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REVIEW PAPER

Process Technology for Phosphoric Acid Production in Saudi Arabia

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Abstract. The development of phosphate fertilizer and the phosphoric acid industries are expected in Saudi Arabia in the near future. The article presents an overview of different process technologies that may be used for phosphoric acid production. Potentialities as well as limitations of conventional and non-conventional techniques are presented to constitute the basis for the process evaluation and selection.

Process Technology of Phosphoric Acid

There are two main commercial processes to produce phosphoric acid: the wet process and the dry [1] (electrical furnace) process. Although, the acid produced (technical grade) with the dry process is pure, its production cost is much higher than that of the wet process phosphoric acid (WPPA or fertilizer grade acid). The capacity use of dry process industry fell to 50 percent from 1970 through 1981 due to the ban of detergent phosphates (sodium polyphosphates) which are produced with technical grade acid. New uses found for technical grade acid (*e.g.* metal surface treatment, phosphorus use in insecticidees, lube oil and polymer additives) helped to increase the use of dry process production in the last decade. However, it seems that solvent extraction of fertilizer grade acid will be more economical than the production of phosphoric acid by the furnace process. In countries where power costs are higher (*e.g.* Japan and Europe) solvent extraction plants have been operating to upgrade fertilizer grade phosphoric acid for sodium tripoly phosphate, production since 1978 [2].

It seems that the use of the electrical furnace process will be limited to the production of phosphoric acid for use in food and pharmaceutical industries. Production capacity of the wet process will still increase in addition to the capacity which already exceeds that of the furnace process.

Wet processes

In these processes, phosphoric acid can be obtained by digesting phosphate rock in mineral acids such as nitric, hydrochloric, phosphoric, or sulfuric. The use of sulfuric acid is the conventional technique and is normally reffered to as "wet process". In this process, calcium sulfate is precipitated as a by-product. Depending on the temperature, as well as P_2O_5 and SO_4 content of the solution, either calcium sulfate dihydrate (DH), hemihydrate (HH) or anhydrite (AH) will be formed as shown in Fig. 1.

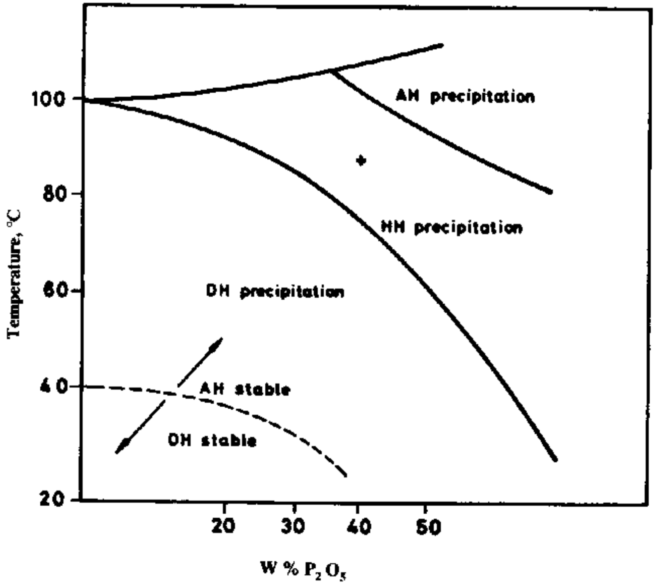

Fig. 1. Regions indicating dihydrate DH, hemihydrate HH, and anhydrate AH gypsum. Regions are defined by temperature and the P_2O_5 content of the phosphoric acid solution [3,4]

Until the early 1970's the dihydrate process (DH) was almost the only process to produce WPPA. After 1973, the increase in energy prices stimulated the use of hemihydrate (HH), hemihydrate dihydrate (HH/DH) [3,4], hemihydrate recrystallization (HRC) and dihydrate/hemihydrate (DH/HH) processes [5,6].

