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## THE FISONS HEMI-DIHYDRATE (HDH) PHOSPHATE ACID PROCESS

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### 1. INTRODUCTION

The hemihydrate dihydrate (HDH) phosphoric acid process is a further development of the FISONS hemihydrate process which was designed to produce 40-54 per cent  $P_2O_5$  phosphoric acid directly without the need for evaporation. The HDH process not only retains the advantages of the hemihydrate process but enhances certain features of the single stage process.

The development of the hemihydrate process which constitutes the first stage of the HDH process is fully reported in previous publications (1, 2, 3, 4) and will be mentioned only briefly in this paper. A plant (4) based on this process was built for WINDMILL HOLLAND BV in 1970 and was designed to produce 60,000 tpa  $P_2O_5$  as 50 per cent phosphoric acid. This plant has been operated successfully for a period of four years and is now capable of production rates well over the design capacity. The process offers the following main advantages over the conventional dihydrate process :

- (i) use of a coarse rock
  - 100% through 10 BSS sieve (1.675 mm)
  - 75% through 30 BSS sieve (0.5 mm)
  - 25% through 60 BSS sieve (0.251 mm)
- (ii) production of 40-54 per cent  $P_2O_5$  acid directly without evaporation
- (iii) production of acid containing lower levels of impurities than dihydrate acid of the same  $P_2O_5$  concentration.

There were two areas in which the hemihydrate process could be improved; these were (a) to increase  $P_2O_5$  efficiency and (b) to improve the quality of the calcium sulphate produced.

$P_2O_5$  efficiencies for the hemihydrate process lie within the range 90-97 per cent for a wide range rocks and the production of acids of 40-54 per cent  $P_2O_5$  concentration. This range compares with 95-97 per cent for conventional dihydrate processes. The possibility of developing a strong acid process with a  $P_2O_5$  efficiency higher than either the single stage hemihydrate or conventional dihydrate process became apparent during FISONS development of the hemihydrate technology in the 1960's. Results from laboratory experiments coincident with the hemihydrate development indicated that by recrystallisation of the hemihydrate to dihydrate  $P_2O_5$  efficiencies in excess of 98 per cent could be obtained. With the recent escalation in phosphate rock prices, high efficiency processes become even more attractive economically.

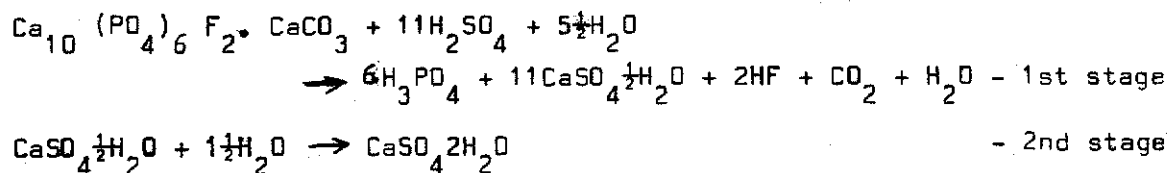
Hemihydrate and dihydrate produced from certain rocks by many of the conventional processes are unlikely to be directly suitable for use as a building material in the form of plasterboard, gypsum block, or as a retarder for cement. The unsuitability is due partly to the relatively high  $P_2O_5$  and fluoride contents of these calcium sulphates. The dihydrate produced in the hemihydrate-dihydrate process contains less  $P_2O_5$  than calcium sulphates produced from hemihydrate or dihydrate processes (0.1-0.3 per cent  $P_2O_5$  compared with 0.5-2.0 per cent  $P_2O_5$ ) and generally less fluoride and should be potentially more suitable for use as a building material. It is realized that the higher purity of the dihydrate from the HDH process can be an advantage only in areas where there is an economic outlet as a building material for the calcium sulphate by-product. However, it is possible that environmental legislation may change and demand a purer effluent or an alternative method of disposal.

Following an initial laboratory investigation of recrystallization of hemihydrate, a pilot plant was constructed to study the feasibility of a hemihydrate-dihydrate process. The results from this pilot plant confirmed the success of the laboratory investigation and have been used in the design of a production plant for RMHK TREPČA in Yugoslavia. This plant is designed to produce 50,000 tpa  $P_2O_5$  as 50 per cent  $P_2O_5$  phosphoric acid from Morocco rock and is now under construction by LURGI CHÉMIE UND HUTTEN-TECHNIK GMBH. Commissioning of this plant is expected early in 1975.

This paper describes the laboratory and pilot plant investigation of the hemihydrate-dihydrate process, the Trepča plant and its expected performance.

## 2. DESCRIPTION OF THE PROCESS

A simplified diagram of the FISON'S hemihydrate-dihydrate process is shown in figure 1. The process occurs in two stages - a hemihydrate stage followed by a dihydrate stage. In the first stage, phosphate rock is dissolved by phosphoric and sulphuric acids to produce phosphoric acid and calcium sulphate hemihydrate which is then recrystallised to calcium sulphate dihydrate in the second stage. The overall chemical reactions which occur in the two stages may be expressed as :



Both reactions are exothermic and cooling is required in both stages to maintain temperatures at the desired levels.

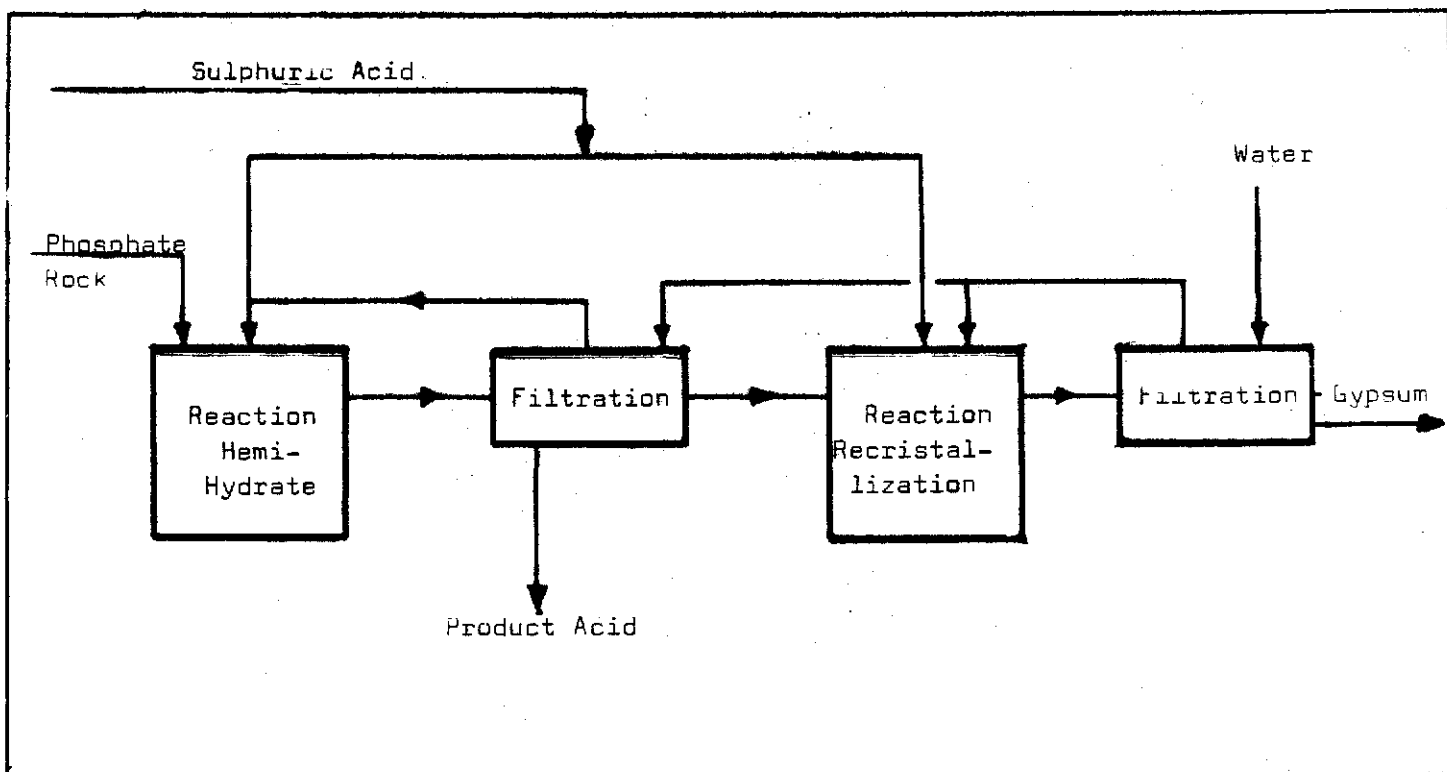


FIGURE 1

## Simplified Flow Diagram of Fisons H D H Process

The hemihydrate reaction is carried out in two reactors. Phosphate rock, 100 per cent passing through 1.6 mm, is fed to the first reactor where dissolution of the rock and partial precipitation of the hemihydrate occurs. The amount of precipitation which occurs is controlled by the amount of slurry recycled from the second reactor. Sulphuric acid and return phosphoric acid from the filter are premixed and fed to the second reactor where dissolution of the rock and precipitation of the hemihydrate are completed. The temperature in both reactors is controlled within 98-102° C by circulating the slurry through a flash cooler to remove the excess heats of reaction and dilution. Fluorine evolved from the slurry in the flash cooler can be recovered by a fluorine scrubber. The slurry overflows from the second reactor to a third vessel which supplies slurry to the hemihydrate filter.

The hemihydrate and phosphoric acid are separated by a standard tilting pan vacuum filter with three wash stages. Part of the acid from the first section of the filter constitutes the product acid from the process and the remainder is mixed with the acid filtrate from the first wash stage and returned to the second hemihydrate reactor. This acid mixture is the hemihydrate return acid. The final wash is filtrate from the dihydrate filter which is known as dihydrate return acid. A special chemical solution is added to the acid in the filter circuit to effectively reduce scaling caused by precipitation of calcium sulphate dihydrate.

