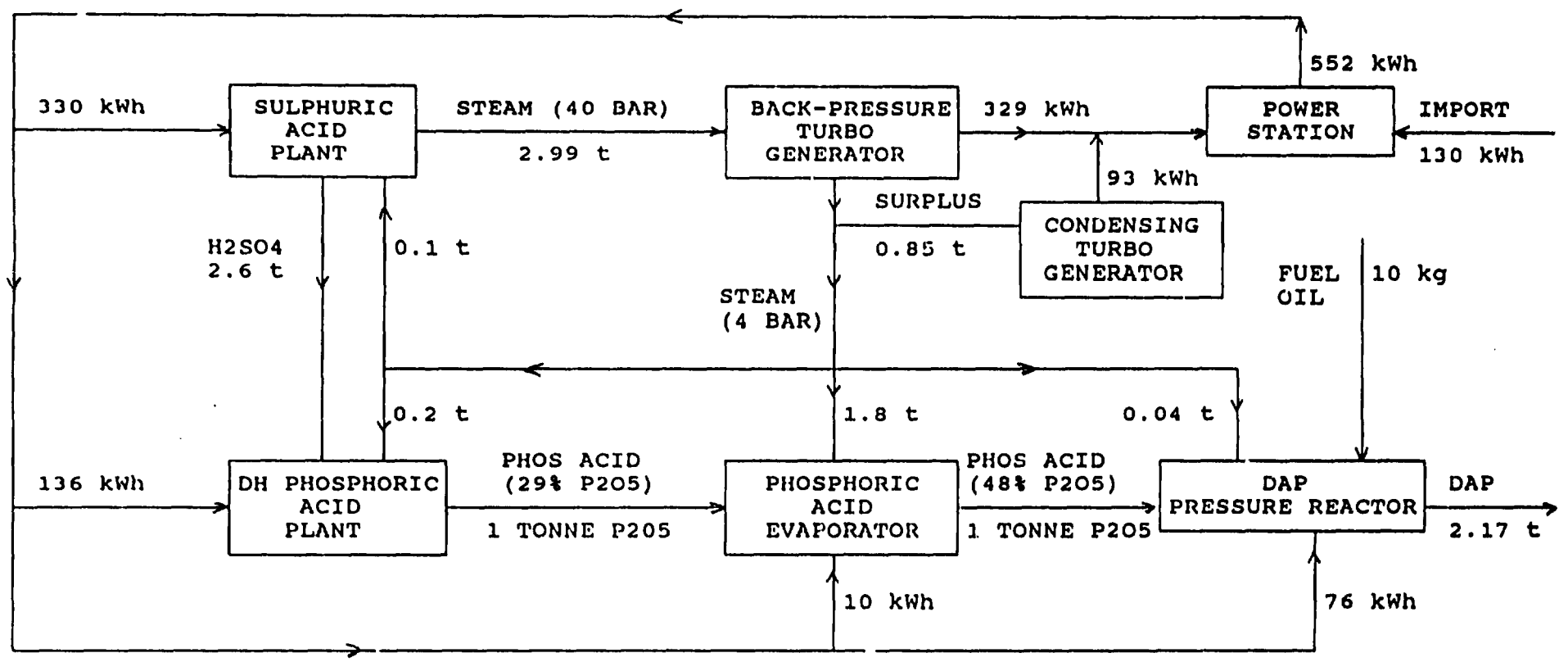
During phosphoric acid concentration, fluorine is evolved in the evaporator. This is normally recovered as fluosilicic acid.

In production of superphosphoric acid (69-72% P_2O_5) by concentrating wet process acid, most of the fluorine is volatilised so that the acid contains only 0.2-0.3% F. By addition of reactive silica during evaporation to enhance fluorine volatilisation, the fluorine content can be further decreased to about 0.1%. Such acid is suitable for manufacture of animal feed supplement products, such as dicalcium phosphate or ammonium phosphate, and is used for that purpose. Other advantages of superphosphoric acid are:

1. Savings in freight occur if the acid is shipped.
2. Sludge is eliminated. The polyphosphoric acids sequester most common impurities; however, in some acids, titanium or magnesium pyrophosphates may precipitate.

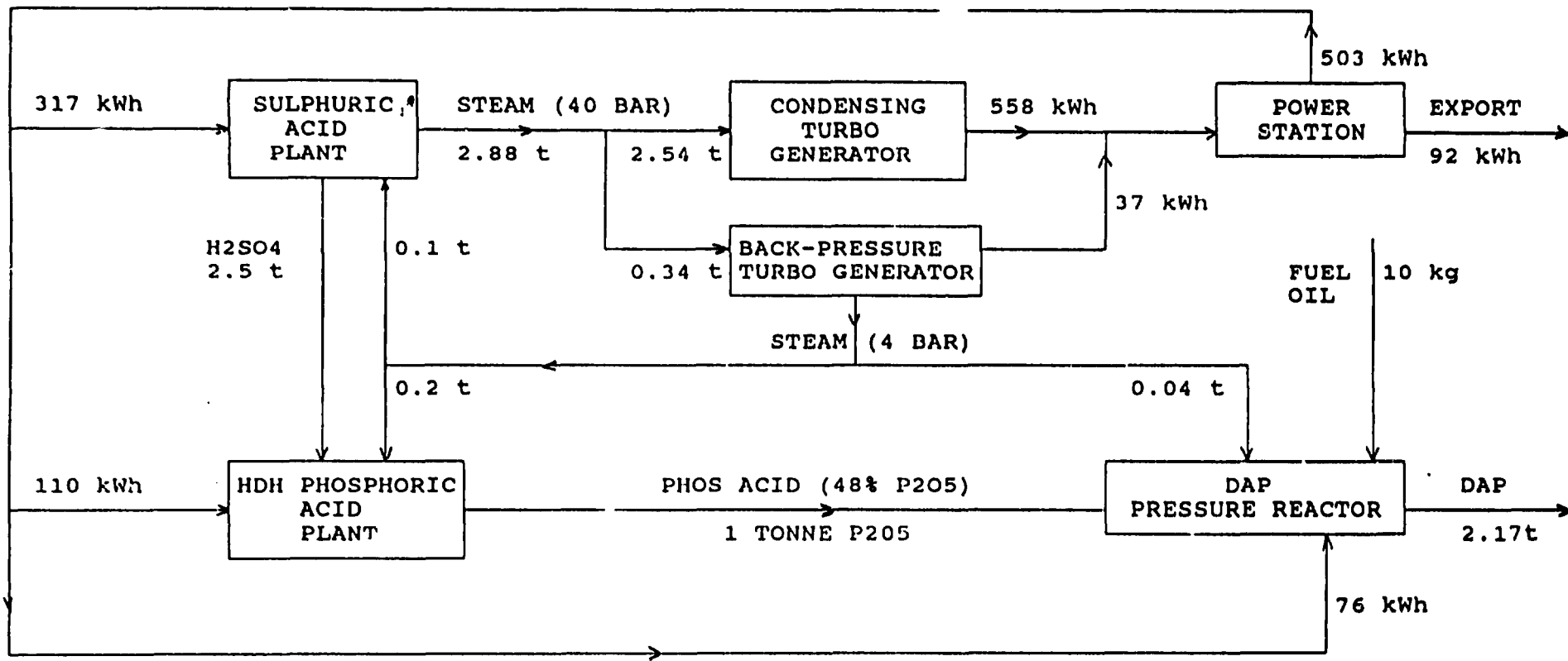
TABLE 7

ENERGY BALANCE - DH PROCESS AND DAP PLANT



BASIS:- PER TONNE ACID P2O5

ENERGY BALANCE - HDH PROCESS AND DAP PLANT



BASIS:- PER TONNE ACID P₂O₅

3. Superphosphoric acid is much less corrosive than lower concentrations.
4. Superphosphoric acid is suitable for production of clear liquid fertilizers (ammonium polyphosphate solutions) since the polyphosphate sequesters impurities that otherwise would precipitate upon ammoniation.
5. Superphosphoric acid can be used to produce compound fertilizers by melt processes in which the drying step is eliminated.

The main disadvantages of superphosphoric acid are the energy requirement, corrosion in some types of evaporators, and the high viscosity. The viscosity depends on temperature, concentration, and impurity content; some superphosphoric acids must be heated to 60°C or higher to permit pumping with centrifugal type pumps.

The compositions of superphosphoric acids produced from several types of phosphate rock are shown in Table 9.

Table 9

Chemical Composition of Superphosphoric Acids

Type of Rock	Florida	Western United States	North Carolina	Morocco	Togo	Taiba
Calcination	No	Yes	Yes	No	No	No
Composition, % by weight						
Total P ₂ O ₅	72.9	72.5	71.2	72.4	73.0	72.1
Ortho P ₂ O ₅	31.8	34.0	37.6	25.1	35.3	27.1
Fe ₂ O ₃	2.2	1.2	1.4	0.6	1.9	2.4
Al ₂ O ₃	1.8	3.0	1.3	0.4	0.9	0.5
F	0.3	0.3	0.4	0.1	0.1	-
SO ₃	2.0	2.1	3.4	2.7	1.7	3.3
MgO	0.3	0.8	0.6	1.1	0.1	0.1
Colour	Black	Green	Green	Green	Dark	Dark
Polyphosphate content, % of total P ₂ O ₅	56	53	47	65	52	62.5

Acid Clarification

Precipitates form in phosphoric acid before, during, and after concentration. Compounds precipitating before concentration are likely to be mainly calcium sulphate and fluosilicates. A wide variety of compounds may form during and after concentration, depending on acid concentration. These compounds are collectively known as "sludge" and cause many difficulties in handling and use of the acid. They also form scale in evaporators. Therefore, many manufacturers clarify the acid and either recycle the sludge or use it in fertilizer products where it causes the least trouble. Acid for shipment, in particular, should be well clarified. Phosphoric acid produced by hemihydrate processes (40-50% P_2O_5) is reported to be relatively free from sludge.

Here are some guidelines to the practice of acid clarification/sludge removal.

Note that when acid is concentrated from 28% to 54% P_2O_5 , it is sometimes done in two steps with a 40% P_2O_5 intermediate product because most of the impurities have lower solubility at the concentration of 40% of P_2O_5 .

It is normal that removal of gypsum from 40% acid is practised. Initial clarification of 28% acid is not practised in all cases.

Ageing of 29% P_2O_5 acid is not in general practice and acid is normally fed to a settling tank of only a few hours hold-up.

Ageing of 40% P_2O_5 acid prior to settling is often practised.

Solid removed from acids up to 40% P_2O_5 content, being gypsum, is suitable for return to the reaction compartments of a phosphoric acid plant. This is not the case of solid removed from 54% P_2O_5 acid which contains a high proportion of iron and aluminium phosphates.

It is normal that solids removed from 54% P_2O_5 acid (mainly iron and aluminium phosphates) are fed to acid consuming plants producing fertilizers as long as it does not dilute the required analysis of the fertilizer.

Ageing is required for 54% P_2O_5 acid to allow metal phosphates to precipitate. An ageing time of 10 days is normal practice.

Ageing is practised solely to provide a clarified acid suitable for transportation.

A clarified 54% P_2O_5 acid containing less than 1% solids content is normally achieved by the use of a centrifuge. Solid bowl centrifuges are not considered suitable for 54% P_2O_5 acid as the crystals are too small. Nozzle centrifuges are used but have a lower solids content in the underflow leading to a greater loss of acid in the underflow.