Dihydrate processes are still the most popular ones because they are simple to operate and have been proven many times to be adaptable to various types of phosphate rocks; therefore, they are considered to be reliable [3-8]. Hemihydrate processes [9-20] can produce phosphoric acid in high concentration; therefore, in many cases the concentration step can be eliminated, which means lower capital cost and lower usage of steam and process water. In many cases, less sulphuric acid and power are required and less aluminum and sludge are found in the product acid. The main disadvantages are the higher reaction temperature which stimulates corrosion and low P_2O_5 yield and higher phosphate rock requirement, and enhanced foaming. The hemihydrate recrystallization process eliminates the disadvantages of the low P_2O_5 yield and produced high purity gypsum but is more complex than the hemihydrate process and the SO_3 content of the product is high.

Hemihydrate/Dihydrate processes also produce phosphoric acid with a high concentration and have the added advantage of high P_2O_5 yield. Therefore, lower capital investment and lower operation cost with savings in concentration storage and clarification are possible [21-24]. In addition, the gypsum produced is free of impurities. The main disadvantages are the corrosiveness due to high temperature in the reactors and the complexity of the process which puts a burden on the operating personnel.

The Dihydrate/Hemihydrate process has almost the same advantages and disadvantages as Hemihdyrate/Dihydrate process except that the reaction temperature is lower and a hemihydrate by-product is produced which may be advantageous when the other sources of gypsum are in short supply.

Generally, in the last two decades the main concern in the wet process phosphoric acid production has been the energy cost. Although, the energy consumption per kg of P_2O_5 produced is not very high, because of the large production rates, the total energy cost is high. The highest energy consuming section in the process is grinding; therefore, processes which can handle coarser rock feeds (*e.g.* hemihydrate and hemidydrate/dihydrate processes) have gained importance. Grinding efficiency can be increased by using wet grinding [6] (with savings of 30-40 percent in power). Another way to save energy is to integrate the steam production units with the sulfuric acid plants. [25].

The important features of each process are listed in Table 1. Additional information which could not be included in this table is given below:

a) Water is needed to cool the reactors, and the evaporator condensers to supply the water of hydration for gypsum and to dissolve phosphoric acid. The amount of water needed in a process is determined by the concentration of the acid, the

Table 1. Comparison of wet process for phosphoric acid production [3-6].

Important factors	DH process	HH process	HRC process	DH/HH process	HH/DH process
Phosphate rock processed	40% 100 Mesh	Dry, 100% 1mm	Dry, Finer than DH	Dry. 100% 0.5 mm	Dry. 100 % 1 mm.
Cake efficiency	95-97 %	90-94% (c)	98-99%	99%	98-99%
Other losses	0.5-1%	1-3%	0.5-1%	0.5-1%	0.5-1%
P_2O_5 recovery	93.5-96.5%	88-93%	95-97%	98-98.5%	98%
H_2SO_4 Used/ton P_2O_5 produced	2.5-3 ton	3-3.5 ton	2.5-3 ton	2.3-2.7 ton	2.4-2.8 ton
Use of dilute H_2SO_4	Yes	90-95% H_2SO_4	60% H_2SO_4	70-80% H_2SO_4	Yes
Water consumption (a)	5-6 tons/ton P_2O_5 in the filter	Low	Slightly higher than DH	Less than DH	Higher than DH
Electrical power cons.	Grinding + Air cooling	Low	Higher than DH	Much lower than DH	Higher than DH
Steam used vs acid strength(b)	High	Lowest	Less than DH	Less than DH	Low
High grade alloys required	316L and 317L	Corrosive	Corrosive	Corrosive	Corrosive
Reaction temp., °C	70-85	85-100	85-100	65-70	90-100
Recrystallization temp., °C	–	-	50-60	90-100	50-65
On line factor, days/year	315-325	315-320	310-320	310-320	305-315
Ease of operation (c)	Easy	Needs care in filtration	Easy	Crystalization acid may be needed	Needs control
Solids content in product	1-4%	0.5%	Lower than DH	0.5-3%	0.5%
Quality of product (d)	See text	1.5% SO_3, 40-48% P_2O_5	High SO_3, 40-45% P_2O_5	Low SO_3, Low Organics 35-38% P_2O_5	1.5% SO_3, 40-45% P_2O_5
Gypsum quality	low quality	Impure	Pure	Pure	Pure

type of $CaSO_4$ obtained (HH or DH) and the moisture content of the phosphate rock.

