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THE PRODUCTION OF 50% W/W P₂O₅ PHOSPHORIC ACIDDIRECTLY BY THE WET PROCESS:FISONS HEMIHYDRATE PROCESS

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1.0 INTRODUCTION

The manufacture of phosphoric acid for fertiliser use is almost entirely carried out by the so-called "Wet Process" in which phosphate rock is attacked by mineral acids. Sulphuric acid is usually used to digest the phosphate rock complex due to the relative ease of separation of calcium sulphate from phosphoric acid solutions. Depending on the temperature and acid concentration in the reaction system the calcium sulphate may precipitate either in the dihydrate, hemihydrate or anhydrous form. The methods by which satisfactory crystals of these forms are obtained, i.e. that will filter and wash economically are of great importance in the successful development of phosphoric acid processes.

Although the dihydrate method, producing 30% P₂O₅ acid is by far the most common of the processes operating today, other wet processes have been under investigation for a long time. In 1927 work under Nordengren (1) at Landskrona was directed towards the development of a strong acid process through a hemihydrate or anhydrite route. This did not reach any industrial application at that time due to technical difficulties and the lack of suitable materials of construction, particularly for the filter. In 1953 after further work at Landskrona a plant was designed (1) having a maximum capacity of 12 - 13 tonnes/day P₂O₅ which was built at Vercelli, Italy. This process was based on the anhydrite method and produced acid of 40 - 45% P₂O₅ concentration. The crystals were in the form of agglomerates and to obtain satisfactory operation it was found necessary to employ a reactor which was intermittently charged. Based on this experience, a larger plant was built (2) at Landskrona in 1956 which was operated at about 30 tonnes/day P₂O₅, first by an anhydrite and then in 1958 by a hemihydrate method. The main reasons given for this change to a hemihydrate process were lower maintenance costs, the avoidance of external heat requirements due to a lower reaction temperature and the elimination of the need for intermittent reactor operation. In 1963 the plant was converted to a dihydrate process producing 30% P₂O₅ acid.

Of more recent years other processes have been described in the literature (3) based on a recrystallisation step and producing acid of approximately 40% P_2O_5 concentration. These processes consist in first forming hemihydrate, filtering this off from the concentrated acid, followed by recrystallisation to gypsum, refiltering and completion of the washing.

Fisons Limited have for many years been carrying out extensive basic studies on the manufacture of wet process acid, with the primary objectives of improving the Company's existing manufacturing plants and also of developing new processes. Work has proceeded \times simultaneously using bench and pilot plant equipment and the results have led to the design and operation of a 40 tonnes/day P_2O_5 plant capable of producing 50% w/w P_2O_5 phosphoric acid directly without the need for evaporation. The development of this process has been published (4) up to the time of the commissioning of the 40 tonnes/day P_2O_5 plant.

The present paper summarises briefly the laboratory and pilot plant development work before describing the operating experiences and results obtained in the small commercial scale plant.

2.0. THEORETICAL CONSIDERATIONS

Following a study of the limits of stability of calcium sulphate in the system $CaSO_4 - P_2O_5 - H_2O$ it was concluded that it should be possible to produce calcium sulphate hemihydrate in a stable form over a wide range of P_2O_5 concentrations. There appeared to be no advantage in operating under conditions favouring the formation of anhydrite. It was also realised at an early stage that one of the main problems to be faced would be to produce hemihydrate crystals in an environment which would promote satisfactory crystal growth. There is no doubt that this was one of the main reasons which had so far prevented the successful development of a concentrated acid process. Other difficulties which are present in all wet process phosphoric acid development work lie in the number and interaction of variables and the need for long residence times within the reaction system. This means that a systematic study of a large number of variables, although feasible, becomes unrealistic in practice due to the extensive time involved. To minimise this disadvantage, rapid test methods were developed to classify the hemihydrate crystals produced under a given set of operating conditions. This allowed test runs to be terminated as soon as equilibrium was confirmed and so shortened the investigation.