Settling tanks are normally flat bottomed with conical rakes.

Some larger tanks have outward scraping rakes.

Lamella settlers represent a real alternative to settling tanks. They require, however, the use of flocculants and regular washing.

Utilization of Sludge--As mentioned previously, sludge impurities precipitate in phosphoric acid before, during, and after concentration. If the acid is used onsite for fertilizer production, it may be possible to use the acid without separating the sludge. However, in some cases the amount of sludge may be so great as to lower the grade of fertilizer products below that desired. The amount of sludge in phosphoric acid depends on rock composition; however the acid from the filters contain about 2% suspended solid. (9).

Sludge solids that form in filter acid (30% P_2O_5) are mainly gypsum and fluosilicates and may, in some cases, be returned to the phosphoric acid production unit without serious interference with its operation. Sludge forming after concentration is likely to contain a high proportion of iron and aluminum phosphate compounds. One example is $(Al, Fe)_3K_{14}(PO_4)_8 \cdot 4H_2O$. Lehr has identified 38 distinct crystalline compounds occurring in sludge from wet-process acids (10). The return of iron and aluminum compounds to the acid-production unit is likely to cause some difficulty. When this sludge must be separated, as is usually the case for shipment, it is often used for production of TSP. Most of the P_2O_5 in the sludge solids is citrate soluble but not water soluble; therefore, this solution is not advantageous when the TSP is sold on the basis of water solubility.

The sludge may be used in the production of nongranular monoammonium phosphate (MAP) which, in turn, is used as an intermediate in the production of compound fertilizers. There is no standard grade for MAP to be used as an intermediate; the user can formulate compound fertilizers on the basis of actual analysis. In this case also, the iron, aluminum, and magnesium compounds are not water soluble. In fact, there is no economical method for utilizing sludge solids in countries where phosphate fertilizer is sold on the basis of water solubility.

Precipitation after concentration to 54% P_2O_5 is slow and never so complete but that more precipitate will form on further storage. However, clarification methods are available that reduce the sludge problem in merchant-grade acids to manageable levels.

Materials of Construction

Choice of materials of construction is very important as it will effect the degree of maintenance and downtime of a phosphoric acid plant.

Corrosion rates in a plant are variable and largely depend on the chloride and free fluoride content of the acid.

There follows a list of typical materials of construction for various items of equipment.

Reactors : Concrete, rubber lined or RLMS (rubber lined mild steel) protected by carbon bricks.

Vessels : RLMS, polypropylene, FRP (fibreglass reinforced polypropylene).

Pipework : RLMS, polypropylene, FRP, rubber.

Agitators : RLMS + polypropylene shield, 20 alloy e.g. 904L, HV9, Sanrico 28, Ferralium 255, 317L.

Pumps : 20 alloy e.g. 904L, HV9, Sanrico 28, high density polyethylene, Ferralium 255, RLMS, 317L.

Recommended alloys for use with Phosphoric Acid production (19)

Type	Cr	Ni	Mo	C	Uses
Stainless steel					
304	18-20	8-12	-	0.08	Only occasionally for splash guards
304L	18-20	8-12	-		
316	16-18	10-14	2-3	0.08	At low speed and matured slurry, low-corrosive rock
316L	16-18	10-14	2-3	0.03	
317	18-20	11-15	3-4	0.08	Agitators, valves, filter with low-corrosive rock
317L	18-20	11-15	3-4	0.03	
446	23-17			0.2	Heat exchanger tubes
Hastelloy C	15.5	54	16	0.08	High Cl ⁻ , agitator, pump impellers; evaporators, hot acid
Hastelloy G	22	44	6.5	0.05	
Hastelloy G ₃₀	29.5	47.5	5.5		
Nionel	21.5	42	3	0.03	Heat exchanger tubes
Sanicro 28	26.0	30.6	3.55	0.015	Pump impeller, agitator turbines when high Cl ⁻
Durimet 20	19-22	27-30	2-3	0.07	Pump, impellers, H ₂ SIF ₆
Durco 100	24-27	4-6	1.7-2.25	0.04	Pump, valves
Uranus					
B6 PM	20	20	4.5	0.02	Agitator turbines, pump impellers
50 M	22	7-9	2.2-2.8	0.07	Pump impellers
55 M	25-27	4.5-6.0	1.5-2.5	0.05	Pump impellers

The cost of 317L alloy is about 10% higher than 316L, and UB6 50% higher.

Phosphoric Acid Production Costs

Approximately 75% of the cost of phosphoric acid production comes from raw material costs, the next highest contributor is energy with 8% (in the DH process).

The operating and investment cost of a 500 tpd P₂O₅ plant is given for the DH, HH and HDH processes, in Table 10. It is based on 1991 West European prices for the production of 50% P₂O₅ acid.

Table 10

1991 West European Costs

	Process		Dihydrate		Hemihydrate*		Hemidihydrate	
	Unit	Cost/ Unit \$	Units/ t P ₂ O ₅	\$	Units/ t P ₂ O ₅	\$	Units/ t P ₂ O ₅	\$
1. Raw Materials								
Phosphate Rock (32% P ₂ O ₅ , 50% CaO)	t	50.00	3.29	164.50	3.29	164.5	3.17	158.50
Sulphuric Acid (93-98%, 100% basis)	t	40.00	2.80	<u>112.00</u>	2.78	<u>111.2</u>	2.74	<u>109.60</u>
				<u>276.50</u>		<u>275.7</u>		<u>268.10</u>
2. Operating Costs								
2.1 Utilities: Cooling Water	m ³	0.04	70.00	2.80	22.00	0.88	27.00	1.08
Process Water	m ³	0.50	7.00	3.50	4.00	2.00	6.00	3.00
Steam (LP): Process	t	12.00	0.15	1.80	0.11	1.32	0.10	1.20
Evaporation	t	12.00	1.75	21.00	0.29	3.48	0.00	0.00
Electric Energy:								
Grinding	kWh	0.06	20.00	1.20	0.00	0.00	0.00	0.00
Process	kWh	0.06	90.00	5.40	70.00	4.20	90.00	5.40
Evaporation	kWh	0.06	10.00	0.60	10.00	0.60	0.00	0.00
Chemicals	-	-	-	2.00	-	3.00	-	2.00
Maintenance	-	-	-	<u>2.00</u>	-	<u>1.75</u>	-	<u>2.15</u>
Materials				<u>40.30</u>		<u>17.23</u>		<u>14.83</u>
2.2 Labour: Operating Personnel	h	20.00	0.25	5.00	0.20	4.00	0.25	5.00
Maintenance Personnel	h	25.00	0.20	5.00	0.15	3.75	0.18	4.50
Laboratory Services	h	25.00	0.05	1.25	0.04	1.00	0.05	1.25
Labour Overheads (70% of above)				<u>7.88</u>		<u>6.13</u>		<u>7.53</u>
				<u>19.13</u>		<u>14.88</u>		<u>18.28</u>
Sub-total Production Costs				<u>335.93</u>		<u>307.81</u>		<u>301.21</u>

Table 10 (Cont.)

1991 West European Costs

	Process		Dihydrate		Hemihydrate*		Hemidihydrate	
	Cost/ Unit	Unit \$	Units/ t P ₂ O ₅	\$	Units/ t P ₂ O ₅	\$	Units/ t P ₂ O ₅	\$
2.3 General: Taxes, Insurance (2% of investment)				4.69		3.75		4.90
Capital Services (17% of investment)				39.84		31.88		41.68
Interest on Working Capital (7%)				<u>1.83</u>		<u>1.05</u>		<u>1.33</u>
				<u>46.36</u>		<u>36.88</u>		<u>47.91</u>
Sub-total Operating Costs				<u>105.79</u>		<u>68.79</u>		<u>81.02</u>
3. <u>Production Costs</u> (excluding any by- product credits)				<u>382.29</u>		<u>344.49</u>		<u>349.12</u>
	* 45% P ₂ O ₅ ex-filter							
	Investment mio US\$		Grinding	1.5		0.0		0.0
			Process	30.0		27.0		38.0
			Evap.	<u>6.0</u>		<u>3.0</u>		<u>0.0</u>
				<u>37.5</u>		<u>30.0</u>		<u>38.0</u>
	Operating Days per Year			320		320		310
Basis = 500 tpd P ₂ O ₅ as 50% P ₂ O ₅ acid.								

Shipment of Phosphoric Acid

A relatively recent development is phosphoric acid from the point of production locations where it is converted into compound fertilizers. Extensive shipment from the United States, mainly by rail, from production areas in North Carolina, and Louisiana to manufacturers located in market areas of compound fertilizers (liquid or solid). There are also substantial amounts of phosphoric acid shipped within or between European countries. In the United States, phosphoric acid is shipped by rail, but shipment by coastal barge through inland waterways is more common.

Overseas shipment is growing rapidly; several countries have built or are building facilities for phosphoric acid intended mainly for export. The major importing countries are Mexico, Morocco, United States, Tunisia, South Africa and Israel. Other countries include India, Brazil, Colombia, several countries in Asia and Japan. Phosphoric acid exports have shown a progressive increase from over one million tonnes in 1975 to 4.4 million tonnes in 1988. In 1989, a decrease was registered to 3.1 and 3.4 million tonnes respectively.

Most of the acid shipped is 54% P_2O_5 concentration, and terminals have been built which handle phosphoric acid (69-72% P_2O_5). Thus SPAP is used. Advantages of shipment of phosphoric acid include rapid loading and unloading of acid at high concentration. Phosphoric acid may be used to produce desired phosphate or compound fertilizers, whereas, TSP or ammonium phosphate is more versatile.

As compared to the importing of raw materials, P_2O_5 as phosphoric acid requires shipment of 1.43 tons of 54% P_2O_5 or 1.43 tons of 70% P_2O_5 acid, which is about 4.3 tons of raw materials (3.3 tons of phosphate plus about 1 ton of sulfur).

Rapid loading and unloading decrease cost by decreasing port time, and decreasing cost of handling. Also, handling of phosphoric acid (or ammonium phosphate) is free, thereby avoiding atmospheric contamination and minimizing losses.

Some disadvantages are the requirement for specially equipped ships and special terminals with storage tanks at both shipping and receiving points for further processing by the importer. Shipment is limited to countries which have sufficient demand and facilities.

Phosphoric acid for shipment should be free of sludge-forming solids, preferably less than 0.1% requirement the acid usually must be clarified previously in this chapter. The amount of sludge depends on the composition of the phosphate rock and the acid production process and, in some cases, the use of such is unnecessary.

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Many liquid chemicals other than phosphoric acid are shipped in bulk, and numerous ships are equipped with tanks lined with stainless steel, rubber, or other acid-resistant materials. Such ships may carry phosphoric acid, as well as various other chemicals. In addition several ships have been built specifically for transport of phosphoric acid, and more are under construction. For long distance shipment, large vessels are preferred, and several have been built recently in the range of 20,000 to over 38,000 tons capacity.