The hemihydrate from the filter can contain from 0.7 to 2.0 per cent insoluble  $P_2O_5$  on a dry basis, the actual amount depending on the rock processed and the  $P_2O_5$  concentration of the acid produced in the first stage. This hemihydrate is discharged from the filter into the recrystallization reactor of the second stage, and the pans washed with dihydrate return acid. These washings are also discharged into the recrystallization reactor.

The recrystallization reactor is a simple vessel with a holding time sufficient to produce and maintain conversion of hemihydrate to dihydrate and produce dihydrate crystals in a filterable form.

Sulphuric acid is fed to the reactor to assist the conversion of hemihydrate to dihydrate and at the same time replace most of the co-precipitated  $P_2O_5$  of the hemihydrate by sulphate ions. The displaced  $P_2O_5$  passes into the recrystallization acid with a proportion of other  $P_2O_5$  components of the hemihydrate such as aluminium, silica and fluoride. A second chemical may be added to the recrystallisation reactor in the case when hemihydrate from a particular rock cannot be completely recrystallized to dihydrate by the addition of sulphuric acid alone. The reaction slurry is air cooled to maintain a temperature in the region of 60-70° C.

The slurry from the recrystallization reactor is filtered on a standard belt or tilting pan vacuum filter with one or two wash stages. The requirement for one or two wash stages depends on the nature of the phosphate rock processed and the method of operation of the first stage. Water is used as the final wash on the filter. The filtered recrystallization acid and the wash acid are mixed to form the dihydrate return acid. Part is used as the final wash on the hemihydrate filter and the remainder is used to wash the filter pans. Three pan washings are returned with the discharged hemihydrate to the recrystallization tank.

The dihydrate which contains less than 0.3 per cent  $P_2O_5$  is either discharged from the filter as a solid or washed into a tank with water before disposal as a slurry. The "dry" dihydrate can be utilized as a building material or transported to a suitable disposal area.

### 3. LABORATORY AND PILOT PLANT INVESTIGATIONS

#### 3.1. Objectives

The objective of the laboratory investigation was to determine conditions under which hemihydrate from different phosphate rocks would recrystallize to dihydrate containing very small amounts of  $P_2O_5$ .

The pilot plant investigation was designed mainly to confirm and extend the laboratory recrystallization data and to determine efficiencies and filter area requirements for the process.

### 3.2. Methods

The laboratory investigation of the second stage of the HDH process was initiated during the pilot plant investigation of the single stage hemihydrate process. (1964-1970). The recrystallization reactor consisted simply of an agitated and baffled vessel surrounded by a water jacket to control temperature.

Hemihydrate from a pilot plant filter and acids were metered continuously into the reactor, and samples of slurry taken periodically from the overflow of the reactor. The solid sample was analyzed for dihydrate,  $P_2O_5$  and other components. The volume of the laboratory reactor was approximately  $1/200$ th the volume of the hemihydrate pilot plant reactors and thus at this stage it was impossible to return acid from the laboratory recrystallization reactor to the hemihydrate filter and maintain a stoichiometric balance.

The pilot plant was designed for a nominal throughput of 8 kg/hr phosphate rock. The existing hemihydrate pilot plant was used as the first stage and the facilities of an existing dihydrate pilot plant were modified to constitute the second stage of the HDH plant. Provision was made for pumping dihydrate return acid from the dihydrate plant to the filter of the hemihydrate plant. The filtration was performed batch-wise.

The HDH pilot plant was operated for periods of up to 200 hours under any one operating condition. Each crystal phase was evaluated by X-ray diffraction, specific surface area measurement and by a filtration test.

The specific surface area gives a measure of the size of the crystals and can be determined in less than five minutes. This result gives a reliable indication of the filtration and washing characteristics of the hemi and dihydrates.

The laboratory filtration tests simulate the operation of a multi-wash stage filter and was used to estimate filter area requirements and  $P_2O_5$  washing losses for both the hemihydrate and dihydrate slurries.

#### 4. RESULTS OF INVESTIGATIONS

The conditions under which large filterable hemihydrate crystals could be produced from many rocks have been well established (2,3), and only brief reference will be made to results obtained from the first stage of the two stage process.

The areas of investigation and results from both the laboratory and pilot plant studies are summarized below.

##### 4.1. Recrystallization of Hemihydrate to Dihydrate

The efficiency of a hemihydrate-dihydrate process depends on the completion and maintenance of the recrystallization of hemihydrate to dihydrate. Partial recrystallization of the hemihydrate to dihydrate results in high insoluble  $P_2O_5$  losses approaching the levels from the single stage process.

The variation of insoluble  $P_2O_5$  loss with conversion of hemihydrate to dihydrate is illustrated in Figure 2. The data were obtained during the processing of Florida rock and show that the insoluble  $P_2O_5$  of the calcium sulphate dihydrate decreases from 2.0 per cent to 0.2 per cent as the dihydrate percentage of the calcium sulphate increases from 0 to 100 per cent.

For a recrystallization process in which 30 per cent conversion of hemihydrate is obtained, the calcium sulphate would contain 1.5 per cent  $P_2O_5$ . This level corresponds to a  $P_2O_5$  efficiency of approximately 93.5 per cent which represents little improvement over the 91 per cent obtained for Florida rock in the hemihydrate process when producing a 50 per cent  $P_2O_5$  acid.

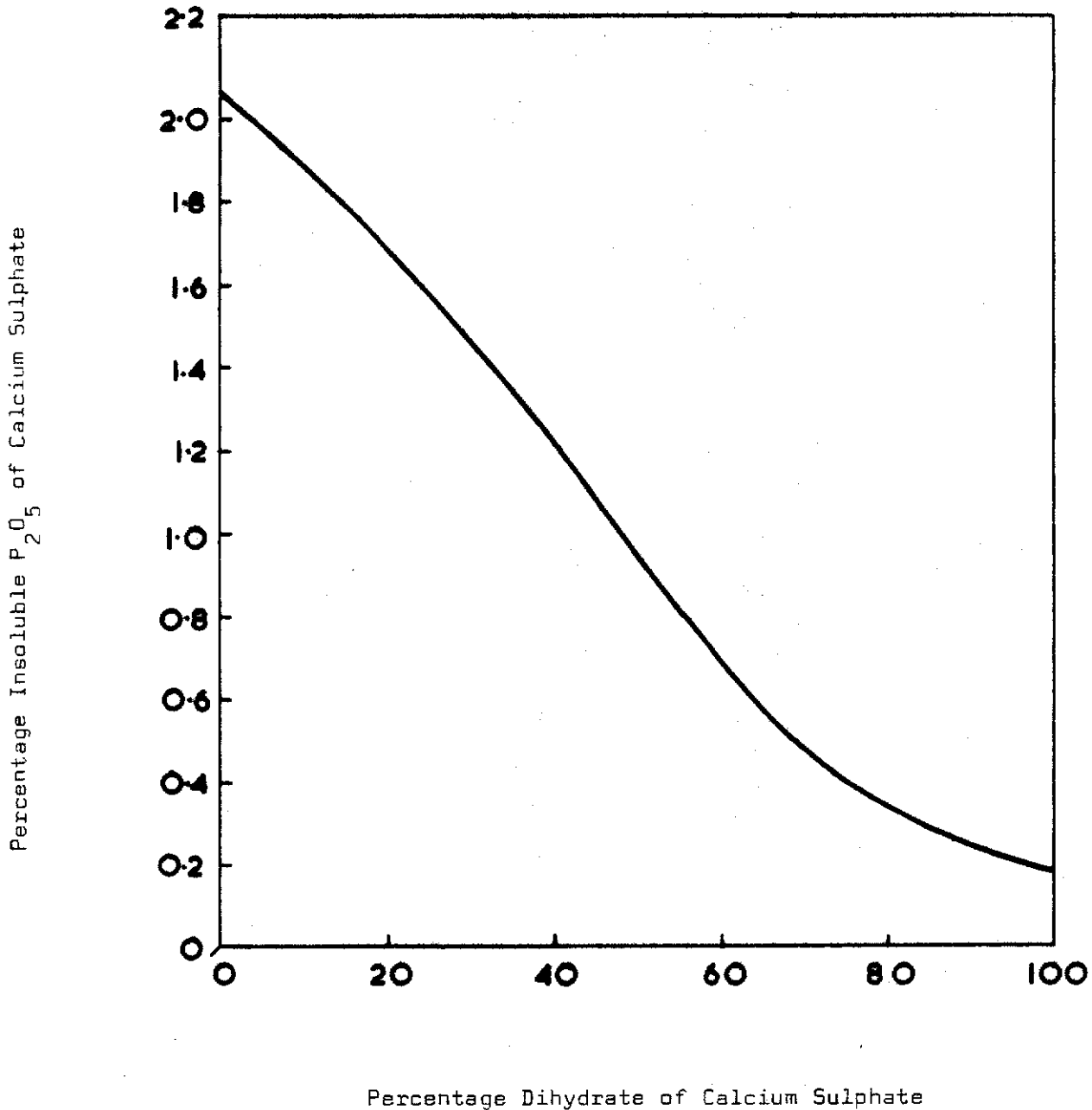


FIGURE 2  
Relationship between Insoluble P<sub>2</sub>O<sub>5</sub> loss and  
Conversion of Florida hemihydrate

In addition to high insoluble P<sub>2</sub>O<sub>5</sub> losses, partial recrystallization may produce problems due to setting of the calcium sulphate during disposal when the recrystallization process would be slowly completed.

#### Effect of Holding Time

The results from the laboratory investigation indicated the wide differences in rates of recrystallization to dihydrate of hemihydrate from different rocks. An illustration of the difference in rates is given in Table 1. For each hemihydrate of Table 1, sulphuric acid was added to the recrystallization reactor to maintain equal concentrations of P<sub>2</sub>O<sub>5</sub>



and  $SO_4$  in the recrystallization acid. The presence of sulphuric acid can in some cases accelerate the recrystallization process and at the same time produce dihydrate which contains low amounts of insoluble  $P_2O_5$  (see section 4.2).