\times All the laboratory and pilot plant work was carried out at the Levington Research Station of Fisons Limited, Ipswich, England.

3.0 TEST METHODS

In general three methods were used to evaluate the crystal phases: X-ray diffraction for identifying the hydrate form, specific surface area measurement, and a filtration test.

Specific surface areas were determined by an air permeability method and gave a measure of the external surface of the crystals. It is possible using this technique to obtain a result within a few minutes once a dried sample of the crystal phase has been isolated. The specific surface area, porosity and permeability data obtained gave a good indication of the filtration and washing characteristics of the slurry.

The filtration test used was specially developed to simulate the operating characteristics of a multi-wash stage filter of the Prayon or Elmco type and has been extensively used on both hemihydrate and dihydrate slurries. By careful design of experiments it is possible to estimate from the test data the filter area required to achieve a given output together with the expected P_2O_5 washing losses. This technique has been used to test slurries on existing manufacturing units and the results gave good agreement with the known performance of production sized filters. Extensive use of the filtration test has also been made to indicate the mode of filter operation likely to minimise P_2O_5 washing losses.

4.0 LABORATORY AND PILOT PLANT INVESTIGATIONS

The laboratory investigation of this process aimed at indicating the most favourable reactor sequences and operating variable ranges which could later be assessed on a pilot plant. Although the main criterion by which trials were compared was crystal size, other factors such as rates of rock dissolution and the nature and magnitude of P_2O_5 losses were also evaluated.

Both the laboratory and pilot plant work were carried out under continuous operating conditions, thus ensuring that precipitation rates and concentration levels approached commercial practice. Samples were taken at regular intervals from the reaction system and the approach of equilibrium conditions was indicated by the trend in specific surface area measurement. Table 1 shows the frequency of sampling and the analyses made.

TABLE 1

Sampling and Analytical Procedures

<u>Sample</u>	<u>Location</u>	<u>Analysis</u>	<u>Frequency</u>
Filtered Slurry	Outlet of first reactor	P_2O_5	2 hourly
		SO_4	hourly
Filtered Slurry	Outlet of second reactor	P_2O_5	2 hourly
		SO_4	hourly
Slurry	Outlet of second reactor	Solids content	2 hourly

<u>Sample</u>	<u>Location</u>	<u>Analysis</u>	<u>Frequency</u>
Dry hemihydrate	Outlet of second reactor	Specific Surface Area	2 hourly
Dry hemihydrate	Outlet of second reactor	P ₂ O ₅	4 hourly
Wash acid	Feed tank	P ₂ O ₅ , SO ₄ s.g.	Every tank changeover
Sulphuric acid	Feed tank	SO ₄ s.g.	Every tank changeover.

The hemihydrate after drying was analysed for total P₂O₅ (T), free acid P₂O₅ (A) and unreacted phosphate rock P₂O₅ (R). From these determinations the insoluble (I) and "lattice" P₂O₅ contents (L) were estimated from the following equations:

$$L = T - (A + R)$$

$$I = T - A$$

The free acid P₂O₅ levels in this case were only used for the above calculation and did not give any indication of the acid losses expected during filtration. These were assessed on pilot plant slurries using a filtration test involving three or four wash stages as described under "Test Methods".

Results

Laboratory trials showed at an early stage that it was not possible to grow hemihydrate crystals to a satisfactory size when using a single reaction vessel. Consequently this led to a study of multiple reactor systems in which all other variables were investigated. For a given P₂O₅ product acid concentration the variables which had the most effect on the hemihydrate crystal size were:-

- (a) the relative reactor volumes,
- (b) the amount and rate of precipitation at different parts of the system,
- (c) reaction temperature,
- (d) mixing.

Apart from the effect of agitation which was investigated only to a limited extent in the laboratory, the most promising operating ranges for the other variables were evaluated and this information was used as a basis for the design of pilot plant equipment.