Obviously, the storage capacity at terminals must be at least equal to the size of the largest shipment although ships may load and unload at more than one terminal. A 1976 world survey showed 46 terminals in operation for shipping and/or receiving phosphoric acid. A more recent survey issued by IFA in August 1991 listed 124 maritime terminals with an aggregate storage capacity of 2.99 million tons. Another IFA report lists 270 ships that are suitable for transport of phosphoric acid (and other corrosive liquids) with cargo capacities ranging from 500 to 39,000 tons. The following tabulation shows the number of ships in various capacity ranges:

<u>Phosphoric Acid cargo capacity in metric tonnes.</u>	<u>Number of Ships.</u>
950- 2,000	17
2,001- 5,000	70
5,001-10,000	90
10,001-20,000	46
20,001-30,000	31
over -30,000	16
	<hr/>
	270
	<hr/>

For construction of storage tanks, rubber-lined steel is commonly used although stainless-steel lining may be used. In some cases, ponds or lagoons are used for storage. The ponds are lined with heavy sheets of rubber or plastic underlaid with gravel with drainage to a sump so that any leakage can be detected and returned to another pond. One such installation, near Tampa consists of four ponds with a total capacity of 11,000 tons. The ponds have inflatable plastic covers to protect them from rain or other contamination. Most storage tanks have facilities for circulating the acid occasionally to prevent settling of solids.

It is difficult to compare the terminal cost for phosphoric acid with that for solid products such as triple superphosphate (TSP) or monoammonium phosphate (MAP). The cost of storage facilities for the same number of tons of solids (30,000 tons) has been estimated to be about 40% of the cost for phosphoric acid (20). However, a substantial investment in mechanical equipment would be required to

reclaim bulk solids from storage and convey them to a ship. In addition, a substantial amount of labor would be required for operating the equipment; whereas, loading and unloading costs are negligible for phosphoric acid. For a receiving terminal in a developing country which may not be well equipped with mechanical devices, the total of unloading and port storage costs might well be higher for solids. On balance, it seems likely that overall terminal storage and handling costs may be about the same for acids as for bulk solids.

Freight rates for ocean shipment of phosphoric acid are not published; the larger cargoes are moved under long-term contracts in custom-designed vessels. Bulk solids are often shipped in tramp vessels; the freight rates fluctuate widely with supply and demand for shipping space. It is reasonable to assume that the freight costs would be higher for phosphoric acid because of the special construction required. A study in 1973 assumed that the cost would be 40% higher for a short haul (north Africa to northern Europe) and 25% higher for a long haul (United States to India). However, at that time, only a few ships were equipped to transport acid. Now that there are a much larger number of ships the differential may well be lower.

Utilisation of By-product Gypsum

The phosphoric acid industry produces about 150 million tonnes of gypsum per annum, of which only about 15% is re-utilised.

Some details of the various uses for phospho-gypsum are given below.

Plaster-board Products

About 14 million tonnes per year of gypsum are used for making plaster or products based on plaster. This is as a substitute for natural gypsum, which in many locations is plentiful and cheaply available.

Production of plaster involves the purification of the phospho-gypsum, usually by simple washing and neutralisation, followed by a dehydration step to form calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$). Dehydration can be carried out in the liquid (slurry) phase in an autoclave to produce alpha-hemihydrate, or in the solid phase in a calcining device to produce beta-hemihydrate.

In either case a large quantity of free water as well as water of crystallisation has to be removed. This is a large energy consumer.

Purification and dehydration methods and conditions are selected to provide the preferred characteristics (setting, hardness, colour, etc.) of the final product.

Plaster-blocks are usually cast with smooth faces of about $\frac{1}{4}$ square meter and 75 to 100 mm thick. They are tongued and grooved to allow smooth surfaced walls to be constructed using plaster "glue" to stick them together. The blocks have limited load bearing capacity and are generally used for internal walls within framed buildings.

There were three commercial operations using phospho-gypsum for plaster-blocks in Europe, but all have now shut down or reverted to natural gypsum.

Plaster-board consists of a sandwich of gypsum between sheets of paper or cardboard. The thickness is about 10 mm and sheets of about 2 m² are produced. The boards are used for internal walls or ceilings, nailed to a usually wooden frame.

In Europe there is only one plaster-board plant using phospho-gypsum. However in Asia, notably Japan, a large proportion of the plaster-board is phospho-gypsum-based - often imported.

Other plaster products e.g. spray plaster, tunnel linings and for dental purposes can and have been produced using phospho-gypsum.

The chemistry of plaster is very complex with setting rate, hardness and other parameters being critically sensitive to impurities. Of particular importance are F and P₂O₅ levels in phospho-gypsum, but there are no generally quoted limits. The experience is that with some ingenuity processes can be adapted to suit different phospho-gypsum sources.

Most phosphate rocks contain minor concentrations of uranium and part of this reports to the gypsum in the phosphoric acid process. Uranium decays to radium which in turn decays to the radio-active gas radon. Radon is released in very small quantities from plaster products. This is of greatest concern from plaster-blocks which contain a larger mass of plaster per unit of wall area. For buildings having limited ventilation, radon concentrations have been detected at levels above those considered safe. This has been used as an argument against phospho-gypsum building materials, although similar levels occur naturally in certain locations.

Where natural gypsum is readily available the use of phospho-gypsum as an alternative is determined almost exclusively by economic considerations. There are unlikely to be overwhelming technical arguments in favour of either product. Economic circumstances have led nearly all phospho-gypsum based operations to close down in Europe, whilst those in Japan continue.

Cement Retarder

Introduction of phospho-gypsum as retarder to cement accounts for about 4 million tonnes per annum.

Portland cement normally contains up to 5% of natural gypsum as a setting retarder and to enhance other qualities of the product.

Phosphate, fluoride and organic impurities in the phospho-gypsum are undesirable and must be reduced to acceptable levels.

Material from double crystallisation phosphoric acid processes is satisfactorily employed in Belgium and Japan.

Sulphuric Acid/Cement

In this process, gypsum is calcined and split into sulphur dioxide and lime. The lime combines with other materials and forms cement clinker (similar to the conventional process).

Sulphur dioxide with other combustion gases is passed to a contact sulphuric acid plant where it is oxidised to sulphur trioxide and absorbed to produce sulphuric acid.

The sulphuric acid can be recycled to the phosphoric acid reaction system to create a virtually closed loop.

In most circumstances this process is uneconomic and applicable in only unique situations. Two plants have operated in Europe and one in South Africa. None are now believed still to be in operation. Such a unit was commissioned in China near Kunming in 1986.

Highways and Paving

Use for highway construction and paving represents a large potential outlet for phospho-gypsum.

Several large-scale trials have been carried out in Texas and Florida USA, where there is a substantial production of phospho-gypsum and a consequent disposal problem. These trials have been carried out on untreated phospho-gypsum, mixed in various ways with clayey and sandy soils. Although apparently successful technically, the techniques do not appear to have been adopted commercially.

An engineering company in Florida has collaborated with the phosphoric acid industry in developing a highway aggregate based on phospho-gypsum. Gypsum and pyrites with waste phosphate clays are calcined on a circular grate roaster to produce the aggregate and sulphuric acid. The economics are not acceptable under present conditions, although the process is technically feasible.

Soil Conditioner

Gypsum, natural or by-product, is effective in combating salinity in soils or to reclaim land which has been flooded by sea water. Calcium from the gypsum replaces sodium from salt water retained by the soil.

Gypsum is also a valuable source of sulphur for sulphur-deficient soils, or of soluble calcium for crops such as ground-nuts.

Miscellaneous

Phospho-gypsum can also be used for production of ammonium sulphate, but this process is rarely economic today.

Recent work has been done in France and Finland to use phospho-gypsum to produce a pigment for paper manufacture.

Gypsum Disposal

The remaining 85% of phospho-gypsum, amounting to about 135 million tonnes per annum is disposed of by dumping or stock-piling systems.

From the environmental protection point of view they can be classified in the order of:

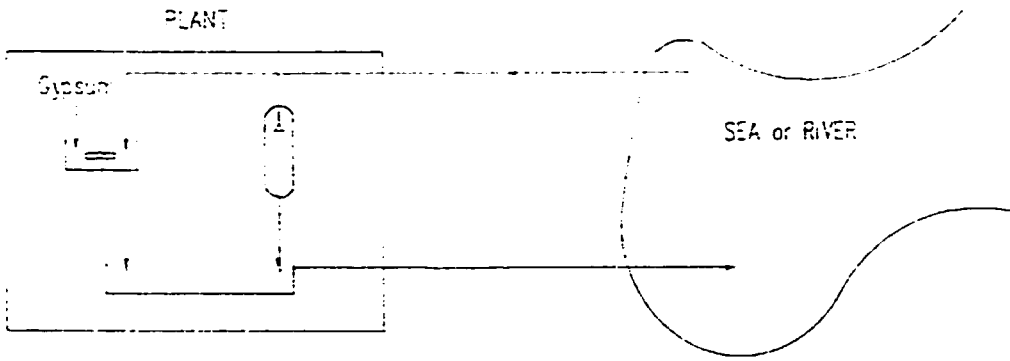
- Clean dry stacking.
- Pumping into sea.
- Impounding on land (pond and pile system).

From the investment costs point of view they can be classified in the order of:

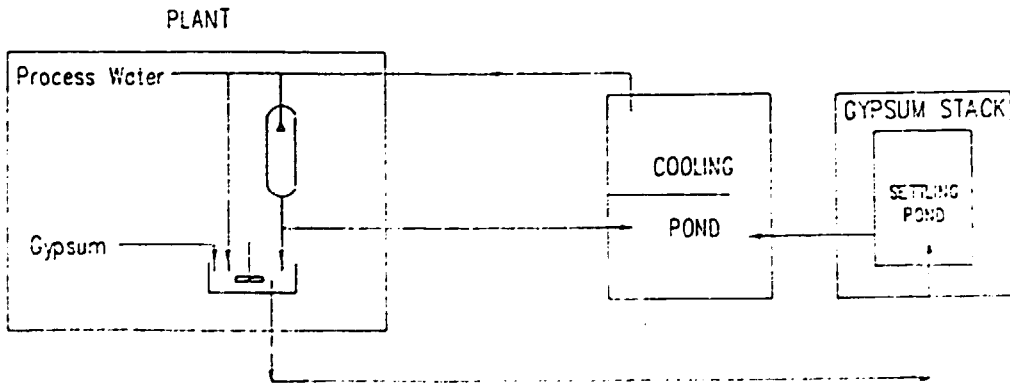
- Pumping into sea.
- Clean dry stacking.
- Impounding on land (pond and pile system).

Figures 7 to 12 depict the gypsum disposal systems in various combination with the cooling water cycle. Although over the past 30 years it has been believed that dispersing into the sea is the best compromise between environmental requirement and economics of investment and operations, this is no longer allowed in many countries. Today the most popular method installed with new plants is dry stacking of gypsum together with a cooling pond or tower system.