TABLE 1

Recrystallization of Hemihydrate - Laboratory Results

Hemihydrate	Holding Time (hr)	Conversion to Dihydrate
Morocco	4	100 %
Togoland	10	Partial
Kola	10	Partial

The relative ease with which hemihydrate from rocks such as Morocco rock recrystallizes to dihydrate is evident from Table 1. In fact, it was found that Morocco hemihydrate would recrystallize within a four-hour holding time without the addition of sulphuric acid, i.e. by the addition of water alone. For hemihydrates from both Togo and Kola rocks, reactor residence times in excess of ten hours are required to complete and maintain the recrystallization process. The use of such large single reactors for a production plant would be costly and in most cases impractical. Methods of acceleration of the recrystallization process were investigated (see Effect of Additives).

The laboratory results with respect to Morocco and Togo hemihydrates were confirmed during the pilot plant investigation.

Effect of Temperature

The recrystallization reactor of the pilot plant was operated at slurry temperatures from 25 to 70° C, and over this range satisfactory recrystallization of the Morocco hemihydrate was obtained. The rate of recrystallization of relatively unreactive hemihydrate from rocks such as Togo and Kola was not increased by this variation in temperature.

It would be expected that as we approach the temperature above which hemihydrate becomes the stable form of calcium sulphate, then the rate of recrystallization will approach zero. For most rocks this temperature is in the range of 90-100° C and the cooling system of the Trepca plant (Section 5) is designed to maintain the temperature of the slurry well below these limits, i.e., approximately 60° C.

#### Effect of Additives

The recrystallization of hemihydrate from rocks such as Morocco rock is virtually completed and sustained by the addition of sulphuric acid alone to the second reactor.

During the pilot plant processing of Togo and Florida rocks, satisfactory recrystallization of the hemihydrate could not be obtained under the conditions used for Morocco hemihydrate. The continuous addition of specially prepared gypsum seeds failed to accelerate the recrystallization. It was concluded that chemical inhibition of the recrystallization process was occurring and, by a suitable choice and continuous addition of a second chemical to the second stage reactor to counter this inhibition, satisfactory recrystallization of the hemihydrate was obtained. It was found, however, that hemihydrate from Kola rock would not recrystallize satisfactorily even under these conditions and to date a satisfactory accelerator for the recrystallization of Kola hemihydrate has not been found.

#### 4.2. Insoluble $P_2O_5$ losses

The major insoluble  $P_2O_5$  loss in the hemihydrate process is that which is co-precipitated with the calcium sulphate. This is often termed "lattice"  $P_2O_5$  but doubt exists as to whether the  $P_2O_5$  actually forms an integral part of the crystal lattice of hemihydrate. The doubt originates from the fact that the dicalcium phosphate isomorph of calcium sulphate hemihydrate has not been identified.

The amounts of "lattice"  $P_2O_5$  contained by hemihydrate range from 0.6-2.0 per cent and depend on the nature of the phosphate rock processes and the product acid concentration.

The minor insoluble  $P_2O_5$  loss is that contained by the unreacted rock filtered with the hemihydrate which normally contains less than 0.2 per cent as unreacted  $P_2O_5$ .

During the recrystallization process, the insoluble  $P_2O_5$  losses are drastically reduced, due mainly to the decrease in lattice  $P_2O_5$  loss. The effect of variables on the amount of insoluble  $P_2O_5$  contained by the dihydrate are discussed below.

Effect of  $\text{SO}_4$  and  $\text{P}_2\text{O}_5$  Concentration of Recrystallization Acid

Figure 3 illustrates the variation of insoluble  $\text{P}_2\text{O}_5$  of dihydrate with the  $\text{P}_2\text{O}_5/\text{SO}_4$  weight ratio of the recrystallization acid. The data was obtained during the laboratory recrystallization of Morocco hemihydrate and refers to conditions when near to 100 per cent conversion of hemihydrate was obtained.

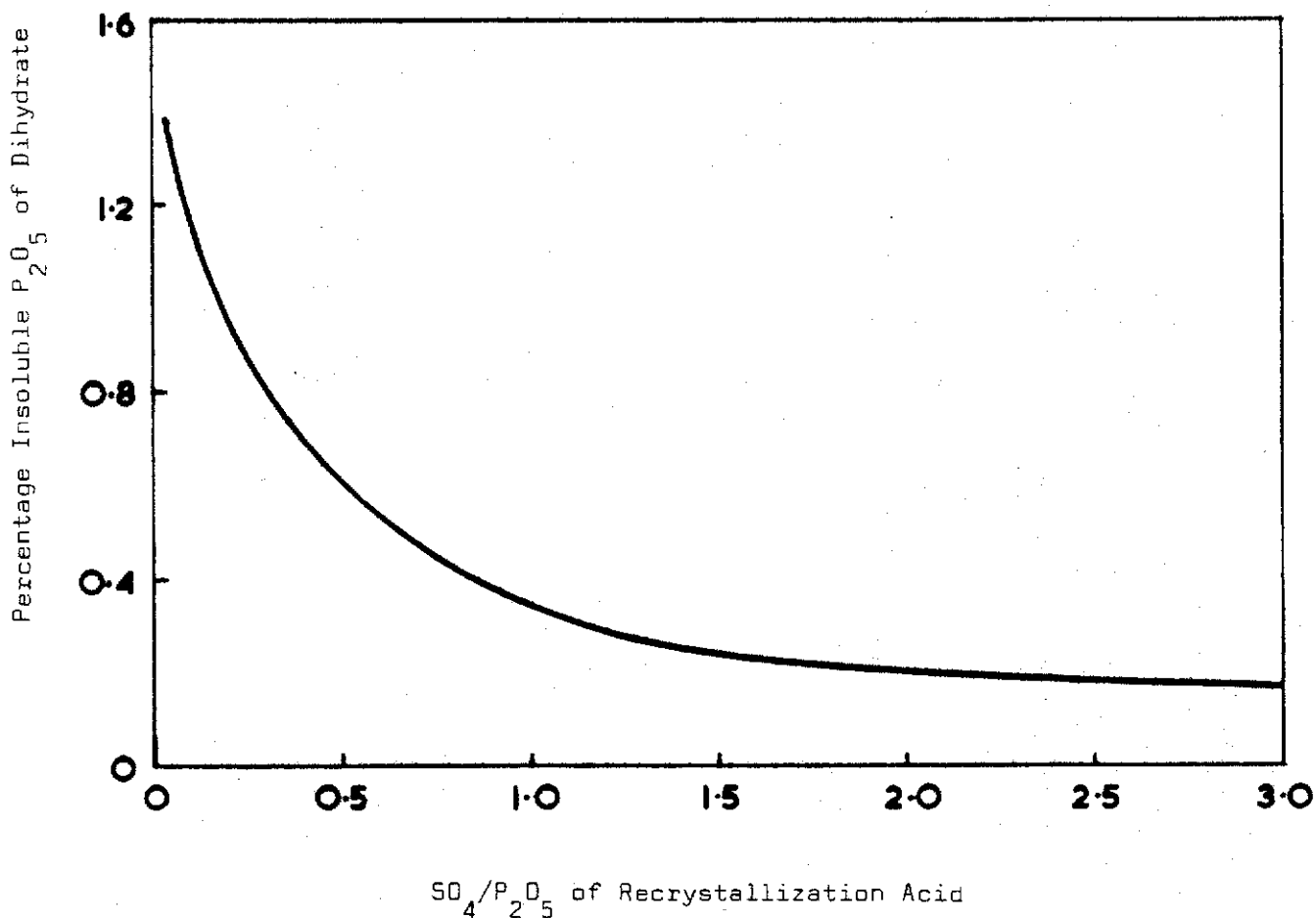


FIGURE 3

Variation of Insoluble  $\text{P}_2\text{O}_5$  loss with  $\text{SO}_4/\text{P}_2\text{O}_5$   
Weight Ratio of Recrystallization Acid

Based on this data, a  $\text{SO}_4/\text{P}_2\text{O}_5 = 1.0$  was chosen as an operating condition for the pilot plant recrystallization reactor. Although lower insoluble losses could be obtained by operation at values of  $\text{SO}_4/\text{P}_2\text{O}_5 > 1.0$ , the benefit would be small and sulphuric acid losses in the dihydrate filter cake would increase.

The levels of insoluble  $P_2O_5$  of the Morocco dihydrate produced in the pilot plant by operation at  $SO_4/P_2O_5 = 1.0$  were lower than the 0.3 per cent indicated by the laboratory results. Small increases in insoluble  $P_2O_5$  were indicated with increases in the  $P_2O_5$  concentration of the recrystallization acid.

TABLE 2

Variation of Insoluble  $P_2O_5$  with  $P_2O_5$  Concentration of  
Recrystallization Acid - Pilot Plant Data

Recrystallization Acid		Dihydrate
$P_2O_5$ %	$SO_4$ %	Insoluble $P_2O_5$ %
3.3	3.3	0.13
4.2	4.2	0.14
7.8	7.8	0.17

Effect of Temperature

The insoluble  $P_2O_5$  of the dihydrate was not significantly changed by operation at temperatures between 25 and 70° C.

Effect of Phosphate Rock Source

The dihydrate produced from the phosphate rocks processed contained from 0.1-0.22 per cent insoluble  $P_2O_5$ . This range is small compared to the 1-2 per cent insoluble  $P_2O_5$  contained by hemihydrates produced with a range of rocks during production of 25 per cent  $P_2O_5$  acid in the single stage hemihydrate process.

Effect of Product Acid Concentration

The level of insoluble  $P_2O_5$  of dihydrate from the second stage is unaffected by the  $P_2O_5$  concentration of the product acid over the range of 43-55 per cent  $P_2O_5$ .

#### 4.3. Dihydrate Crystals and Filtration

The shape of the crystals of the dihydrate from the second stage of the process was similar to the shape of the crystals of hemihydrate from the first stage, i.e. approximately spherical. Typical crystals of hemihydrate and dihydrate produced from Morocco rock are shown in Figure 4. Although the shapes of the two crystals are similar, the dihydrate crystals are smaller in size than the hemihydrate crystals. This can be illustrated by reference to typical values of specific surface area obtained during the pilot plant investigation;

#### Specific Surface Area ( cm<sup>2</sup> / g )

Hemihydrate	940
Dihydrate	1410

Although the dihydrate crystals were smaller in size, the filtration rate of the dihydrate slurry was much higher than the filtration rate of the hemihydrate slurry produced in the first stage. For example, results from the filtration tests indicated that the filter area required for the filtration of the dihydrate from Morocco rock would be approximately 25-35 per cent of the area required for the first stage filter. The higher filtration rate of the dihydrate slurry can be explained by the lower viscosity of the recrystallization acid compared to that of the product acid and the use of one wash stage on the dihydrate filter compared the use of three wash stages on the hemihydrate filter.