b) Steam consumption is high when evaporation is needed. Concentration from 30 to 54 percent P_2O_5 requires about 1.9 tons of steam; concentration from 54 to 70 percent needs about one ton of high pressure steam per ton of P_2O_5 processed. Concentrated acid is not always needed, but when there is no low cost steam source and the fuel cost is high, then a high strength acid (*i.e.* HH/DH) process is advantageous.

c) The ease of operation will depend on the familiarity of the plant personnel with the behaviour of the phosphate rock. If the phosphate source is changed too often it will be difficult to reach optimum operation in a short time. This factor is closely related to the on-line factor which is a measure of how often the process is interrupted by a malfunction of any of the equipment (*e.g.* excessive scaling on the filters or evaporators, problems associated with sludge transportation, difficulties in crystallizer control, etc.) or lack of access to spare parts (*e.g.* rubber lining, or high-grade construction material).

d) The quality of the product is strongly influenced by the impurities in the phosphate rock. However, analysis of phosphoric acid obtained in the DH process can be taken as a basis for comparison: (Percent by wt) P_2O_5 : 50-55 (before evaporation 28-30% P_2O_5), SO_3: 2.5-3, F:O.3-1, A_2O_3 : 0.1-1.7, Fe_2O_3 : 0.3-1.5, MgO : 0.2-0.7; Total sludge: 20-150 kg/metric tons.

e) The scaling effect on the filter in the HH process causes serious problems with many types of rocks. It is not due to hydration of the hemihydrate but to the formation of fluosilicate scale in the strong wash filtrate section. Steam injection is usually a helpful remedy. However, there are chemicals [26] which can given successful results.

Nonconventional acidulation processes

As mentioned above, the basic objective of any acidulation process is to obtain the highest concentration of phosphoric acid possible with the maximum yield. In addition, this should be done economically and in an environmentally sound manner. In this regard, several techniques have been examined by different researchers as potential substitutes for the conventional wet process (using sulfuric acid). The proposed processes are described below.

Davison clinker process [27, pp. 387-394]

In this process, phosphate rock is acidulated with a strong sulfuric acid. The reaction products are heated to give a clinker-like material which can be leached to give highly concentrated phosphoric acid. This process was proposed to eliminate filtration and evaporation steps in the wet process. However, the difficulties in clinker extraction (due to low porosity) and solids heating have to be overcome so that this process can be a candidate for commercialization.

Fuming sulfuric acid process

In an attempt to avoid heating the acidulated mixture, TVA researchers [28, pp. 395-404] used fuming sulfuric acid (oleum) for acidulation which led to a relatively high temperature 232°C. The overall chemistry of this process is presumed to be essentially the same as in the clinker process.

This process has not been tested on a larger scale. In addition, SO_3 recovery needs to be determined. Most importantly, the sensitivity of this process to the grade of phosphate rock and the acid stoichiometry seems to be the main disadvantages. These two parameters need to be studied further before any commercial consideration of this process.

The foam process

This is a hemihydrate process by which phosphoric acid with more than 40% P_2O_5 concentration can be obtained in a short retention time (less than one hour). It was developed in the laboratories and pilot plants of the Tennessee Valley Authority (TVA) [29, pp. 369-382]. The published data indicates that control of sulfate concentration in the reactor is not critical for good filtration. In addition, gentle agitation is sufficient and recirculation of the slurry is not required.

The process uses a layer of foam on the slurry in the reactor. This layer is the key to the formation of large, washable agglomerates of hemihydrate. A flow diagram of this process is shown in Fig. 2.

The phosphate rock, mixed with a weaker recycle acid is fed underneath the foam layer and an antifoam agent is used to control the thickness of the foam. Best filtration results are obtained by feeding sulfuric acid at the top of the layer. Gentle stirring is a key factor in the performance of this process. Another important parameter is the feed rate. Higher feed rates cause vigorous boiling which lead to transfer of the phosphate particles into the foam layer (high sulfate concentration) where calcium sulfate coats the rock leading to decreased rock conversion.