GYPSUM DISPOSAL AND COOLING WATER SYSTEMS



Cooling and Gypsum Sludge Water from Sea (or River)

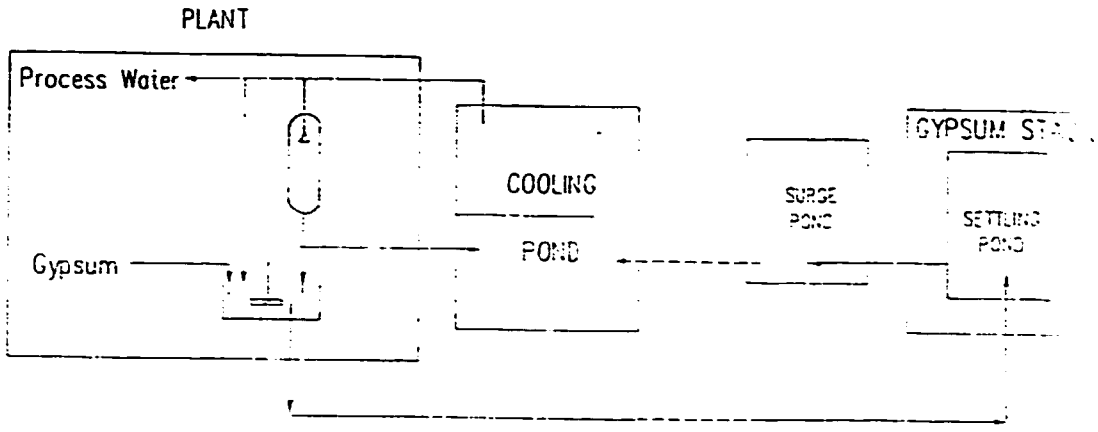


Combined Cooling and Gypsum Settling Pond Close to Plant

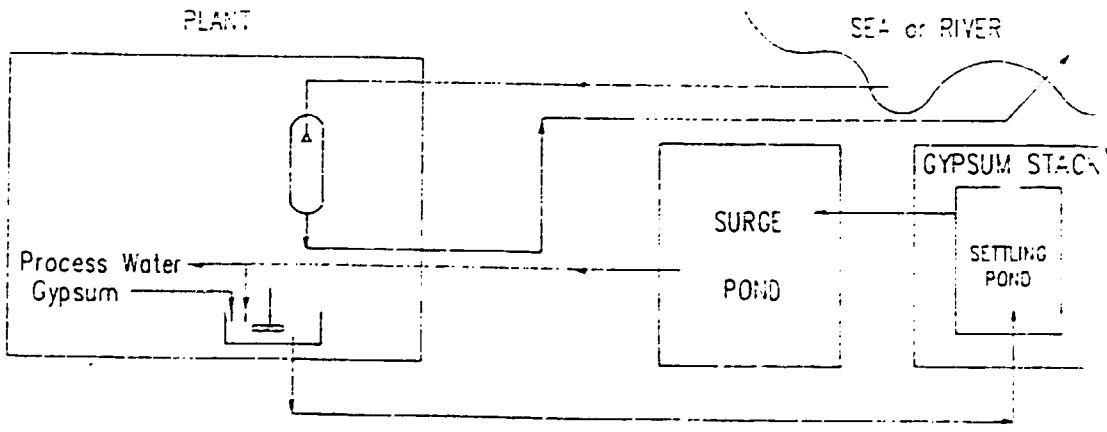
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Gypsum Disposal and Cooling Water Systems



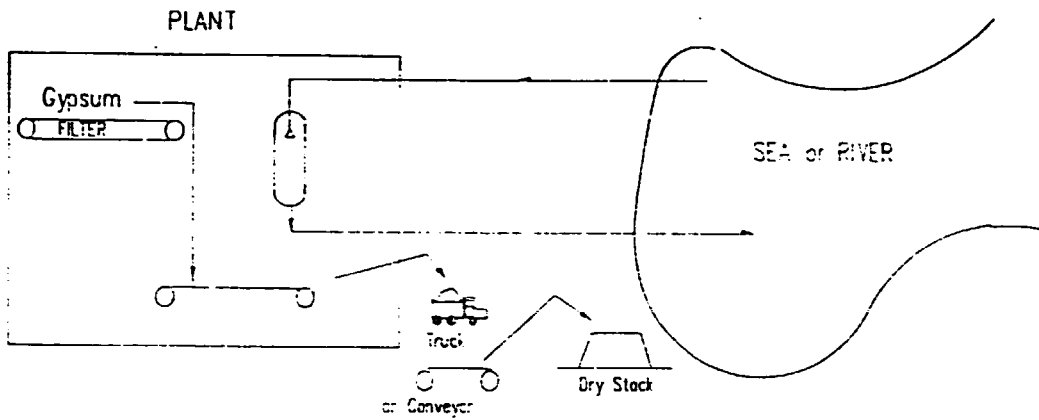
Cooling Pond Close Gypsum Settling Pond Far From Plant



Cooling Open Loop Sea Water Settling Pond on Separate Cycle

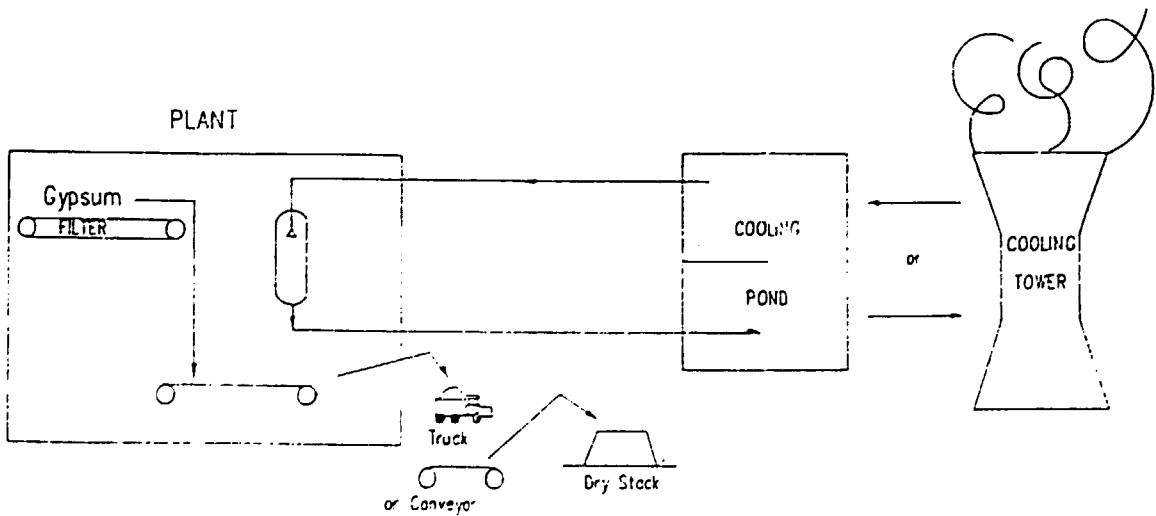
Gypsum Disposal and Cooling Water Systems

11



Cooling Open Loop Sea Water Gypsum Dry Stacking

12



Closed Cooling Loop Gypsum Dry Stacking

Modes of Disposal

Pumping into Sea or River

Advantages - Disadvantages of Sea/River Disposal

Advantages: No technical problems to be expected.
 Low operating costs.
 Low investment.

Disadvantages: Dredging if intense settling disturbs navigation.
 Easy target for environmental critics.

Dispersion into sea/river is common in European and North African countries, although it has been criticised in some cases. Morocco has completed the world's largest phosphoric acid factory at Jorf Lasfar with a gypsum disposal arrangement of pumping 20,000 mt per day into the Atlantic Ocean. Similar is true for Tunisia.

From the Hydro Agri Rotterdam plant in Holland a gypsum/water slurry is pumped into the nearby river.

Gypsum transportation and dispersion into the sea/river is operated via sluice water pumping through pipe-line. The pipe end should be located some distance off-shore where sufficient depth and possibly current, will prevent from visible effects of the disposal and achieve rapid dissolving effects.

Most of the gypsum will dissolve in sea water, the solubility of gypsum in sea water is 3.5 g/l.

Some of the components will not dissolve: silica (which will add sand to the beach), and unreacted phosphate rock.

With moderate to strong current (above 0.5 m/sec.) or a strong swell, the disposed material will disperse and dissolve in the sea/river water.

The most environmentally - hostile effects in a clear sea are the organic materials coming along with the gypsum crystals. They can build up foam or oil-like patches on the sea and effect cloudy water. Organic material originates from phosphate rock and depends on the rock origin.

Nevertheless, organics can be prevented either by flocculation before disposing of, or by a skimming off operation before pumping the slurry into the sea.

Calcium Sulphate Impounding on Land

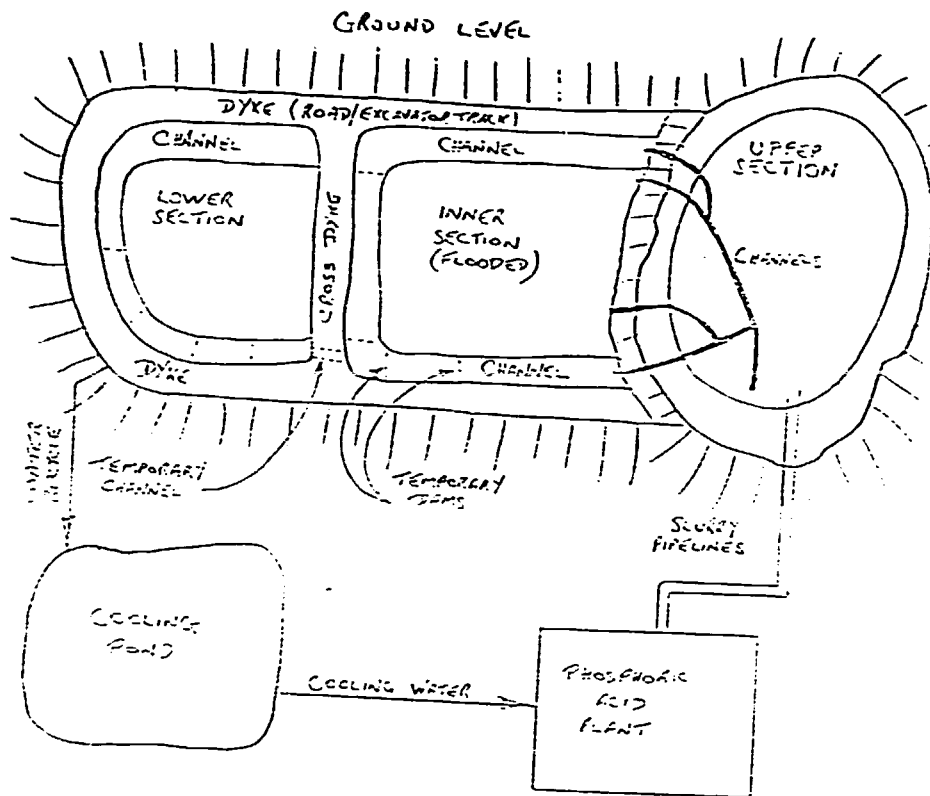
Common practice in the United States is land disposal of gypsum. The solids are pulped with sluice water and pumped into a settling pond. The settling pond is located on the top of the gypsum pile. Settling elevates the solids level of the pile.

Usually, settling and cooling pond are combined within one inter-connecting system. This allows better water balance management.

The settling operation is controlled by the so-called rim-ditching technology. It is based on excavating rim ditches (3) with flat bottoms, so that the large crystals settle in the ditches, filling them up gradually.

The small crystals eventually settle in the centre of the pond. Another ditch leads the clarified pond water via an overflow opening to the cooling pond from where it is recycled to the plant.

Figure 13
Gypsum Pile and Pond - Plan View



The stack, located immediately adjacent to the phosphate factory and the water cooling pond, is of an elongated shape with a higher section at one end occupying about 25% of the total area. The upper and lower sections are surrounded by gypsum banks, or dykes, which contain the liquid covering a majority of the surface area. The lower section is divided into two by a further gypsum dyke.

Figure 14
Excavation of Gypsum



The method of operation is for slurry to be fed to the higher section from which it flows down channels to the lower section. Initially a channel is excavated near the edge of the lower section, parallel to each dyke, eventually leading to the centre. Slurry is first fed to one channel down which it slowly flows. Gypsum deposits in the channel gradually filling it, whilst clear liquor flows to and collects in the central area, eventually draining to the cooling pond. The stack serves the dual purpose of decanting and cooling (by evaporation) of the liquid phase.