The dihydrate crystals exhibited excellent washing characteristics. For Morocco rock and other similar rocks, only one wash stage should be necessary on the second stage filter. Other rocks such as Togo and Florida rocks could require two wash stages.

The dihydrates from the pilot plant filter contained 20-30 per cent water on a wet basis. This level is similar to that of hemihydrate from the single stage process filter but lower than the 30-40 per cent water found in dihydrate after filtration in a conventional dihydrate process. The lower water of the dihydrate from the two stage process and of the hemihydrate is a further illustration of the superior washing characteristics of the type of crystal formed in these processes.

#### 4.4. Hemihydrate Crystals and Filtration

The return of diluted recrystallization acid from the second stage through the hemihydrate filter to the hemihydrate reactors can reduce the growth rate of hemihydrate crystals. This reduction is attributed to an effect of impurities such as aluminium, fluoride and silica contained by the diluted recrystallization acid. For example, when 50 per cent  $P_2O_5$  acid was produced from Morocco rock by the two stage route, the crystals of hemihydrate were smaller than crystals produced in the hemihydrate process (HH) under similar conditions. This difference can again be illustrated by reference to the results of specific surface area.

<u>Process</u>	<u>Hemihydrate Specific Surface Area (<math>cm^2/g</math>)</u>
HH	500-700
HDH	840-940

This comparative decrease in crystal size of the hemihydrate from the HDH process was reflected in the results from the laboratory filtration test. These results indicated that the filter area required for the Morocco hemihydrate from the HDH process would be 25-30 per cent higher than the filter area required for the hemihydrate from the single stage process. If a product acid of less than 50 per cent  $P_2O_5$  is required, this increase in filter area could be minimized by dilution of the acid from the hemihydrate stage with dihydrate return acid. For an effective product concentration of 43 per cent  $P_2O_5$ , the relative increase in filter area could be limited to 10 per cent.

For some rocks other than Morocco, the relative increase in the hemihydrate filter area was much lower than the 25-30 per cent.

The area of the hemihydrate filter could be reduced by using fewer wash stages and shorter drying times than are currently used. These modifications, however, would increase the  $P_2O_5$  concentration of the acid in the second stage and increase the dihydrate filter area requirement.

#### 4.5. Corrosion

Table 3 gives some laboratory results of corrosion of stainless steels by typical acids produced in the dihydrate, hemihydrate and HDH processes.

TABLE 3

Corrosion of Stainless Steels

Stainless Steel	Corrosion Rate (mm/yr)		
	Dihydrate Acid	Hemihydrate Acid	Recrystallization Acid
A	0.02	0.4	0.00
B	0.10	3.5	0.02
C	1.3	3.9	0.03
Temperature of acid ° C	80	100	70
P <sub>2</sub> O <sub>5</sub> % of acid	31.5	50	6

The results indicate that corrosion rates of stainless steels by the acid of the second stage of the HDH process are likely to be very low and far less than is normally experienced in either the dihydrate or hemihydrate processes.

4.6. Scaling

Some scaling due to deposition of sodium silicofluoride and potassium silicofluoride occurs in the second stage of the process. However, this is not expected to be any worse than the degree of scaling normally experienced in dihydrate processes.

Scaling due to precipitation of dihydrate in the hemihydrate filter circuit is effectively reduced by the addition of a scale inhibitor.

4.7. Product Acid

The expected analysis of 50 per cent P<sub>2</sub>O<sub>5</sub> which will be produced in the Trepsa plant from Morocco rock is given in Section 6.

In general, phosphoric acid produced by the hemihydrate-dihydrate process is expected to retain the advantages in quality (4) of hemihydrate acid compared with acid of the same P<sub>2</sub>O<sub>5</sub> concentration produced by the dihydrate process. These advantages are :

- a) lower solids concentration
- b) lower sulphate concentration
- and c) lower aluminium concentration

Acids produced by the HDH process are expected to contain slightly larger amounts of aluminium than the corresponding acids from the single stage hemihydrate process. This is due to the return to the first stage of additional aluminium contained by the dihydrate return acid from the second stage filter. For example, acids produced from Togo rock ( $\text{Al}_2\text{O}_3 = 1.1$  per cent) had the following analyses.

<u>Process</u>	<u>Acid Composition</u>	
	<u><math>\text{P}_2\text{O}_5</math> %</u>	<u><math>\text{Al}_2\text{O}_3</math> %</u>
HH	50	0.3 - 0.4
HDH	50	0.5 - 0.7
DH	50	0.9

For all components other than aluminium, analyses of acids from HH and HDH processes are expected to be similar.

#### 4.8 By-product Dihydrate

The expected analysis of dihydrate which will be produced in the Trepca plant is given in Section 6.

The direct use of by-product calcium sulphate as a raw material for the manufacture of building materials is restricted by the amounts and nature of certain impurities, e.g., phosphate and fluoride, contained by the calcium sulphate. If the amounts of phosphate and fluoride exceed certain levels, the setting and other properties of the building materials are adversely affected to an unacceptable extent.

Table 4 shows a typical analysis of dihydrate produced from Morocco rock in the two stage process. For comparison, analyses of calcium sulphates produced by the single stage hemihydrate (HH) and dihydrate (DH) processes are included.

TABLE 4  
Analyses of Calcium Sulphate Hydrates

Process	Acid $\text{P}_2\text{O}_5$ %	Hydrate	Percent w/w			
			$\text{P}_2\text{O}_5$	F	$\text{CaSO}_4 \frac{1}{2}\text{H}_2\text{O}$	$\text{CaSO}_4 2\text{H}_2\text{O}$
HDH	50	Dihydrate	0.2-0.3	0.4-0.6	NIL	97-98
HH	50	Hemihydrate	1.3-1.5	0.8-1.2	91-93	NIL
DH	30	Dihydrate	0.6-0.8	0.8-1.0	NIL	94-95



The analyses of table 4 indicate the highest purity of the calcium sulphate dihydrate from the HDH process. In particular, the relatively low phosphate and fluoride is highly likely to make the dihydrate from the HDH process the most potentially suitable for use in building materials.

## 5. DESCRIPTION OF THE TREPICA PLANT

The plant is being built in the chemical complex of RMHK TREPICA at Kosovska Mitrovica, about 200 km South of Belgrade. The plant site is 500 m above sea level.

The plant will start up early in 1975.

The reaction section of the plant is located outdoors ; the filter, control room and electrical gear are enclosed in asbestos clad and brick buildings.

Figure 5 shows the model of the plant used for design, erection and training purposes and illustrates the compact layout.

Figure 6 is a simplified flow diagram.

### 5.1. Rock Feeding

Standard equipment is provided to screen the rock feed to the plant and crush the particles of over 1.5 mm diameter in a roll crusher.

Rock is supplied to the weigh-belt from a constant head hopper. The metered flow is divided into two equal streams and fed to the first reactor of the hemihydrate stage. Rubber flap valves prevent reactor fumes entering the rock chutes and causing blockages.

Dust emission is prevented by ventilating the equipment through a bag filter unit.

### 5.2. Hemihydrate Reaction System

The hemihydrate reaction system comprises :

Two reactors and a filter feed vessel.

Slurry cooling system.

Fluorine scrubbing systems.

Ventilation system.

The reactors are fully baffled vertical cylindrical vessels with flat bottoms and integral sloping roofs.

The first reactor is equipped with 4 open turbine agitators each with 6 flat blades pitched at 45°. Two agitators pump upwards and two downwards, thus ensuring complete mixing of the contents.

The second reactor and filter feed vessel each have one large downward pumping agitator of the same type.

Slurry is pumped from the second reactor to the flash cooler where water is evaporated. Vacuum is maintained by the cooler condenser and vacuum pump. A metered quantity of slurry discharged from the cooler is recycled in two equal streams to the first reactor. Excess slurry is returned to the second reactor.

A fluorine scrubbing system is located between the flash cooler and the condenser. It consists of a vertical void tower subdivided into two Swift type -spray chambers. Each chamber is equipped with 3 centrally located spray nozzles mounted one above the other through which fluorosilicic acid is circulated.

### 5.3. Hemihydrate Filtration Section

The hemihydrate filter is a standard tilting pan machine having an effective area of 65 m<sup>2</sup>. Three counter-current wash stages are used. The associated equipment is similar to that of a conventional dihydrate plant, except the cloth drying fan which is not necessary.

The filter discharges the hemihydrate into the recrystallization reactor and the pans are washed with dihydrate return acid.

Any acid spillage is collected in the plant sump, located in the hemihydrate filtration area. This acid is pumped to the wash acid tank from which it is metered into the return acid stream.

### 5.4. Dihydrate Section

The dihydrate system comprises :

Recrystallization reactor.

Dihydrate filter

The disposal equipment.

The recrystallisation reactor is of similar construction to the second hemihydrate reactor but having a taller aspect ratio. It is equipped with a large single agitator having two open turbine impellers. Each impeller has 6 flat blades pitched at 45° and pumping downwards.

Cooling air provided by a small fan is injected just below the slurry surface through cooling air nozzles. The reactor is ventilated to the scrubber system.

The dihydrate filter is a standard belt filter with an effective area of 18 m<sup>2</sup>. A single water wash is employed and this is the only point where water enters the process. Cooling water discharged from the vacuum pumps is collected in a small tank and re-used as the dihydrate cake wash water. Two filtrate separators are provided for alternate operation to enable on-stream cleaning of any scale formed in the filtrate lines. Filtrates from the separators are collected in a seal tank and form the dihydrate return acid which is pumped to the hemihydrate filter as cake wash, cloth wash and cake slurrifying liquor.

The dihydrate filter is suitable for "wet" or "dry" discharge of the filter cake to provide the flexibility required by local conditions.