Pilot plant testing of this process has confirmed the bench-scale results as shown in Table 2 and 3.

As shown in Table 3 the extraction of P_2O_5 from the rock was significantly lower when the feed-rate was increased. This was attributed to the boiling in the reactor. The overall conclusions from these tests show that the foam process could be prom-

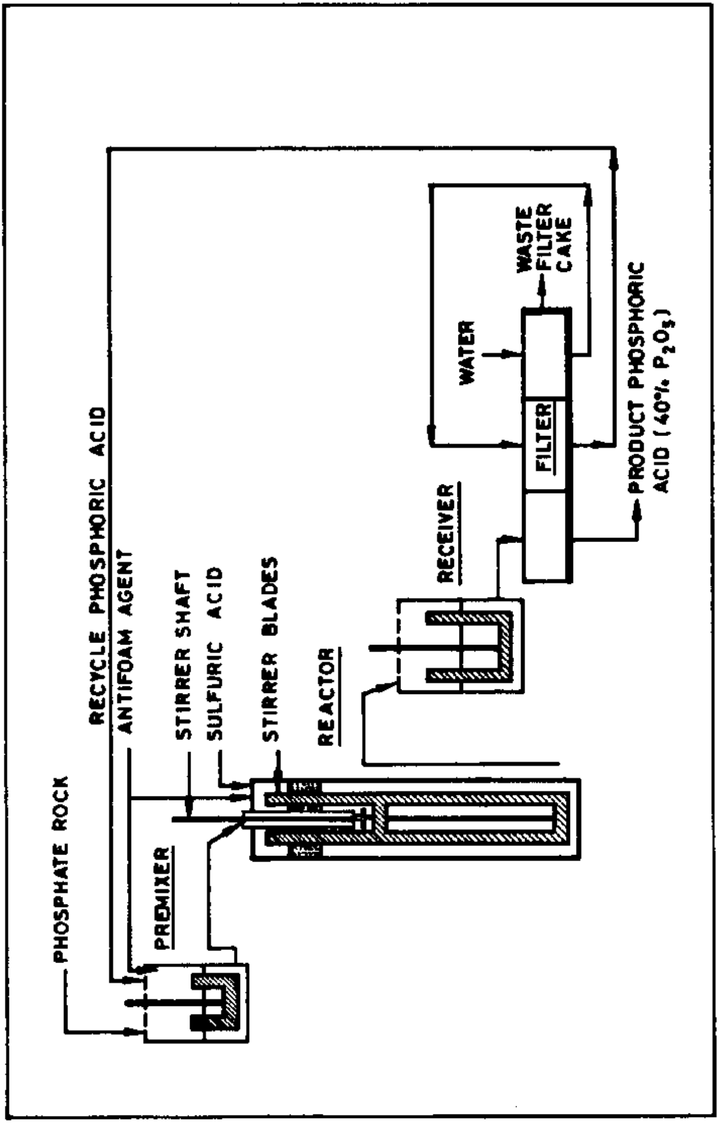

Fig. 2. Schematic diagram of foam process [31].

Table 2. Operating conditions and results obtained in the foam process pilot plant [29]

Florida phosphate rock, P_2O_5 content %	30.5 – 33.5
Sulfuric acid, %	93
Feed rate, phosphate rock, kg/hr	227 – 318
Recycle phosphoric acid, kg/kg rock	1.5 – 2.2
Antifoam agent (sulfonated oleic acid), kg/ton rock	0.9 – 2.2
Feed-flux, kg rock/hr-m^2	342 489
Retention time in premixer, min	5 – 10
Retention time in reactor, hr	1.5
From layer thicknessm cm	12.7 – 76.2
Depth of distributor plate below foam-slurry interface, cm.	5.1 – 30.5
Wash water, kg/kg rock Temperature, °C	0.8
Premixer Reactor	46 – 57
Foam-slurry interface	107 – 115
Slurry	102 115
Slurry to filter	93 – 99
Peripheral speed of agitator, m/min product acid analysis, %	30.5
SO_3	0.2 – 1.5
P_2O_5	40
CaO	0.5
F	1.5
Al_2O_5	0.8
Fe_2O_5	1.6
Filtering rate, m^3/hr-m^2	4.07 – 7.74
Filtering rate, kg product P_2O_5/hr-m^2	244 – 489
P_2O_5 distribution, % of total fed	
Product acid	93
Water soluble in cake	3
Lattice-bound in cake	2
Unreacted rock in cake	2