When the first channel is full of solid, the flow is diverted to the other and solid removed by drag line to build up the dyke (which also acts as an excavator track and access road (see Figure 14)). The process is repeated for each channel alternately until the dyke has been built up to sufficient height to create a rim. The slurry is then fed to the central area until it is full, then the whole process is repeated. In this way the stack gradually grows, with steeply sloped sides.

The recycled pond water is fed back into the gypsum slurring tank, to return again to the pond within the closed loop.

Process water (filter water) taken from the loop contains P_2O_5 and consequently improves the overall recovery of the phosphoric acid plant (the water cycles 3-4 times).

Consistent water balance management must be monitored. The water balance of the system depends on several factors, which are difficult to control:

- Rainfalls.
- Evaporation.
- Seepage (percolation into soil).

If there are seasonal rainfalls and high evaporation periods, pond level monitoring must compensate between higher and lower water intake periods.

Advantages - Disadvantages of the Piling System

Advantages

- Recycling of cooling water and part of the soluble P_2O_5 losses, back into production. (Also a small part of co-crystallised P_2O_5).
- Calcium sulphate can be recovered if any economical use should be found in future. (Construction material recycling into sulphuric acid and manufacturing, etc.)

Disadvantages

- Gypsum pile needs a large area which will be unsuitable for any economical utilisation in future.
- Possibility of acidic pond water percolation into local water table, if the soil has no neutralisation or cementation effect.

However, water percolation can be arrested by means of laying a suitable membrane under the pile but would call for an additional investment of 10 million dollars.

- Can become expensive, especially when location is far from production units (pumping costs, pipe-line maintenance, pipe pluggings, etc.).

View of a pile and pond system in Florida are shown in Figures 15 and 16.

Pile and Pond System, Florida USA

Figure 15



Figure 16



Pile System Requirements

Surface Requirements

A 500 mt/day P_2O_5 plant will produce about (depending on phosphate rock quality), 736,000 tonnes/day of gypsum equal to about 650,000 m³ of material to be stored (bulk density is related to crystal shape).

The required surface for the pile depends on the mechanical properties of the soil which will permit different stacking heights. Strong soil like the area near Tampa, Florida, support 60 metre high stacks. The average, nevertheless, hold some 20-30 metres.

The angle of repose of gypsum is about 45°. However for safety reasons, in a pond system, it is normally limited to 26.5°.

By comparing with other pond/pile systems elsewhere, it is estimated that the normal annual elevation is approximately 0.5 m. Therefore after 20 years the pile height should be no more than 10 m.

The gypsum in the pile has water retention properties which aid the stack management regime and restrict problems with windblown particles. It is far less dusty than sand.

In order to improve the external appearance of a gypsum pile it is common practice to landscape it. Thus with a top dressing of nitrogen fertilizer and sufficient irrigation, it is possible to grow grass and shrubs on a gypsum pile.

Maintenance Equipment and Labour

Gypsum stacking needs a permanent maintenance team (two operators on day shift) for:

- Rim ditching.
- Levelling.
- Access roads.
- Pump and pipe maintenance.

The equipment needed will be:

- One drag line for rim ditching.
- One bulldozer for levelling and access roads.

Dry Stacking

When gypsum leaves the battery limits of a phosphoric acid plant it contains approximately 25% w/w water. If it is discharged untreated in this form it is known as "dry discharge". One of the simplest methods of disposal is to discharge this "dry" gypsum to an area where it is stacked. It can be transported by conveyor belt or truck, depending on the distance of the stack from the plant. The use of conveyor belt is the more economical. However, stack management includes control of stack height and shape by bulldozers or similar equipment.

Again there is still the possibility of percolation although this will be limited due to the lower moisture content of the gypsum; and again percolation can be avoided by lining the area with an impermeable membrane before stacking.

problems with fly blow particles of gypsum are not normally experienced. As before, landscaping of the stack is possible.

As with the pond and pile system, the increase in the height of the stack can be restricted to less than 0.5 m per year (depending on area of stack) so after twenty years the stack will be less than 10 m high for a 500 mt P_2O_5 /day plant.

One of the advantages of this method is that the gypsum will be available for other uses. Normally this includes as a cement retarder, soil conditioner, raw material or plaster-board, back-filler for roads, etc.

The moisture containing properties and the phosphate contents make the gypsum suitable as a soil conditioner.

The main disadvantage of the dry stacking method is that it utilises a large area of land which may otherwise be used for a preferred and profitable purpose.

A dry stack at a phosphoric acid plant is shown in Figures 17, 18, 19 and 20.

Dry Stacking System, Australia

Figure 17



Figure 18



Figure 19



Figure 20



Fluorine Recovery and Utilisation of Fluorine

Many phosphate rocks of the fluorapatite-type contain a significant quantity of fluorine (say 4%). In some cases up to 50% of this can be evolved during the manufacture of wet process phosphoric acid. If active silica is present the evolution is in the form of SiF_4 and HF.

The fluorine is evolved from various stages of the phosphoric acid process: from the reactor slurry surface, in the flash cooler or other cooling system, in the concentration plant.

In a DH process the proportions are:

Slurry Surface	:	3-5%
Flash Cooler	:	8-10%
Concentration Plant	:	15-20%
(up to 45 P_2O_5)		

In a HH or HDH process (producing 45% P_2O_5 acid at the filter) the proportions are:

Slurry Surface	:	12-15%
Flash Cooler	:	15-20%

Where there is a demand for fluorine compounds, for example, for fluoridation of public water supplies or aluminium fluoride production, it may be economic to recover fluorine as fluosilicic acid from a phosphoric acid plant.

For example, the Hydro process for fluorine recovery from a phosphoric acid concentration unit consists of a void vessel with a bank of spray nozzles, operating under the same vacuum as the evaporator. The product can contain a small quantity of P_2O_5 but is suitable for sodium fluosilicate manufacture, fluoridation etc. Where fluosilicic acid is required for aluminium fluoride manufacture it is necessary to remove P_2O_5 . Hydro have developed a system which reduces the P_2O_5 content to less than 100 ppm.

This involves a two-stage unit, the first stage is the purification operation when P_2O_5 droplets are removed by cyclonic effect; the second stage is the standard fluorine recovery unit. The fluosilicic acid can be produced at between 15% and 20% H_2SiF_6 with a P_2O_5 content as low as 50 ppm.

When a HH or HDH phosphoric acid process is used Hydro has developed technology to remove fluorine from the reactor and flash cooler off-gases. The resulting fluosilicic acid is suitable for AlF_3 manufacture. Details are given below.

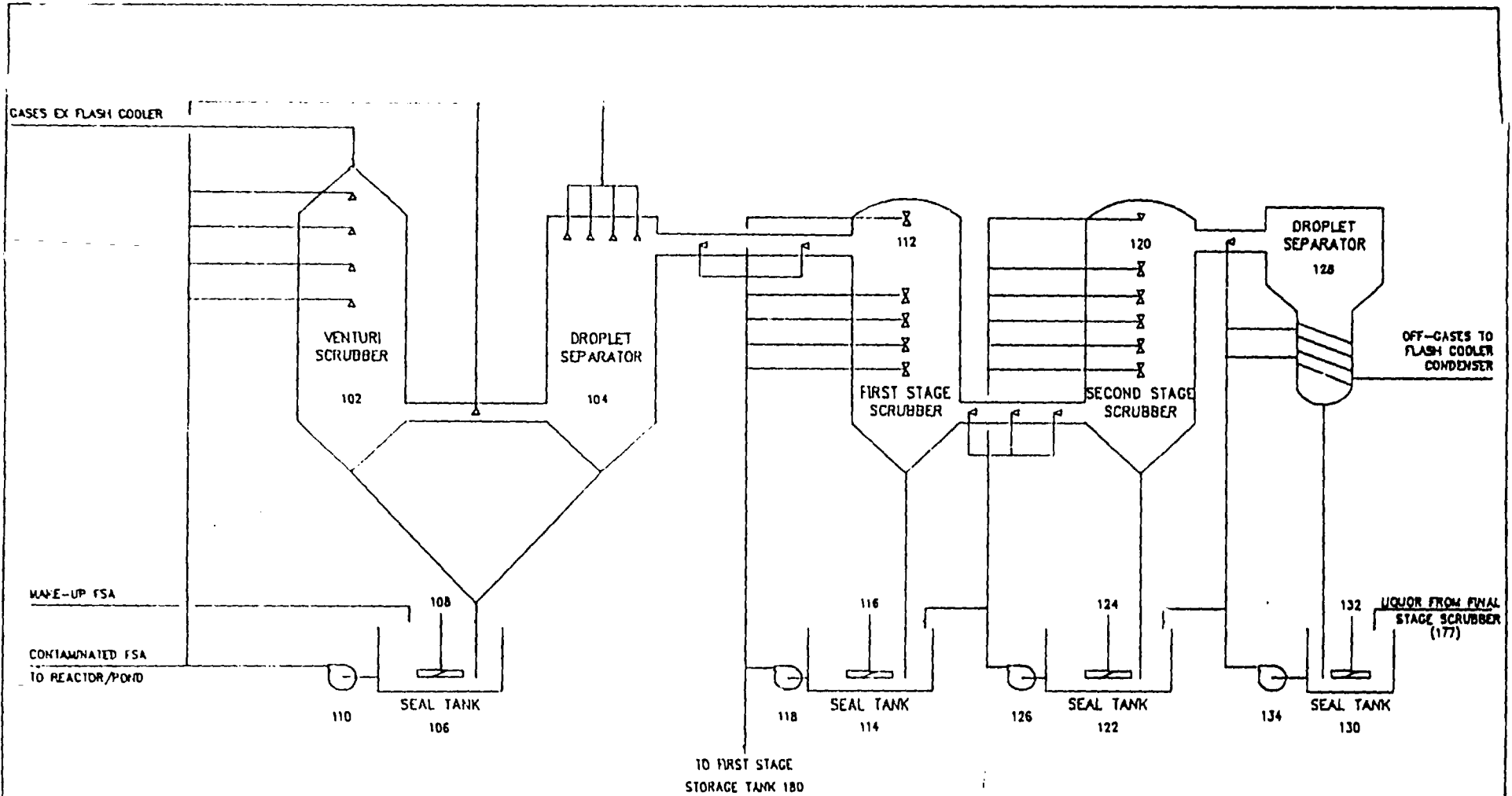
On phosphoric acid plants where vacuum cooling is employed two scrubbing units are normally required. One unit is required to treat the reactor off-gases and a second to treat the flash cooler vapours. The units are very similar in terms of the process flow diagram although equipment sizes will vary due to the different operation conditions.

A simplified diagram is given in Figure 21.

Gases first pass from either the flash cooler or reactors to a venturi scrubber and then to a droplet separator. In these vessels the gases are contacted with a recirculating high strength (approximately 28%) fluosilicic acid solution. Any phosphoric acid, phosphate rock or entrained foam in the gas streams is removed. The liquor recirculated is an azeotropic solution and therefore absorbs only a small amount of fluorine from gas phase, however any entrained liquids or solids are completely removed.

For the flash cooler unit no make-up liquor is added as there is sufficient water addition through condensation and seal water in-leakage. However on the reactor units fluosilicic acid from a phosphoric acid evaporation plant, if available, can be added to the seal tank. Fluosilicic acid from phosphoric acid evaporators contains a stoichiometric excess of fluorine. This excess fluorine is used to reduce the amount of silica passing to the next stage.