For wet discharge, the cake falls into an agitated slurrifying tank where it is mixed with water previously employed for cloth washing and waste water from elsewhere in the process. A slurry containing 20-25 per cent solids is pumped to the disposal area.

For dry discharge, the filter cake is collected on the first of a series of conveyors which transport it to the disposal area. The conveyors are specially designed to avoid damage to the bearings caused by ingress of dihydrate crystals.

#### 5.5. Pumps

Horizontal centrifugal pumps are employed for all duties except for the sump which has a vertical unit. For slurry service, centrifugal shaft seals are fitted. All pumps have short horizontal suction piping to eliminate the possibility of blockages. Expansion bellows are fitted where necessary.

Installed spares are provided only for the large pumps and when not in use these are piped-up on the suction side only.

#### 5.6. Materials of Construction

The hemihydrate and recrystallization reaction vessels are of standard phosphoric acid plant design. Carbon steel is lined on site with a neoprene based rubber lining and carbon bricks set in phenol-furane cement for the bottom and walls.

For other smaller vessels, natural rubber has been used and has generally been applied before delivery. Additional linings of carbon brick were applied on site to the flash cooler and the return acid seal tank.

The impellers of the reactor agitators are made of solid 25/5/2/3 CrNiMoCu stainless steel ; the mild steel shafts are covered with the same stainless steel. For most of the pumps, the 25/5/2/3 CrNiMoCu material has also been used. The few exceptions are the wash water pumps of cast iron, and the fluorosilicic acid pumps of high density polyethylene.

The filter pans of the hemihydrate filter are made of AISI 317 L stainless steel, and the central valve of 20/25/4.5/1.5 CrNiMoCu stainless steel. For the filter cloth support a glass fibre reinforced polyester resin has been used.

For the dihydrate filter, natural rubber and 17/14/4 CrNiMo stainless steel have been selected for the belt and the suction box respectively.

Filter cloth materials are polypropylene for the hemihydrate filter and polyester for the dihydrate filter.

The gas ducts and the gas scrubber have been constructed of polypropylene and glass fibre reinforced resin sealed polyester.

Materials of construction for process pipework are :

- slurry line : mild steel, with a double (hard plus soft) rubber lining.
- acid lines : glass fibre reinforced polyester with a synthetic fibre reinforced liner where necessary.

The majority of the valves both in acid and slurry lines are of the diaphragm type . Natural and synthetic rubbers have been used for the flexible diaphragms.

## 5.7. Plant Control

The instrumentation of the plant is typical of that used in modern phosphoric acid plants. The equipment used in the WINDMILL plant has been described previously (4).

For the additional dihydrate section, the main control parameters are :

- a)  $SO_4$ ,  $P_2O_5$  and solids levels of the recrystallization slurry.
- b) Temperature of the slurry
- c) Dihydrate filter flows.

The types of instrument employed are identical to the hemihydrate section. The transformation temperature is maintained at approximately 60° C by regulation of the cooling air flow to the reactor and/ or the number of nozzles in use. The flow of slurry to the dihydrate filter is controlled by the level in the recrystallization reactor. The cake wash water is controlled by the level in the filtrate seal tank, which also serves as the wash tank for the hemihydrate filter. Thus, the flow of the filtrate from the dihydrate filter to the hemihydrate filter (as cake wash liquid) determines the flow of cake wash water to the dihydrate filter.

## 6. EXPECTED PERFORMANCE OF THE TREPCA PLANT

### 6.1. Production Rate and Acid Quality

The HDH plant of RMHK TREPCA is designed to produce 50,000 tpa  $P_2O_5$  as 50 per cent  $P_2O_5$  phosphoric acid from Morocco rock. After deduction of two weeks for the annual shut-down of the plant, an annual utilization of 88 per cent is expected, i.e. 310 days (24 hours) of actual production.

The following analysis of the product acid is expected :

<u>Component</u>	<u>Per cent w/w</u>
$P_2O_5$	50.0
$SO_4$	2.0
$Fe_2O_3$	0.36
$Al_2O_3$	< 0.1
MgO	0.65
F	0.8

The solids content of the acid is not expected to exceed 0.5 per cent provided the filter cloth is properly maintained.

### 6.2. $P_2O_5$ Efficiency

based on the total  $P_2O_5$  of the dihydrate cake, a  $P_2O_5$  efficiency of 99.0 per cent is expected.

### 6.3. Dihydrate Quality

The dihydrate filter cake is expected to contain approximately 25 per cent free water on a wet basis. On a dry basis, the following analysis of the dihydrate is expected:

<u>Component</u>	<u>Per cent w/w</u>
$P_2O_5$	0.20-0.22
$SO_4$	54-55
CaO	32-33
$Fe_2O_3$	< 0.02
$Al_2O_3$	0.3-0.4
MgO	< 0.02
F	0.4-0.6

#### 6.4. Raw material and Utility Consumptions

The following consumptions of raw materials and utilities are expected :

Phosphate rock (33.7 % $P_2O_5$ , 51.9% CaO, dry basis)	:	3.02 t/t $P_2O_5$ produced
Sulphuric acid (min. 93 % $H_2SO_4$ , 100 % basis)	:	2.65 t/t $P_2O_5$ produced
Cooling water (27°C, 3 Kg/cm <sup>2</sup> )	:	32 m <sup>3</sup> /t $P_2O_5$ produced
Process water (2-27° C, max 200 ppm Cl)	:	6 m <sup>3</sup> /t $P_2O_5$ produced
Steam (8 Kg/cm <sup>2</sup> g)	:	approx 5 t/hr for start-up average approx 5 Kg/t $P_2O_5$ produced
Electric power (including rock preparation and product storage)	:	150 KWh/t $P_2O_5$ produced
Anti Scaling Chemical (cost)	:	£0.6 (pounds Sterling)/t $P_2O_5$ produced.

#### 6.5. Operators and Maintenance Costs

The plant will be operated by 3 skilled operators per shift under the supervision of a shift foreman.

A maintenance cost of £1.50 (pounds Sterling) per ton  $P_2O_5$  produced is expected. This cost allows for direct labour and material. Overheads are excluded, as they vary from plant to plant.

#### 7. CONCLUSIONS

The results from laboratory and pilot plant investigations of a hemihydrate -dihydrate process have been utilized in the design of a plant to produce 50,000 tpa  $P_2O_5$  as 50 per cent  $P_2O_5$  phosphoric acid from Morocco rock. This plant is now under construction for RMHK TREPICA of Yugoslavia at Kosovska Mitrovica and will be commissioned during the early part of 1975. Experience obtained from the four years operation of a plant operated by WINDMILL HOLLAND BV on the FISON'S hemihydrate process has been utilized in the design of the TREPICA plant.

The investigations which were carried out at the Levington Research Station of FISON'S have shown that the HDH process is likely to be suitable for many of the phosphate rocks which are currently used in the conventional dihydrate process.

The HDH process offers the following advantages over the hemihydrate process and the conventional single stage dihydrate processes :

- (i) For a given rock, the  $P_2O_5$  efficiency (> 98 per cent) of the HDH process is higher than the  $P_2O_5$  efficiency of either the hemihydrate or dihydrate process. The relatively high efficiency of the HDH process strongly influences the expected production cost of  $P_2O_5$ .

<u>Process</u>	<u>Manufacturing Cost Index</u> (per ton $P_2O_5$ )
HDH	100
Hemihydrate	103
Dihydrate	104

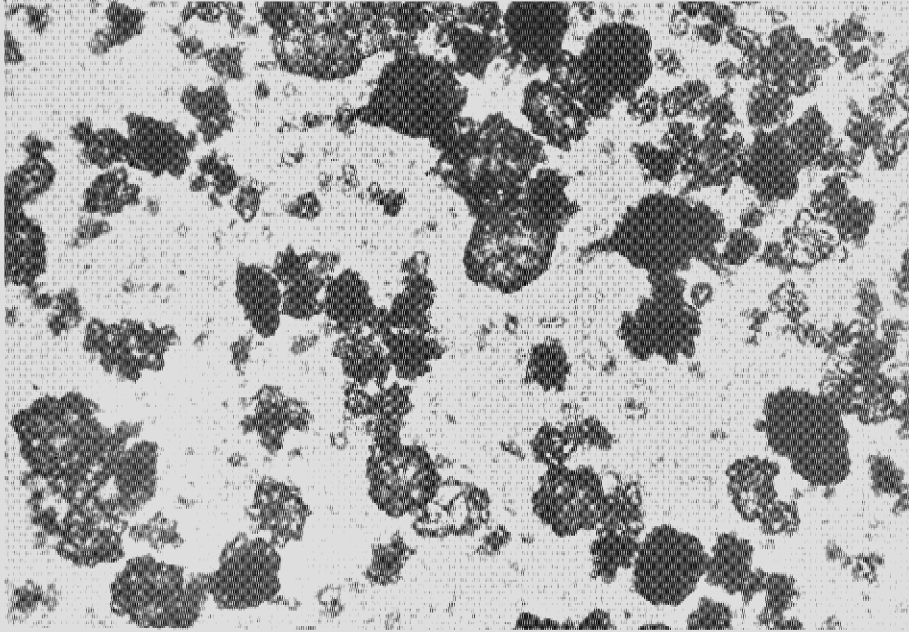
These costs are based on Morocco rock and typical European experience in the production of 50 per cent  $P_2O_5$  acid.

- (ii) Compared to the dihydrate process, the product acid from the HDH process contains smaller amounts of impurities such as solids (< 1 per cent),  $SO_4$  (1.5-2.0 per cent) and aluminium. The acid can be stored and shipped without further treatment. This advantage also applies to acid from the hemihydrate (HH) process.
- (iii) The HDH process produces a calcium sulphate which contains smaller amounts of impurities (e.g.  $P_2O_5$  and F) than the calcium sulphates produced in the hemihydrate and dihydrate processes. This can be an economic advantage only when there is an outlet for the calcium sulphate as a building material and has not been considered in the calculation of the production cost indices given in (i).
- (iv) Compared to the dihydrate process, the HDH process is more flexible. Acid of any concentration between 40 and 54 per cent  $P_2O_5$  can be produced directly without an evaporation stage or modification of the hemihydrate plant.