Table 3. Effect of feed-flux[a] on extraction of P_2O_5 from rock [29]

Feed-flux kg rock/hr-m^2	Rock feed rate, kg/hr[a]	water-soluble P_2O_5 extracted from rock, %
342	227	96
416	272	92
489	318	92

a. Rock-feed rate per unit of cross-sectional area of reactor kg/hr-m^2

ising for production of high concentration phosphoric acid. However, further investigations are needed to alleviate the existing problems of limiting feed-rate, sensitivity to the point of sulfuric acid addition, foam control, and increasing P_2O_5 recovery.

Acidulation with phosphoric acid

There is a growing concern about the influence of heavy metals on human health. Phosphoric acid produced by conventional methods contains cadmium. The use of phosphogypsum is limited in Europe because of its impurity content, especially cadmium. Studies initiated and sponsored by some European governments are aimed at looking for new processes to produce clean phosphogypsum and clean phosphoric acid.

Acidulation with phorphoric acid is claimed to be one of the most promising methods, where the phosphate rock is digested in an aqueous solution containing 40 percent P_2O_5 and 1.8 percent H_2SO_4. After the separation of the insoluble ore residue and minor amount of calcium sulphate hemihydrate, calcium-di-dydrogen-phosphate (CDHP) solution is obtained. From this solution Cd^{++} ion can be separated by ion exchange. Calcium ions are removed by adding concentrated sulphuric acid to the CDHP solution at 90°C to obtain clean phosphoric acid and clean calcium sulphate hemihydrate [30,31].

If phosphate ore is digested by phosphoric acid, the following reactions take place [26]:

$$Ca_{10}(PO_4)_6F_2 + 4H_3PO_4 \longrightarrow 10CaHPO_4 + 2HF \longrightarrow$$

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF \longrightarrow$$

Temperature and concentration of phosphoric acid are important parameters which can determine the amount of dissolution as well as type of products.

If sulfate ions are present, then calcium sulfate will precipitate. Higher concentrations of sulfate should be avoided, otherwise calcium sulfate would coat the ore particles leading to reduction in P_2O_5 recovery. S.V. Sluis *et al.* [31] conducted a study to investigate the effect of such parameters as temperature, phosphoric acid concentration and ore particle sizes. Based on the laboratory data a kinetic model was developed to describe the digestion step. The results indicated that digestion can be completed in one hour to give a concentrated acid at 60-90°C. However, it seems that this process is sensitive to the presence of impurities such as sulfate and carbonate ions. Also, based on the authors' experience with similar systems, filtration rates of product acid from solids present in the feed ore (*e.g.* silica) can be very slow which may render this process impractical in such cases.

Acid/Alcohol leaching process [32,33]

Direct acidulation of unbeneficiated phosphate ores may have the benefits of higher recoveries due to elimination of losses during the beneficiation steps. However, dissolution of impurities such as aluminum, iron and magnesium could be a problem in these cases. In addition, filtration of leach liquor from solid residues could be a difficult operation. To overcome these problems, a method has been developed [32] and is being investigated further by U.S. Bureau of Mines [33] in which acid-alcohol mixtures are used as the leaching agent. In this technique, a phosphate matrix is slurried with a mixture of sulfuric acid and methyl alcohol and leached at 65°C for 1 hour [33]. Iron and aluminum impurities are not very soluble in this mixture. After leaching, the slurry is filtered to separate the residue from the leach solution, which contains the desired phosphoric acid. The residue has been found to filter more readily than the slurry resulting from a leach using only sufluric acid. The methyl alcohol contained in the leach solution is subsequently recovered by vacuum distillation for reuse in the leaching step. In laboratory experiments [33], phosphate extractions as high as 88 percent have been achieved. The leach slurry can be filtered using conventional equipment, with filter rates of greater than 200 kg/h per square foot of filter surface area being obtained. Iron and aluminum impurities also have been held to within tolerable limits. Studies of the effect of such parameters as temperature, alcohol-to-acid ratio, and particle size on phosphate extraction are continuing. A small-scale continuous unit is being designed to obtain engineering data required for the design of a full-scale plant.