Figure 21



					 Norsk Hydro Licensing	Hydro Fertilizers Limited, Levington Research Station, Ipswich, Suffolk, IP10 0LU, United Kingdom.		TITLE SUPRA SCRUBBING SYSTEM FLASH COOLER SYSTEM PROCESS FLOW DIAGRAM		
1	11-1-90	UPDATE	NO			CLIENT	PROJECT	DRAWN BY	DATE	APPROVED
ISSUE	DATE	DESCRIPTION	BY	APPRVD	PROJECT NO	SCALE	JMG	21-7-89		P00/064
AMENDMENT RECORD							ACod Ref	MX0001		

If evaporator acid is not available then the make-up is taken from the product acid stream. Discharge liquors from the flash cooler and reactor systems pass to gypsum disposal system or to the phosphoric acid reactors.

From the droplet separator the gases pass to the first stage scrubber. Here the gases are washed with a recirculating fluosilicic acid solution (approximately 20% H_2SiF_6). Some recirculating liquor is bled off as a product stream to an agitated storage tank. The strength of fluosilicic acid is maintained by a density controller which effects the water make-up to the scrubbing system.

The gases then pass to the second stage scrubber, where the gases are scrubbed with recirculating scrubber liquor of between 5 and 10% H_2SiF_6 . Some of this liquor is fed to the first stage scrubber whilst the level in the seal tank is maintained by the addition of liquor from the droplet separator seal tank.

The gases then pass to a droplet separator which eliminates any liquid carryover to either flash cooler condenser or to the Final Stage Scrubber. Liquor collected in separator passes to a seal tank where liquor is recirculated to flush the separator and some is bled off to the second stage scrubber. The level in the seal tank is maintained by a feed of scrubber liquor from the Final Stage Scrubber on the reactor gas scrubber unit.

In the flash cooler system the cleaned vapours pass to the flash cooler condenser where the water vapour is condensed. The remaining gases are then vented to atmosphere, by the flash cooler vacuum pump.

In the reactor off-gas scrubber system the cleaned gases are extracted by a fan and then mixed with fumes extracted from the Transformation Tank (if it is a HDH plant) and general fume extraction. These fumes are extracted by a separate fan after having been scrubbed in a duct scrubber.

The mixed gases pass to the Final Stage Scrubber where the gases are further cleaned by a recirculated liquor. The gases are then exhausted to atmosphere via the stack.

The product fluosilicic acid is pumped from the first stage storage tank to a semi-continuous belt filter. Here silica is removed to ensure a solids free product. From the filter the acid is pumped to final storage. See Figure 22.

The process recovers a high quality fluosilicic acid product meeting the following specification:

Concentration	:	20-23% H_2SiF_6
P_2O_5	:	less than 100 ppm
Sludgs	:	less than 500 ppm

The recovery of these by-products results in a significant reduction in the overall production costs of the phosphoric acid process. The saving is typically about US \$4/tonne P_2O_5 produced.

Fluosilicic acid can be used as a raw material for the manufacture of a number of different compounds:

Fluosilicates

Sodium or potassium fluosilicate are valuable salts which can be produced from the recovered fluosilicic acid. The salts are employed as flux in the metallurgical industry, an additive to drinking water, insecticides, opacifying agents, and as a protective agent in the casting of light metals.

Fluorides

Ammonium, magnesium, zinc, copper, barium and aluminium fluoride can be produced from fluosilicic acid and find many uses within industry.

Cryolite

Cryolite ($3NaF.AlF_3$) can also be produced from fluosilicic acid. Cryolite is used in the production of aluminium and forms the electrolyte in the electrolytic reduction of alumina.

Fluosilicic acid is also used directly in the brewing industry as a disinfectant for copper, brass and wooden vessels.

For most fertilizer production processes, purification of wet-process phosphoric acid is not necessary. However, there are two common fertilizer uses that may call for partial purification:

1. "Merchant-grade" acid which is shipped by rail, barge, or ocean vessels and is often stored at shipping and receiving terminals should be purified sufficiently so that formation of insoluble precipitates (sludge) during shipping and storage is minimized.
2. Phosphoric acid to be used for production of liquid fertilizers, such as ammonium polyphosphate solution, sometimes requires partial purification to prevent formation of precipitates upon ammoniation or during storage of the ammoniated solution.

Although ammonium polyphosphate sequesters most of the common impurities, excessive amounts of some impurities (especially magnesium and organic matter) cause precipitate formation. Superphosphoric acid usually do not form sludge, but magnesium or titanium have been known to cause sludge-forming precipitates.

A major fraction of sludge in most merchant sludge acids is the compound $(Fe, Al)_3 KH_{14} (PO_4)_8, 4H_2O$. It precipitates slowly over a period of several weeks; therefore, long storage periods are needed to ensure reasonably near completion of the precipitation reaction. Methods for clarification of merchant-grade acid have been discussed in a previous section of this chapter. A recently developed method of "stablizing" the acid is to concentrate it to 40% P_2O_5 (a point of minimum impurity solubility), treat the acid by undisclosed means, and then concentrate the acid further to 60% P_2O_5 . This method is said to be successful in preventing further sludge formation.

Several solvent extraction methods have been developed, and some are in commercial use. Such processes usually separate the phosphoric acid into two fractions, a cleaner fraction and a dirtier fraction containing most of the impurities. The cleaner fraction can be used for production of liquid fertilizers and the less pure fraction for TSP or mono-ammonium phosphate. One exception is a process developed by Garrett Research that selectively extracts acid dissolved in kerosene (24). The objective is to upgrade acid made from low-grade rock; 94% to 97% of the P_2O_5 is recovered as partially purified acid.

Methods have been developed for removing organic matter by flocculation or copolymerization during digestion (23). The agglomerated carbonaceous matter is removed along with the gypsum filter cake. Many other methods are under study; for further details see the following references; (22, 23, 24). Possibly further development of acid purification methods will permit utilization of low-grade rocks that cannot be utilized because of their high impurity content.

Production of Phosphoric Acid Using Acids Other than Sulfuric

Phosphate rock can be dissolved by several organic and inorganic acids to produce phosphoric acid. The use of nitric acid for this purpose is described in chapter XV, Nitrophosphates. Commercially used nitrophosphate processes produce phosphoric acid containing nitrates and, hence, are used to produce compound NP and NPK fertilizers. It is technically feasible to produce phosphoric acid substantially free from calcium or nitrates by separation methods involving solvent extraction. One such process using tertiary amyl alcohol as the solvent has been developed in Finland and described by Lounmaa (21). However, no commercial use has been reported.

Several processes using hydrochloric acid have been developed or patented, but only that developed by the Israel Mining Industry (IMI) has been used commercially. The IMI process has been described in a UNIDO publication (20). The following description is a condensation from that publication. The main stages of process are:

1. Dissolution of phosphate rock by hydrochloric acid, resulting in an aqueous solution of calcium chloride and phosphoric acid;
2. Liquid-liquid contacting in a number of solvent extraction steps to obtain a solution of substantially pure phosphoric acid; and
3. Acid concentration to obtain 95% H_3PO_4 (69% P_2O_5).

The raw materials and reagents used are as follows:

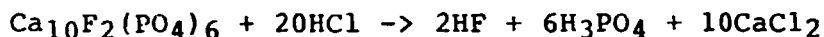
1. Phosphate rock (any commercial grade). The P_2O_5 recovery is over 98%.
2. Hydrochloric acid for acidulation can be used as a solution of 20% HCl or higher or in gaseous form by combining absorption with reaction. For reasons of economy, concentrated acid is preferred because most of the water accompanying the

acid must be evaporated in a later stage of the process. Acid consumption is dependent on the composition of the rock. Acid consumption for Florida rock of 34% P_2O_5 is about 2 tons HCl (calculated as 100%) per ton P_2O_5 .

3. Solvent. Several solvents can be used for extraction. Those preferred are technical isoamyl alcohol or n-butanol or a mixture of both. Solvent makeup is 4 kg/ton P_2O_5 .
4. Process water.
5. Auxiliary reagents. Depending on the type of rock and the method of separation of insoluble residue from dissolution liquor minor quantities of filter aids or flocculating agents may be required.

Dissolution and Mechanical Separation of Insoluble Residue

The dissolution of phosphate rock is essentially decomposition of fluorapatite by HCl according to the equation:



Other acid-soluble components of the rock, such as $CaCO_3$, decompose simultaneously.

The rock is dissolved by hydrochloric acid. The insoluble residue amounts to a small percentage of the rock feed and consists mainly of silica, silicates, insoluble organic matter, etc. The insoluble matter can be separated from the dissolution liquor by filtration, followed by washing of the cake or by sedimentation in a thickener, followed by countercurrent decantation washing of the sediment. The choice of the proper method of separating solids depends on the character of the insoluble residue and on economic considerations. The dissolution liquor is fed to the subsequent section.

Figure 22 shows a typical flowsheet of the process.

Liquid-Liquid Contacting

This stage consists of a number of operations; extraction, purification, washing, and stripping.

Extraction--This is performed by a countercurrent contact of dissolution liquor with the selected solvent. Phosphoric acid transfers selectively from the aqueous dissolution liquor to the organic solvent phase, giving the extract and a calcium-chloride brine (raffinate) containing substantially all the impurities, such as fluorine and iron.

Purification--The solvent extract, which contains small amounts of Ca^{++} and some other impurities, is purified further by countercurrent contact with an aqueous phase.

Washing--The acid of the purified extract is transferred into water. The solvent leaving this stage is virtually free of acid.