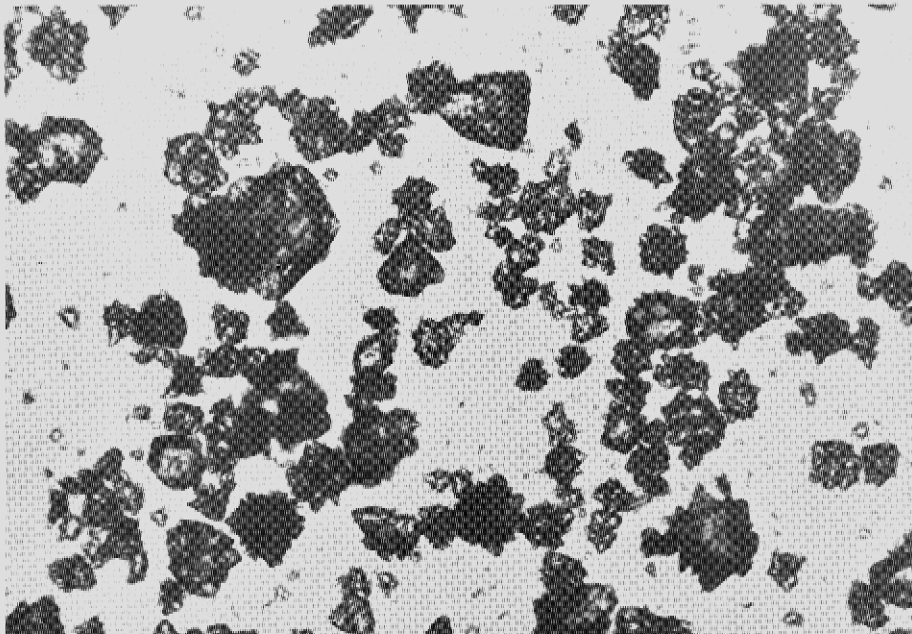
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  2. Robinson N. and Janikowski S. M. - "The Production of 50 per cent  $P_2O_5$  Phosphoric Acid Directly by the Wet Process : Fisons Hemihydrate Process", ISMA Technical Conference, Brussels, 1968.
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Hemihydrate Crystals from Morocco Rock - Pilot Plant



Dihydrate Crystals from Morocco Rock - Pilot Plant

FIGURE 4

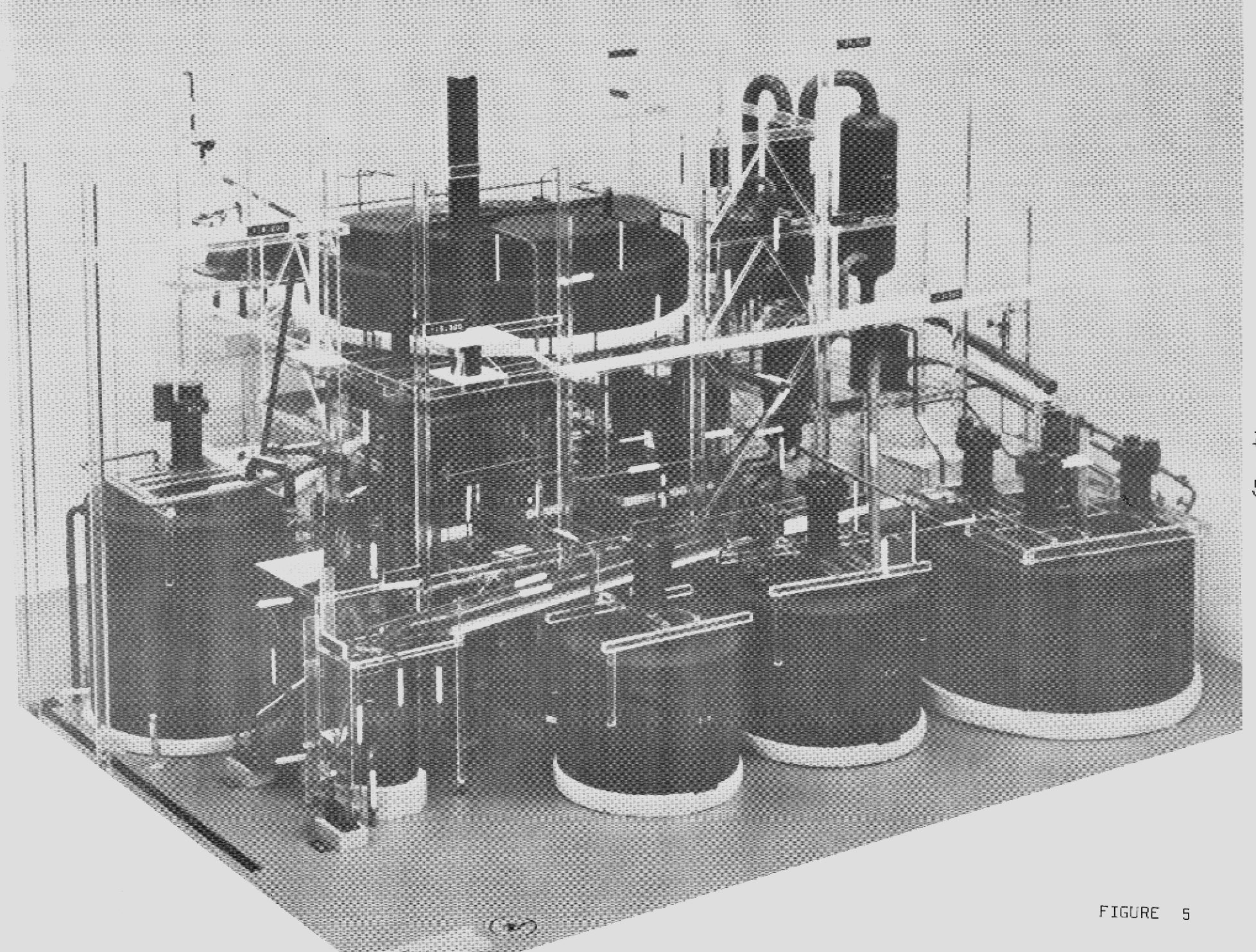


FIGURE 5

PROCESS WATER  
H<sub>2</sub>SO<sub>4</sub>

14 - 26

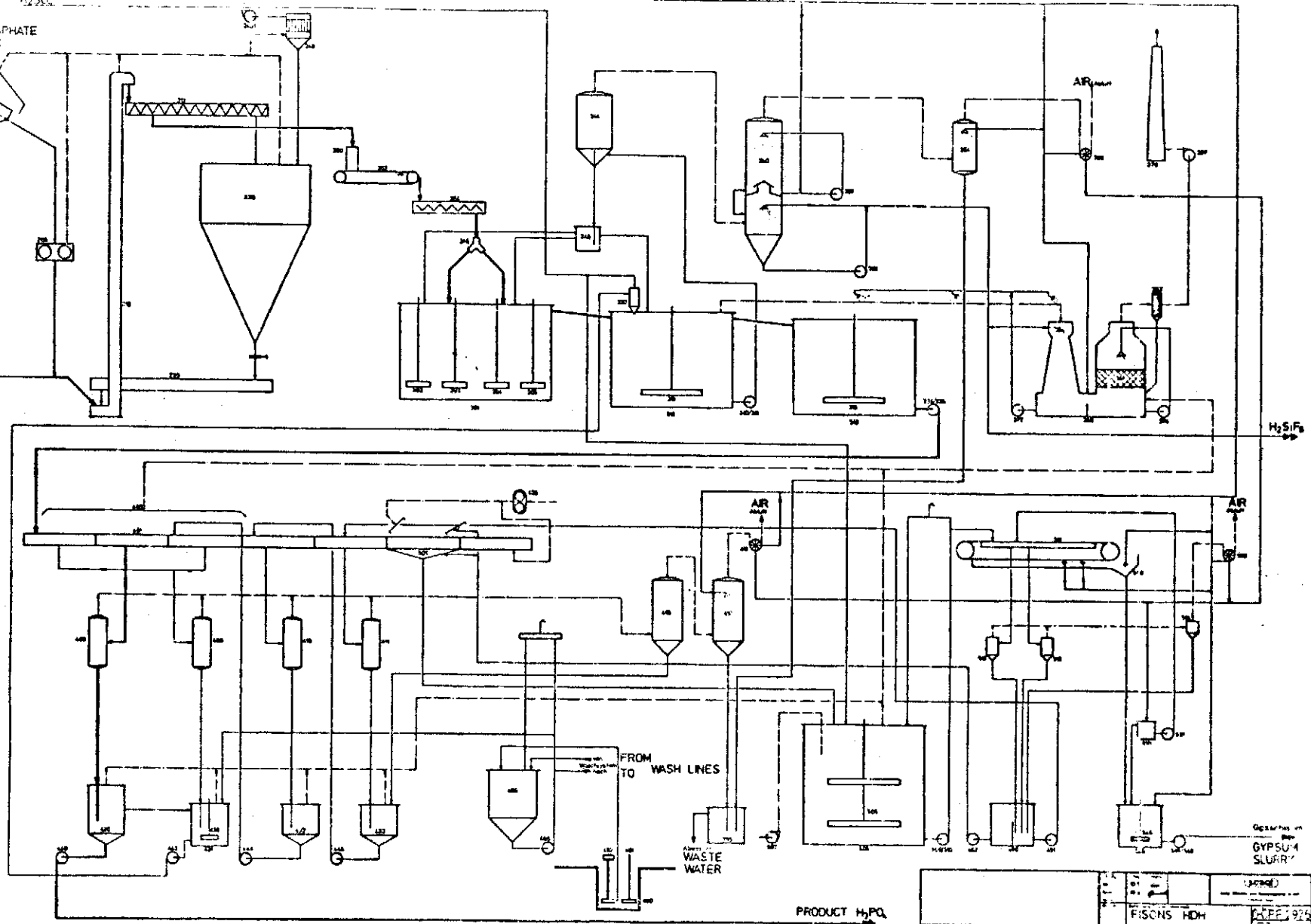


FIGURE 6

OPERATION		DATE
FISONS HDH		02/27/92
PHOSPHORIC ACID		
PROCESS		

COMMUNICATION N° 14M. CRERAR (Fisons, U.K.)