It should be mentioned that in the patented process [32] low recoveries (up to 63%) were obtained. This could be the reason for the hesitation of phosphate producer to adopt this technique commercially. In addition, the solid-liquid separation step could constitute the difficulty in scaling up this process. On the other hand, the available data from Bureau of Mines [33] work indicate higher recoveries (88%) and good filtration rates. Thus, on the bases of the data to be generated in the continuous unit, a phosphate producer may decide to have another look at this technique.

Acidulation with hydrochloric acid [34-43]

The Israel Mining Industries (IMI) has pioneered the development of the hydrochloric acid process [34-38]. In this process, phosphate rock is leached with hydrochloric acid and the resulting phosphoric acid is extracted from the clarified leach liquor by contacting with an immiscible organic solvent:

$$Ca_{10}(PO_4)_6F_2 + 20HCl \rightarrow 10CaCl_2 + 6H_3PO_4 + 2HF$$

$$(H_3PO_4)_{aq} + \underset{\substack{\text{Solvent} \\ \text{(Alcohol)}}}{ROH} \rightarrow (H_3PO_4)\ \text{(dissolved in solvent)}$$

Dissolution of phosphate rock in hydrochloric acid is rapid. The concentration of P_2O_5 and $CaCl_2$ in the leach liquor are a function of the rock grade, the HCl concentration, and the water balance in the system [34].

Phosphoric acid is separated from the leach liquor by solvent extraction. The solvents used are C_4 and C_5 alcohols. Recently, it has been proven that tributylphosphate (TBP) is an effective solvent too [41-44]. It should be mentioned that the presence of $CaCl_2$ in solution is essential for the extraction process. The concentrated organic phase is stripped by water to obtain pure H_3PO_4 solution which is evaporated to the desired concentration. The stripped solvent can be reused. The brine solution containing $CaCl_2$ is treated to recover the dissolved organic solvent and then $CaCl_2$. This process has the advantage of producing high purity phosphoric acid as well as higher recoveries of P_2O_5 from low grade and unground rocks. However, one should pay attention to several technical and economical aspects such as: **a)** availability and cost of HCl; **b)** cost of solvent and solvent recovery; **c)** material of construction type and cost; **d)** environmental problems related to disposal of HCl containing waste; and **e)** water balance especially when treating low grade ores.

Purifying wet-process phosphoric acid

Depending on the phosphate rock, wet process phosphoric acid may contain a variety of impurities including calcium, magnesium, sulfate, iron, aluminum, fluorine, heavy metals such as arsenic, lead and mercury, other trace metals, and organics. Many different techniques have been investigated for removal of all or some of these impurities [43-64]. These techniques include ion exchange resins [50;51, pp 100-103], crystallization [52], and solvent extraction [44-48, 53-61]. The latter has been most widely employed and forms the basis of the majority of commercially operated purification units.

There are several factors that should be considered before choosing the required solvent. This may include: **a)** higher extraction efficiency and high selectivity towards phosphoric acid; **b)** ease in separating the two phases (organic phase and the raffinate) as well as recovering pure acid from the organic phase; **c)** efficiency of reclaiming solvent from different streams; **d)** cost, availability and stability of the solvent. Table 4 presents a list of solvents tested or used for the extraction of phospohric acid [44].