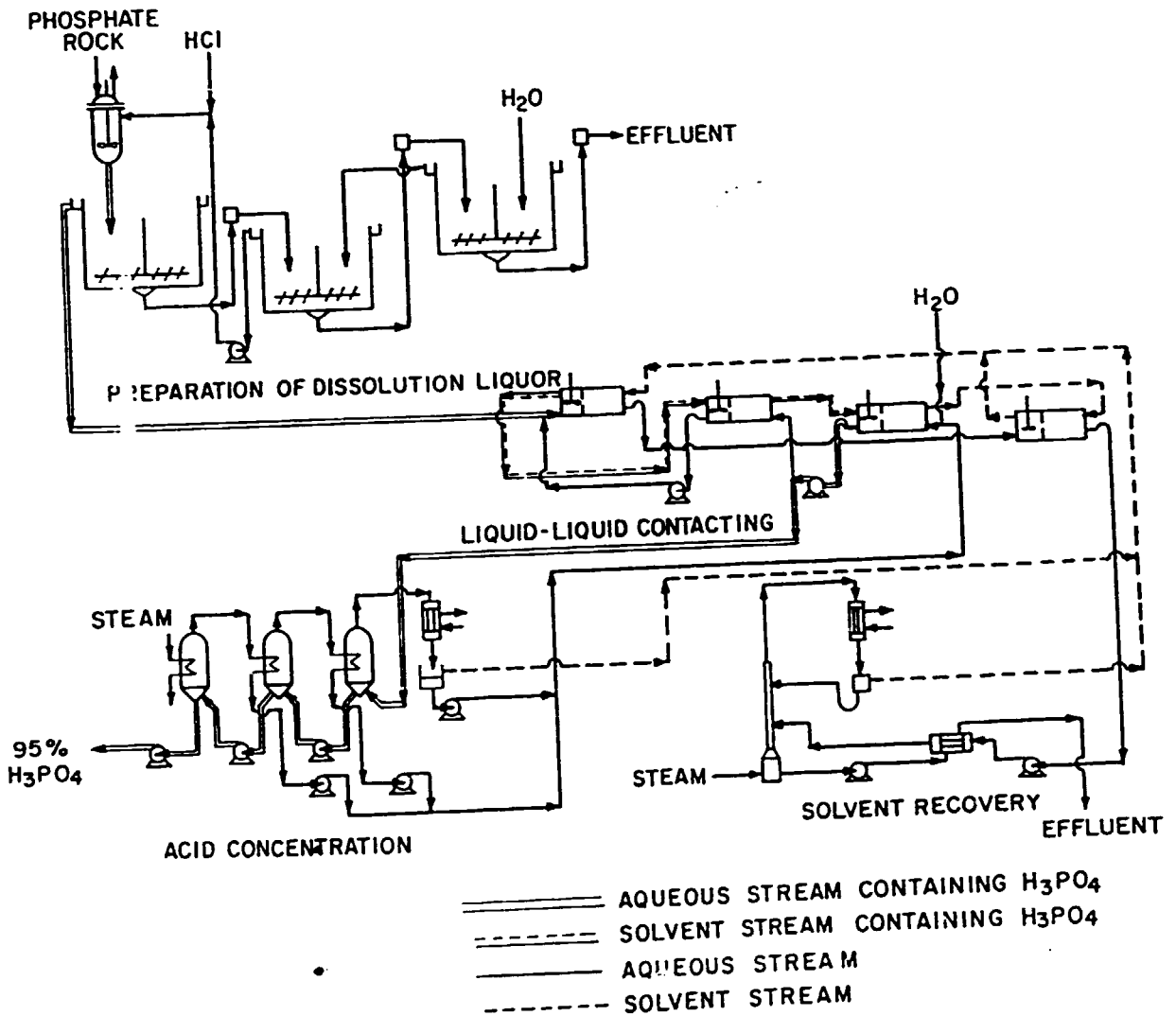


Figure 22 Typical Flowsheet of the IMI Phosphoric Acid Process (HCl-route).

Stripping--The acid-free solvent stream extracts the residual acids present in the raffinate and is recycled to extraction. The spent calcium-chloride brine is stripped by steam to recover any dissolved solvent.

Acid Concentration

The dilute aqueous acids emerging from washing consist of an aqueous solution of H₃PO₄, HCl, and some dissolved solvent. This solution is concentrated to 95% H₃PO₄, which is the end product. The separation of H₃PO₄ from other components of the solution is essentially a distillation operation; this permits a full recovery of the minor quantity of solvent that is dissolved in the aqueous phase on washing and of the HCl both maintained in closed cycle in the process.

The main requirement of this operation is heat economy, and a multiple-effect evaporator is used to achieve this. The amount of steam used is less than 0.5 ton/ton of water evaporated. The complete absence of dissolved solids in the solution being concentrated permits maintenance of high heat-transfer coefficients. All the volatile streams from the system are recycled to the previous steps of the process.

Solvent Recovery From Spent Calcium Chloride Brine

The residual brine leaving the stripping stage contains a small amount of dissolved solvent, which has to be recovered for economic reasons. The solvents used form an azeotrope with water on rectification so that the simplest system to be applied is steam stripping. The costs of this operation are reduced by the recovery of heat from the brine leaving the system. The recovered solvent is recycled to the liquid-liquid contacting section, and the brine is discarded.

Construction Materials

The process requires the use of acid-resistant construction materials that are solvent resistant, as well, in those parts of the process where solvent is present (i.e. the liquid-liquid contacting section and a part of the sections where acid is concentrated and where solvent is recovered from the brine).

For the dissolution and mechanical separation of insoluble residue, rubber-lined steel is the least expensive material. In the liquid-liquid contacting section, rigid polyvinyl chloride (PVC) is very satisfactory. In the parts of the system operating at elevated temperatures, impervious graphite can be used for the heat exchangers. Other construction materials include thermosetting resins and lined steel.

Quality of HCl-Route Phosphoric Acid

HCl-route phosphoric acid is much purer than wet-process acid, and its analysis is similar to that of thermal acid (table 11). By slight adjustments in the process, food-grade acid can be obtained. The composition of wet-process acid is dependent on the rock as raw material; whereas, almost the opposite is true for HCl-route phosphoric acid.

TABLE 11 COMPARISON OF ANALYSIS OF HCl-ROUTE
PHOSPHORIC ACID AND WET-PROCESS ACID

<u>Component</u>	<u>HCl-Route Phosphoric Acid (%)</u>	<u>Wet-Process Acid (%)</u>
H ₃ PO ₄	95	69-77
P ₂ O ₅	69	50-56
Heavy metals ^a	0.002-0.01	0.5-1.5
CaO	0.008-0.04	0.014-0.35
Fe ₂ O ₃	0.003-0.05	0.86-2.30
Al ₂ O ₃	Traces	0.3-2.45
Mg	Traces	0.0-0.8
H ₂ SO ₄	Traces	1.0-5.6
SiO ₂	Traces	0.04-0.10
F	Traces	0.25-1.10

a. Calculated as Pb.

Capital Investment

The capital investment required for a plant may vary from location to location. However for comparative purposes it will be noted that the capital cost for the HCl process is about 35% higher than for the standard (H₂SO₄) wet process when production of the acid (HCl or H₂SO₄) is excluded.

If HCl were available as a by-product from another process, the capital cost would be lower than for a wet-process plant including H₂SO₄ production facilities. However, when using byproduct, HCl from another process, the capital cost would be lower than for a wet-process plant including H₂SO₄ production facilities. However, when using byproduct HCl, the scale of the operation would be limited by the amount of byproduct HCl available.

Process Requirements

Operating cost may be estimated from the process requirements which are given in table 12 for a plant of 100-tpd capacity:

Table-12 Process requirements for estimating production costs per ton P₂O₅ in a plant with a capacity of 100 tons per day:

<u>Item</u>	<u>Requirement</u>
<u>Raw Materials</u>	
Phosphate rock 34% P ₂ O ₅	3 tons
HCl (calculated as 100%)	2 tons
<u>Requirement for Variable Costs</u>	
Solvent (isoamyl alcohol) makeup	4 kg
Steam	4.3 tons
Power	100 kwh
Cooling water (25°C)	165 m ³
Process water	3 m ³
Total variable costs	
<u>Requirement for Fixed Costs</u>	
Labour: 4 men/shift (including shift supervisor) 4 shifts/day	
Overhead: 100% of labor.	
Maintenance: 5% of fixed capital investment (FCI)	
Depreciation: 6.7% of FCI	
Insurance and taxes: 1.3% of FCI	

In addition to the process requirements given in table-12 the expense of disposal of the byproduct calcium chloride brine must be considered. If the plant is located adjacent to the sea, disposal in the sea may be acceptable and economical; for an inland location disposal may be difficult and expensive.

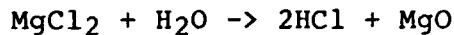
HCl-route phosphoric acid has certain disadvantages as compared with wet-process acid. Its production is economic only in places where HCl is available or where it can be produced at a moderate price. Transport of HCl in the form of an aqueous solution of perhaps 33% HCl is possible only in pipes or railcars lined with rubber, PVC, or similar materials.

However, HCl-route phosphoric acid has some advantages over wet-process acid. Unlike wet-process acid, it contains no scale-forming components, and its composition and quality are practically independent of the type of phosphate rock used. Superphosphoric acid (70%-72% P₂O₅) can easily be produced from HCl-route phosphoric acid.

Wet-process acid would be suitable for the manufacture of tripple superphosphate of about 44%-46% P₂O₅ and of diammonium phosphate with a grade of 18-46-0. Diammonium phosphate (21-53-0) can be manufactured directly from HCl-route phosphoric acid owing to its high concentration and purity.

HCl can be used where it is available as a byproduct. This is important for developing countries producing NaOH, where there is no captive market for the chlorine that is produced simultaneously. Byproduct hydrochloric acid is sometimes available from other sources and may even create disposal problems. In such cases the production of phosphoric acid by the acidulation of phosphate rock with hydrochloric acid can be advantageous if the quantity of the byproduct is adequate for an economical scale of operation and disposal of or utilization of the calcium chloride brine is economically feasible.

An interesting possible source of hydrochloric acid is through calcination and hydrolysis of magnesium chloride according to the equation:



This possibility is under study in Israel using magnesium chloride from the Dead Sea. The magnesium oxide could be useful for production of refractories.

Another possible source of hydrochloric acid is from the production of potassium phosphate from phosphoric acid and potassium chloride (see chapter XVI).

At present the only plants using the HCl process are relatively small ones, and most of the product is used to make industrial phosphates rather than fertilizers.

Phosphoric Acid Production by the Electric Furnace Process

The first step in the production of furnace acid is to produce elemental phosphorus in an electric furnace (see figure 23). Phosphate nodules or other lump phosphate material, silica pebble, and coke are mixed and fed to the furnace. The electric current which enters the furnace through carbon or graphite electrodes fuses the rock and silica, and the carbon in the coke reduces the phosphate. A mixture of phosphorus vapor and carbon monoxide gas is withdrawn continuously from the furnace.

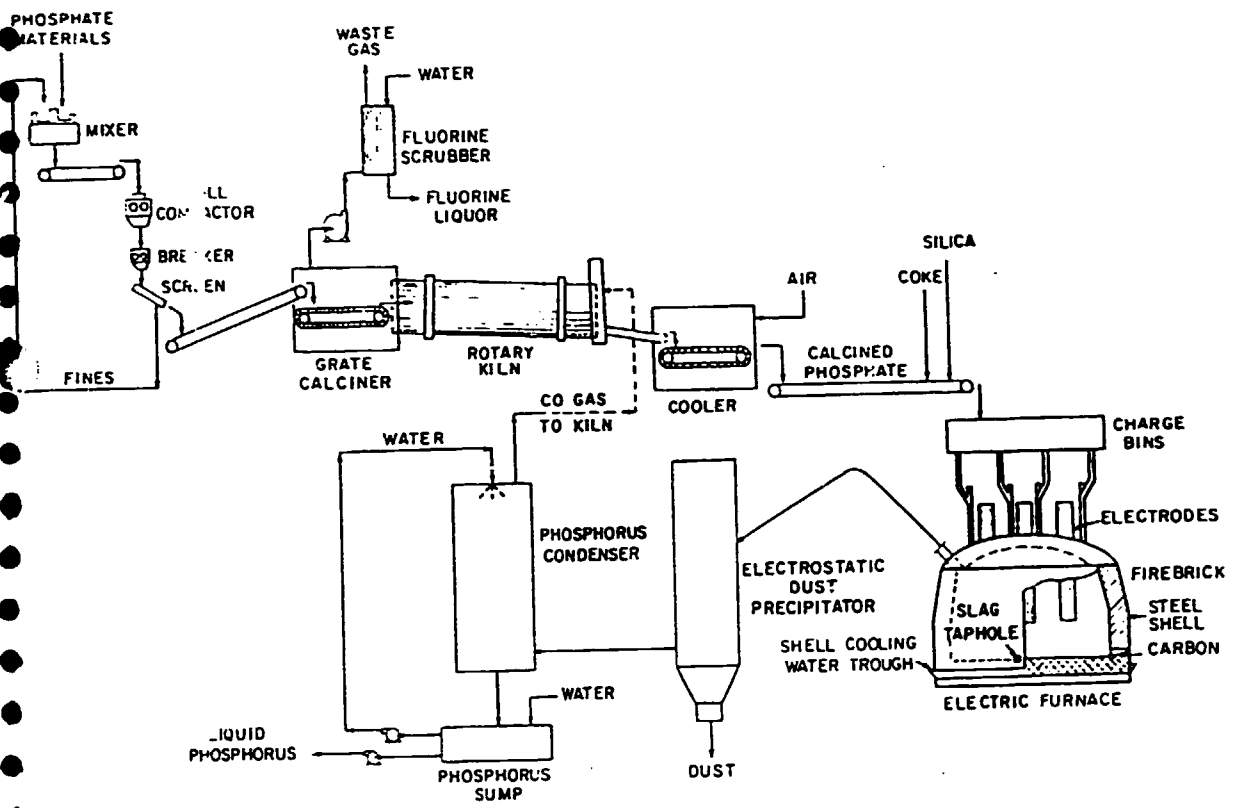


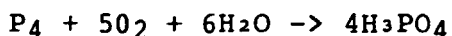
Figure 23 Manufacture of Elemental Phosphorus.

instance, 1 ton of elemental phosphorus is equivalent to the phosphorus content of 5 tons of TSP or DAP or 7 tons of high-grade phosphate rock.