Producers of phosphoric acid always throw away significant proportions of their raw material. Recoveries of 97 % and less - even 90 % - are accepted. Attempts have been made for many years to improve the efficiency of phosphoric acid processes. With the current high price of phosphate rock there is a great incentive for improvement.

The paper I am presenting today describes the progress we have made in developing a phosphoric acid process with a  $P_2O_5$  efficiency of 99 %: the Fisons Hemi-dihydrate Process.

The Fisons single-stage Hemi-hydrate Process was described at the Seville Technical Conference two years ago. Its advantages are: the direct production of 50 %  $P_2O_5$  acid without evaporation; low solids, low sulphate and low aluminium content of the product acid, an ability to process coarse rock.

What demanded improvement? - The  $P_2O_5$  efficiency generally in the 90 - 97 % range.

During the development of the single stage process, laboratory work was going on into the recovery of the phosphate rejected in the filter cake - both soluble and insoluble  $P_2O_5$ .

The new process has two stages - A hemihydrate stage followed by a dihydrate stage. Each stage has its own reaction system and filter - perfectly straightforward phosphoric acid practise.

The first stage is identical to the single stage hemihydrate process.

The Hemi-hydrate filter cake contains up to 2 %  $P_2O_5$ , mainly as co-precipitated phosphate. It is discharged to the dihydrate reactor.

A little sulphuric acid is added and conditions controlled to promote the conversion of hemihydrate to the dihydrate crystal form. As the conversion proceeds  $P_2O_5$  is released into the liquid phase.

The reaction slurry is filtered to remove the dihydrate - or gypsum - which contains about 0.2 %  $P_2O_5$ . The filtrate contains all the phosphate released in the dihydrate stage.

How is this  $P_2O_5$  recovered? The filtrate is used to wash the hemihydrate cake on the first stage process. It eventually enters the hemihydrate reaction system from the filter.

What is the  $P_2O_5$  efficiency of this process? About 99 %.

Extensive laboratory work has been performed to determine the optimum conditions for the transformation to dihydrate. Pilot plant trials have been carried out to confirm laboratory tests and to determine the filter areas required and the practical  $P_2O_5$  efficiencies.

The increase in efficiency over the single stage process is directly related to the degree of transformation from hemihydrate to dihydrate. Clearly a conversion approaching 100 % is desired. How is this achieved? - Holding time is the main factor which affects the degree of transformation. A retention time of about 4 hours was found necessary for Morocco hemihydrate. Togo and Kola needed 10 hours - too long to be considered practical. An additive was found to accelerate Togo to 4 hours; but Kola has been rejected for the time being as unsuitable for the process.

To ensure maximum efficiency the quantity of  $P_2O_5$  co-precipitated with the dihydrate must be minimised - even at 100 % conversion. How is this controlled? The ratio of free sulphuric acid to  $P_2O_5$  in the dihydrate reaction slurry is the major factor.

$P_2O_5$  losses decrease as the ratio of sulphate to  $P_2O_5$  increases until the ratio reaches unity. After this point little benefit is gained by further addition of sulphuric acid. A sulphate to  $P_2O_5$  ratio of 1 is the preferred operating condition.

4 %  $P_2O_5$  in the dihydrate stage is typical for Morocco rock. A 4 % free sulphate is therefore maintained by adjustment of the sulphuric acid feed.

The filterability of the dihydrate slurry depends on the crystal size range and shape. The crystals are similar to the hemihydrate crystals: Spherical agglomerates of smaller crystals. They are typically a little smaller than the hemihydrate. Filterability is good, however, and usually requires only one water wash. What filter area is required for this stage? About one-third of that for the hemihydrate stage. What about corrosion? No special problems are met in the second stage of the process - standard materials for phosphoric acid can be used.

What about scaling? Some deposition of fluosilicate scale occurs in the second stage. This is similar to the conventional dihydrate process.

The first commercial example of the HDH process is due to come into operation early next year in Yugoslavia. It will be operated by RMHK Treppa at its fertilizer complex in Kosovska Mitrovica.

It will produce 50 000 tons of  $P_2O_5$  per annum as 50 %  $P_2O_5$  acid. The efficiency will be 99 %.

Simplicity has been the keynote of the plant's mechanical design. Equipment, instruments and materials employed have all been industrially proved. There will be no abnormal maintenance requirements.

How are the reactors constructed? Hemihydrate and Dihydrate reactors are fabricated in Carbon steel and lined with rubber.

Carbon bricks are also installed.

Agitation is by pitch blade turbines similar to those used in the Windmill plant.

What filter area is provided? 65 sq.m. for hemihydrate using a standard tilting pan filter with 3 washes. An 18 sq.m. belt filter with a single wash stage is installed for dihydrate filtration.

The reactors and some other equipment will be vented to a multi-stage scrubber. Thus a high standard of environmental protection will be ensured.

A high proportion of the fluorine in the rock is evolved and recovered. Fluosilic acid with a low level of  $P_2O_5$  will be fed to a new Aluminium Fluoride unit.

Which materials of construction are used? Ferralium stainless steel for most agitators and pumps, 317L for the hemihydrate filter pans and Uranus B6 for the central valve. Butyl rubber lining is used extensively to resist temperatures up to 100°C in the hemihydrate stage.

How much saving can the process show? The manufacturing cost of 50 % phosphoric acid by the Fisons HDH process is 4 % less than by the standard dihydrate route. This cost saving is mainly contributed by the higher efficiency of raw material usage and savings of steam consumption. Raw material costs are about 8 dollars less per tonne

of  $P_2O_5$ . Trepca will save at least 400 000 dollars per year. To summarize, what are the advantages of the process?

Relatively coarse phosphate rock can be used.

Acid of 50 % concentration can be produced without the necessity for evaporation.

The product quality is superior to dihydrate acid - only 2 %  $SO_4$  compared with 4 to 6 %, less than 1 % solids compared with over 5 %, low aluminium content.

The by-product gypsum has a quality suitable for the production of building blocks, plaster-board or cement.

Finally, the HDH process makes more efficient use of phosphate rock. Phosphate rock that is rapidly becoming more expensive and less readily available.

M. WENNBERG (Supra, Sweden)

After studying the lecture-paper I have come to the following "three questions" and would like to inform you thereof in order to get our mutual opening of the discussion as good as possible.

1. Considering the supply of phosphate rock it is very essential for most producers of phosphoric acid to have flexible processing units in which different kinds of rock can be used. My first question is therefore: which experience Fisons have in using low grade rock in this particular process?

Which are e.g. limitations to the HDH process in respect to aluminium, fluorine, silicon and in what proportions do the impurities divide to acid and gypsum?

2. The report gives us a detailed description based on the use of Khouribga rock. It would be interesting to have some information of costs for both investment and production when using other commercial rock-phosphates in relation to Khouribga. I am particularly interested in the volume which is necessary for recrystallization, the filter area one needs and if crystal modifying additives can be of use.
3. You mention in your report that the gypsum can be used for further refinement.

Which tests have been made to examine if the gypsum is suitable for production of plaster board and as additive to cement?

M. QUINTON (Fisons, U.K.)

I assume that by low grade rock, Mr. WENNBERG means those rocks containing 32 % and lower amounts of  $P_2O_5$ . Our pilot plant experience in the HDH process has been limited to those rocks which contain 33 % and more  $P_2O_5$ . However, our single stage hemihydrate pilot plant investigation has embraced many rocks from different parts of the world including low grade rocks. During these investigations of all rocks we included an investigation of the method at disposal of the hemihydrate. We found that in general the hemihydrate which has been difficult to transform in our disposal test has been also difficult to transform in the second stage of this two stage process. In general, the hemihydrates from the low grade rocks have been transformed with not too much difficulty during the disposal test and

it is expected similarly that for the low grade rocks we have tested transformation in the second stage or two stage process also does not present too much difficulty. Provided we can transform, it is expected that the efficiencies of recovery  $P_2O_5$  would be in excess of 98 %.

On the question of limits, it is difficult to set firm limits on aluminium, fluorine and silicon with respect to the HDH process. We believe that in some cases it is a combination of these elements which affect crystal growth and filtration in the first stage and transformation in the second stage. Other components also affect both filtration and transformation and it is only by pilot plant testing each individual rock prior to plant design that the magnitude of this effect can be established and this is all current practise. As an example of the proportionation of aluminium, fluorine and silica between acid and gypsum, and I should include the vapour as well, we take the case of a rock containing relatively high amount of aluminium; - this in fact was one of the rocks containing 33 % or more than 33 %, - aluminium levels 0.9 % expressed as aluminium oxide  $Al_2O_3$  and a normal F level of 3.9 % F, silica around 3 %. For the components the proportionation is as follows : for aluminium we find that 27 % remains in the acid phase, 73 % is found in the dihydrate. For fluorine approximately 8 % of F fed in the phosphate rock remains in the acid but 27 % of the F remaining in the dihydrate or gypsum and approximately 60 - 65 % is evolved in the vapour. Silica in the acid is less than 1 %, gypsum 63 %, vapour 37 %. This refers to an occasion when we produce 50 %  $P_2O_5$  from the rock containing  $P_2O_5$  in excess of 33 %.

On to the third part of the question which referred to dihydrate suitability in building materials we have carried out laboratory tests. This has been confined to plasterboard suitability. We have determined setting rates, compression tests, water requirements to make a paste adhesion test, ability to adhere to paper and a circle slump test which is the ability to spread over paper. The results from these tests were most favourable compared with dihydrate prepared from the same rock in a single stage dihydrate process.