Even though solvents of type B are much cheaper than type A, they are considered to have several disadvantages including the need for more washing which leads

Table 4. Solvents tested or used for extraction of phosphoric acid [44]

A.	Nonmixable with water (low solubility)
	Di-isopropyl ether
	Tributyl phosphate
	Methyl-isobutyl ketone
B.	Highly mixable with water
	n-butanol
	Isobutanol
	Propanol
	Isopropanol
C.	A mixture of both
	Di-isopropyl ether/butanol
	Tributyl phosphate/isopropyl ether

to dilute acid product requiring expensive concentration (evaporation) steps. In addition, expensive solvent recovery systems are needed which are not very efficient in most of the cases, leaving traces of solvents in waste disposal streams. Nevertheless, they are being used commercially.

As mentioned above, there are several different commercial purification processes. The design of these plants depends on factors such as feed acid strength, end-use of the purified acid, methods of raffinate disposal, etc. Details of commercial processes can be found in related references [44-63]. Nevertheless the names of these processes will be mentioned for the sake of completeness:

Prayon Process [39-41] (di-isopropyl ether and tri-n-butyl phosphate mixture is used as solvent),

Rhone-Poulenc Central Liquor Process [44,57] (tri butyl phosphate is used as solvent)

IMI Process [34,44] (di-isopropyl ether or a mixture of isopropyl ether and butanol are used as solvent).

Discussion and Conclusions

Until the necessary data and experience are accumulated on the non-conventional and extraction processes it would be wise to select a process among the wet processes described in selection I. When a decision is to be made about a process for a specific industrial application there must be enough data to prepare a table similar to Table 1. Preliminary selection of the process can be carried out by giving a certain weight [5] to the important factors in such a table. By adding up the negative or positive points given to each factor, a quantitative basis is obtained for comparison. In this respect, the importance of the type of phosphate rock to be used must be pointed out. The raw material (phosphate rock) effects the plant operation in many ways, and this is very unpredictable. Complete mineralogical and chemical analyses of the rock gives clues about its usefulness as a raw material. A comprehensive pilot plant study constitutes the basis for a reliable evaluation of the rock and the process selection.

It is always desirable to have a process design which includes sufficient flexibility to permit the use of rocks from various sources. Even when the source of the rock is from a known mining area, it is always preferable to allow for the variations in the rock characteristics in the design. Example for such allowances could be: extra grinding capacity for harder rock, additional filtration capacity for rocks with slow filtration rates, flexible slurry handling systems for higher acid-insoluble impurities in the rock, high corrosion resistance materials of construction for variations in impurities which cause corrosion.

Economics of the production will be highly influenced by the proximity of the phosphate mine to the plant (*i.e.* transportation cost), presence of a sulfuric acid plant nearby (for availability of low-cost steam and H_2SO_4), location of the plant in an already industrialized area (to have the infrastructure and possible availability of water for wet grinding) and the end use of the phosphoric acid which determines the load on concentration units. Concentration of acids required for various processes are: triple superphosphate: TSP-den process, 50-54; TSP-slurry process, 38-40; diammonium phosphate (DAP), 40; mono-ammonium phosphate (MAP), 40-50; and merchant grade for shipment, 54; superphosphoric acid for liquid fertilizer production, 69-70.

Among the non conventional acidulation processes mentioned in section II the most promising one seems to be the foam process where short residence times are reached for the acidulation and crystallization. Acidulation with phosphoric acid can be considered when cadmium pollution is important and acid/alcohol leaching process can be important when the phosphate rock contains high proportions of aluminum iron and magnesium. Complexity of latter two processes should be noted against the simplicity of the foam process. Acidulation with hydrochloric acid should only be considered when this acid is in abundance and cannot be utilized otherwise. Processes developed for the purification of the wet process acid are intended to increase the competence of the wet process against the furnace process to produce high purity phosphoric acid. Before indulging in such processes great care must be exercised because these are relatively new processes.

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تقنية عمليات إنتاج حامض الفوسفوريك في المملكة العربية السعودية

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ملخص البحث. من المتوقع أن تقوم صناعات الأسمدة الفوسفاتية وحامض الفوسفوريك في المستقبل القريب في المملكة العربية السعودية. هذا البحث يشتمل على مسح لمختلف العمليات التقنية المستخدمة في إنتاج حامض الفوسفوريك. كما يشتمل البحث على إمكانات وقصور التقنيات التقليدية والحديثة المستخدمة لتلك الصناعة.