Another advantage of the furnace process is its ability to produce high-grade products. Superphosphoric acid (76%-80% P₂O₅) may be made without extra cost and, from it, ammonium polyphosphate (15-60-0), high-analysis superphosphate (54% P₂O₅), or high analysis liquid fertilizer (11-37-0). Diammonium phosphate made from furnace acid has an analysis of 21-53-0 compared with 18-46-0 for the wet-process product.

The main drawbacks of the furnace process are the relatively high capital cost of the plant and the scarcity of locations where low-cost electricity is available. For this reason the electric furnace process is used almost exclusively to produce phosphorus and phosphoric acid for industrial chemicals, insecticides, detergents, and food or animal feed additives.

Production of phosphoric acid from elemental phosphorus is relatively simple. It is carried out by burning liquid elemental phosphorus in air and hydrating the resulting P₂O₅ to H₃PO₄. A diagram of a typical plant is shown in figure 24. All process equipment is made of stainless steel, usually type 316. The overall reaction is:



Typical process requirements per ton of P₂O₅ recovered as phosphoric acid assuming 86% overall recovery for a plant of about 100,000 tons P₂O₅/year capacity are:

- | | | |
|-----|--|--------------------------------|
| 1. | Phosphate rock, 31.2% P ₂ O ₅
(or equivalent amounts of rock of
other grade) | 3.73 tons |
| 2. | Silica rock or pebble, 95% SiO ₂ dry
(Less silica is needed if the
phosphate rock is high in silica). | 1.1 tons |
| 3. | Coke, screened & dried, 86% fixed carbon | 0.6 tons |
| 4. | Carbon or graphite electrodes | 25 kg |
| 5. | Electricity | 6,700 kwh |
| 6. | Cooling water (once through basis) | 110 tons |
| 7. | Steam | 1 ton |
| 8. | Operating labor | 4 man-hours |
| 9. | Maintenance (labor & materials) | 10% of plant cost
per year. |
| 10. | Fuel, negligible to 1.2 million kcal
depending on efficiency of use of
byproduct carbon monoxide gas. | |

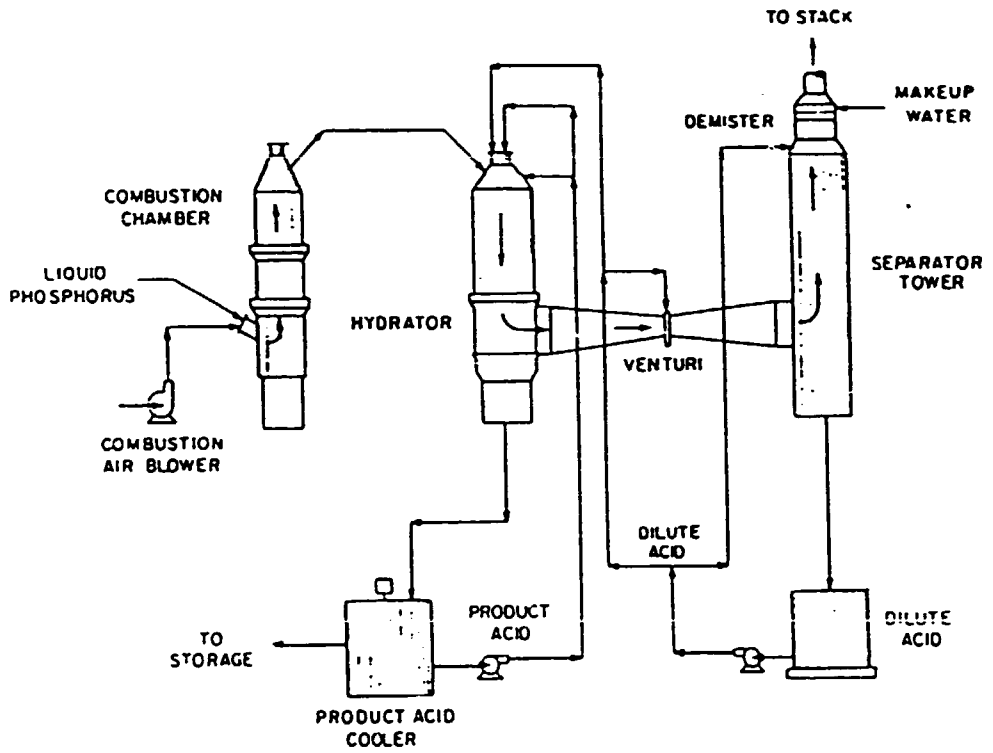


Figure 24 Manufacture of Phosphoric Acid from Elemental Phosphorus.

Some rocks that have been used successfully in electric furnaces without agglomeration, calcining, or sintering are screened Florida pebble (plus 6 mm), Florida hard rock, and Montana hard rock (crushed and screened). Use of uncalcined rock may increase the electric power consumption in the furnace by as much as 10%, depending on the CO₂ and combined water content.

The Tennessee Valley Authority (TVA) began development of the electric-furnace process for producing phosphate fertilizers in 1933 and produced phosphorus and phosphoric acid from 1934 to 1977. At one time five furnaces were in operation. In 1977 operation of all furnaces was discontinued by TVA since the process could no longer compete with the wet process for fertilizer production. Numerous publications are available from TVA on production of elemental phosphorus and phosphoric acid by the electric-furnace process; selected references are included at the end of this chapter (11, 12, 13, 14, 15, 16 & 17)

PHOSPHORIC ACID PRODUCTION BY THE BLAST-FURNACE PROCESS

A flow diagram of a TVA pilot plant for producing phosphoric acid by the blast-furnace process is shown in figure 25. The scale of the pilot plant was about 1 ton of P₂O₅/24 hours (18).

In general, the blast-furnace process differs from the electric furnace in the following respects:

1. Coke is used for both fuel and phosphorus reduction. The estimated coke requirement for large-scale unit is 2.5 tons/ton of P₂O₅ recovered as phosphoric acid (allowing for ferrophosphorus losses). About 0.6 ton of coke is consumed in reduction of P₂O₅ to phosphorus, and the remainder generates heat by combustion with pre-heated air to form carbon monoxide.
2. As with the electric furnace, the charge--phosphate rock, coke and silica--must be in lump or agglomerated form but it is not necessary to calcine or dry the charge since there is sufficient heat in the ascending gases in the furnace shaft for this purpose.
3. The gas from the furnace contains about 37% CO and 1.0%-1.5% P₄ by volume. The remainder is mainly nitrogen. Although recovery of elemental phosphorus by cooling and condensation is feasible, it would be difficult to recover a high percentage because of the low concentration in the gas. In the TVA pilot plant, phosphoric acid was recovered after preferential oxidation of the phosphorus in the gas with air.

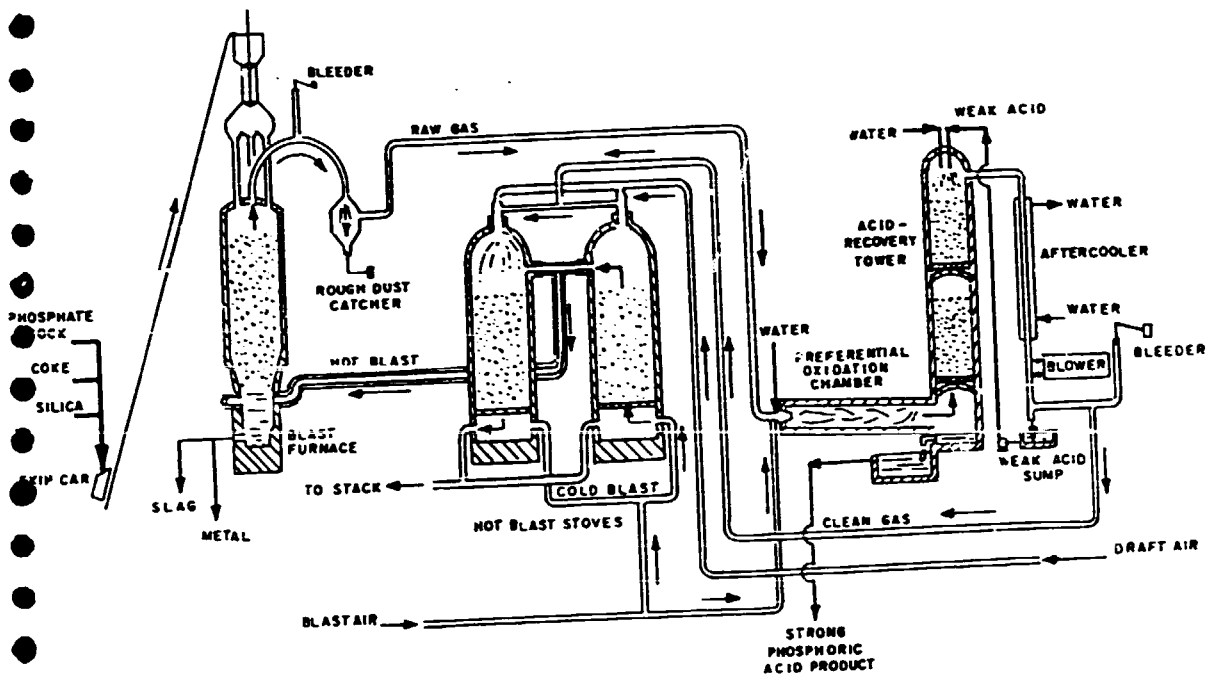


Figure 25 TVA Experimental Phosphate Blast-Furnace Plant.

4. The gas remaining after phosphoric acid recovery contains about 34% CO, 1%-2% O₂, and the remainder N₂ (dry basis). About 40% of this gas can be used advantageously for preheating the air to the blast furnace. The remainder would be available for other uses.

The blast-furnace process was used commercially to produce phosphoric acid for industrial and chemical products from 1929 to 1938 by the Victor Chemical Works, now Stauffer Chemical Company. The plant was located at Nashville, Tennessee (United States).

The use of the blast furnace to produce phosphoric acid for fertilizer purposes seems unpromising at present due to the high cost of coke. However, with some improvements it might be considered in certain circumstances 19. As does the electric furnace it can utilize low-grade siliceous ore with moderately high alumina and iron oxide content.

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