Dr. BLUMRICH (Lurqi, Germany)

Concerning the second question relating to costs and the use of phosphate other than Khouribga rock, more precisely. Now will the equipment change, how will the investment cost change and how will the production cost be influenced by change to other rocks. The equipment : we have under certain circumstances to adapt the filter sizes to rocks where the hemihydrate or the dihydrate have worse filter characteristics and where it is necessary to have a second washing stage on the second gypsum filter. This is all we intend to change on the equipment side. The influence of these changes on the investment cost will be in the order of 6 to 8 % of the equipment, which means in the order of 4 to 6 % for total investment cost within plant battery limit. This has a certain influence on production cost but it is very small, nearly negligible, in the order of 0.3 % at the maximum and we have to consider of course cases of plus and minus. Other rocks may have smaller filters. There is

a second point, it might be necessary to use additives to promote the conversion of hemihydrate in the dihydrate. These additives are simple compounds easily available and the cost will be in the order of 3 to 5 DM/t  $P_2O_5$ . Let's take a round figure for production cost under today's conditions of approximately 800 DM. Then the influence of the investment cost will be in the order of 3 DM and let's add the 3 to 5 DM/t of  $P_2O_5$  for the additives, this means a total change from 800 DM to 808 DM on the plus side or to 797 on the minus side. This does not change the cost comparison given on page 22 of the paper.

M. GOSSE (Heurtey, France)

You indicate that in the TREPCA plant, the effective gypsum filtration surface area is 18 m<sup>2</sup>, which is quite a reasonable figure for an output of about 160 t/d, quite comparable to the area needed for a good conventional gypsum process. However, the filtration area for hemihydrate would be 65m<sup>2</sup> for the same 160t/d  $P_2O_5$  production. This figure is on the high side. So my question would be : how do you visualise the hemihydrate filtration for a 800 t/d unit which could be considered as a normal present capacity and what is the effective area of the biggest filter existing in the world ?

My second would be : you seem to have serious scaling problems with the hemihydrate filter since you use a few additives or solutions to prevent scaling. Don't you think that this problem is mainly due to your washing the hemihydrate with a fairly weak acid solution which is in fact the filtrate of the gypsum sector? I would like to ask you the following question : what is the life-time of the filter cloth you use for hemihydrate and finally a question which, in my opinion, is very important : what is the total investment cost of your process as compared to the conventional gypsum process? I mean starting from the same rock in the same condition to reach a comparable acid, for instance 54 %.

M. CRERAR

On the question of the filtration surface area provided in the TREPCA plant, you are quite right in your comments that 65m<sup>2</sup> is provided for the hemihydrate section and this refers to the 160t/d of  $P_2O_5$ . We realize that this area is rather on the high side. It is difficult to provide exactly the filter at the surface area that one predicts from the laboratory tests. because filters are not made in a complete range of sizes. This is a EMCO 90 filter that has been provided with a EMCO 620 and is about adequate for the duty here, but since it was the first commercial unit, we decided that we had to provide some safety factor here and put in a larger filter that was actually required. We expect we shall get substantial overcapacity from that.

The area required for a plant of 800 t/day brings us to the limit of the availability of this process and the requirement of filter area here coincides with the very large filters that are being made. The largest tilting pan type filter is about 190 m<sup>2</sup> and the largest filter VC type is about 200 m<sup>2</sup> so that we would be using a filter of this maximum size for a plant of the order of 800 t/d. You asked a question about the life of filter cloth. On the experience that we have from full scale plants producing hemihydrate which is the plant operated by



WINDMILL in Holland. their experience there is that filter cloth life is determined mainly by mechanical considerations rather than any scaling within the fabric of the cloth and in that particular filter mechanical considerations give a filter life of 2 months.

Dr. BLUMRICH

As a basis of comparison for the capital cost, let us define a plant including grinding, the phosphoric acid plant proper and the evaporation plant and for this total plant the cost for a HDH plant is comparable to a conventional dihydrate plant including evaporation.

M. COATES (Albright and Wilson, U.K.)

My question is also an economic one. Could the authors give us an indication of the incremental value of phosphoric acid recovered from the gypsum conversion stage in relation to the capital cost of the incremental plant expressed as a payback period.

M. CRERAR

The second stage of the process accounts for about 18 % of the total installed cost. On the single stage hemihydrate process one could expect an efficiency of around 94 %. In the two stage process we are expecting efficiencies of 99 % so that 5 % of  $P_2O_5$  recovery is effected in the second stage of the process.

Dr. DEKKER (Windmill, Netherlands)

I would like to come back to Mr. Wennberg's point about changing the rock and I think we have a general problem for today's contractors in a seller's market in which we are for phosphate rock. It seems to me that if you want to be rather independent as a  $P_2O_5$  producer, you must have the flexibility to use other rocks. My question is : the point is for the contractor to speak with the client what he really wants because if the client wants to change his rocks once every so often because of economic reasons, then the process must be able to follow and if we then also include that the same client may have commitments for his gypsum disposal to the construction industry. My question is, how could you as a contractor and as a licensee give certain guarantees so that the client does not get into difficulties with his own operations and with his by-product gypsum ?

M. QUINTON

On this point of negotiations with the prospective client, it is often the case that more than one phosphate rock is tested and in this case we test more than one rock and give guarantees on the number of rocks we test.

M. UUSITALO (Kemira Oy, Finland)

We had in use about the same system hemihydrate dihydrate process several years and we have got quite a lot of experience about that and we have found one very critical point; this point is to change the hemihydrate to dihydrate; so I want to ask when you have made pilot plant tests, what has been the time you have needed for Kola phosphate compared to Morocco phosphate, to change the hemihydrate to dihydrate. Then when you tell that you are getting a yield of about 99 %, how much have you calculated that you have changed from hemihydrate to dihydrate? If you are not reaching the whole 100 %, how much this is affected? I can mention that in our system we have never reached more than 80 % change from hemihydrate to dihydrate.

M. CRERAR

In our paper we mention that our work with different phosphates had given different times for transformation from the hemihydrate to the dihydrate in the second stage of the process. In the case of Morocco and Florida rocks times of 4 hours are easily achieved. In the case of Togo, we found an additive which would accelerate the rock transformation. However, we could not find an additive to do this with Kola rock and we found that the hemihydrate of Kola rock is extremely stable and at the moment we would not be prepared to offer our process to handle this material. I know that you've had the experience of using Kola for a two stage process but with Kola we found a transformation time of 10 hours. It does not seem to be economically worthwhile. The yield depends on the degree of transformation and we are expecting, based on our pilot plant and laboratory tests, to be working in the region of 100 % conversion in the plant using Morocco rock and the other rocks I mentioned, so that we do not expect to be substantially below the 99 % by virtue of having insufficient transformation.

M. ARCACHE (Société de Prayon, Belgium)

After all these commercial considerations, I would like to ask commercial questions : I see in your table N°3 corrosion of stainless steel, that the rate of corrosion in the hemihydrate section is in the order of 20 - 35 times higher than the dihydrate section. I don't understand why you chose 316 for the 65m<sup>2</sup> filter nor the figure given for the maintenance cost in conjunction with such corrosion. A second point is that the validity of the final gypsum which contains little P<sub>2</sub>O<sub>5</sub> is adversely affected by its 25 % free humidity and involving a very costly drying.

M. CRERAR

The corrosion figures you refer to indicate certainly that the corrosion rates are much higher in the hemihydrate section of the plant than in the dihydrate. This is fairly obvious. In fact, the material for the filter we are using on the TREPICA plant is 370 and not 360 now. The condition, the corrosion environment that the filter has to withstand is less severe than parts continuously immersed in the 50 % medium.

For example, pumps exhibit much greater corrosion than the filter does, but nevertheless, 370 is used on the filter and we don't expect to have any corrosion with that at all. The value of the by-product dihydrate as a building material has not been given any credit for in our economic comparison. So really the basis of the economic comparison between the dihydrate and the two stage hemihydrate processes is based only on making phosphoric acid and having to dispose of the cake and waste material; this shows a benefit for the two stage process and if there is an outlet for the by-product material which there could be in certain countries, this is a bonus and the cost of drying is something one could consider and determine the value in this particular case.

Dr. RAISTRICK (Cremer and Warner, U.K.)

Could we be told a little of the behaviour of this process on rocks which are high in chloride for example 0.3 to 0.4, 0.4 % Cl?

M. QUINTON

There is no doubt that rocks high in chloride create heavy corrosion problems in the hemihydrate stage, so we have to limit this. The process is limited to rocks with about 0.06 of this region of chloride in the rock. The second stage of course is not influenced. This applies to the one stage hemihydrate and to the HDH processes.

M. CREERAR

Yes, using a rock with 1 000 ppm of chloride, one can avoid only by careful design of the equipment, the points of corrosion on stainless steel items and one should minimise the use of stainless steel in the case of Togo rock. In the Windmill plant we have used agitators covered with rubber which is not a solution one would like to use in all cases. In the situation of high chloride one can use this as a means of combatting the problem. Pumps would obviously corrode rapidly. One would have to use exotic material, even to hastelloys and be prepared to change this on a fairly regular basis.

M. JUSTA (Chemoprojekt, Czechoslovakia)

Up-to- now we were informed that the recommended concentration of phosphoric acid produced on a commercial scale with the aid of FISON'S processes either hemihydrate or dihydrate is about 50 %  $P_2O_5$ ; this figure is usually given as the subject of guarantee and the conclusions of the previous paper and not only there was reported that the concentration can vary in wide ranges up to 54 %  $P_2O_5$ . I have two questions concerning this matter. Is it possible to expect that the concentration 54 %  $P_2O_5$  can be easily achieved and maintained during the long term operation of the commercial plant supposing Morocco rock is processed? and the second one: what changes in the production cost or life of equipment, and reliability of the process can be expected when the concentration of phosphoric acid is increased from the normal 50 %  $P_2O_5$  to the desired 54 % ?

M. QUINTON

The process can be operated up to 54 % with control over a long period at 54 %, but there are penalties if we operate at this high concentration. We find that 54 % or over 50 % going up to 54, there is a sharp increase in insoluble  $P_{205}$  in the hemihydrate. This of course is reflected in a high  $P_{205}$  concentration in the second stage which affects the size of crystal and the filtrability in that stage and, of course, in this particular case, will require a higher filter area in the second stage of the process. The other penalty is that we also get an increase in required filter area inasmuch that, although the crystals produced at the 54 % are of about the same size as at 50 %, there is a decrease in filtration rate due to an increase in viscosity of the acid. The results with the increase both in the hemihydrate filter size and the dihydrate size this should increase the actual investment cost.