The pilot plant was designed for a nominal throughput of 20 lb/hr. phosphate rock and comprised reaction vessels arranged as a cascade, followed by a filter feed tank. This size of plant had been found from previous work to be adequate for investigating the rate determining factors affecting reaction, crystallisation, and the size (for sizing) of large units. Provision was made for recycling slurry from the second or third vessel to the first and the hemihydrate produced was removed by means of a batch filter.

Up to July, 1967 the total experience obtained on pilot plant operation amounted to over 7,000 hours. Generally the pilot plant results confirmed the effects of process variables indicated from the laboratory unit. There was one main difference, however, in that the hemihydrate produced on the pilot plant filtered and washed more rapidly than in the laboratory. Reasons for this were the differences in impurity levels between the two systems and the fact that on the pilot plant the slurry had a much higher solids content. Both these factors influence the crystallisation of hemihydrate.

VARIABLES AFFECTING CRYSTAL SIZE

Precipitation

Both laboratory and pilot plant results showed that where precipitation of calcium sulphate occurred substantially in one vessel, hemihydrate of a very high specific surface area was produced. By allowing the precipitation to occur stepwise in a multi-reactor system, a means was found of substantially reducing the surface area and obtaining satisfactory filtration and washing properties. Figure 1 illustrates this effect by relating the specific surface area to the amount of hemihydrate precipitated in the first vessel of a multi-reactor system.

Reactor Sequence

There appears to be no advantage in using more than four reaction stages. For most phosphate rocks two stages are normally sufficient and better crystals are obtained when the first stage is larger than the second.

Recycle

To provide the right degree of hemihydrate crystal seeding it is necessary in this process to recycle slurry from a later stage back to the first reaction vessel. This influences the sulphate level in the first reactor and this must be allowed for to ensure that precipitation remains in the optimum region as illustrated in Figure 1.

Reaction Temperature

The specific surface area of the hemihydrate is influenced by a change in reaction temperature. The optimum level depends on the P_2O_5 concentration within the reaction system, but will fall within the range 85-110°C.

Mixing

At all points where precipitation occurs the degree of mixing can influence the size of hemihydrate crystals produced. On the pilot plant many agitation systems were investigated and these included variation in impeller design and the total number of agitators. The most promising were single or multiple turbines

which give higher flows for a given power than the more conventional flat bladed designs.

VARIABLES AFFECTING P_2O_5 LOSSES

The major P_2O_5 loss in the wet process is that contained in the calcium sulphate crystal lattice. This is termed "lattice" P_2O_5 but other definitions are used which indicate broadly the same thing, i.e. "nitrate - soluble P_2O_5 " or "co-precipitated P_2O_5 ". For similar conditions of precipitation, hemihydrate will contain much less "lattice" P_2O_5 than gypsum. This is usually attributed to the fact that gypsum and dicalcium phosphate dihydrate are isomorphous.

In the hemihydrate process there are two main process variables which affect "lattice" P_2O_5 losses for a given phosphate rock, these are:-

- (a) Product and P_2O_5 concentration;
- (b) Ratio of SO_4/CaO fed to the first reaction stage.

Other variables such as reaction temperature and sulphate ion concentration in the recycle slurry also affect lattice P_2O_5 losses but only to a small extent.

Figures 2 and 3 illustrate the variation of lattice P_2O_5 loss with product acid P_2O_5 and SO_4/CaO ratio respectively.

The product acid P_2O_5 concentration also influences the rock P_2O_5 losses (Figure 4) and filtration wash losses (Figure 5).

Hemihydrate Crystals and Filtration

Under the correct operating conditions the hemihydrate produced on the pilot plant was fast filtering and could be washed economically. Four wash stages are normally required and the stability of the crystals is such that there is no danger of any transformation to gypsum either in the reaction system or on the filter during washing. This is due to the complete absence of gypsum seed which catalyses the transformation and to the large size of the crystals themselves.

5.0 40 TONNES/DAY PLANT AT KING'S LYNN, ENGLAND.

The successful outcome of the laboratory and pilot plant development led to the design and erection of a plant having a nominal design output of 40 tonnes/day P_2O_5 . This was completed and commissioned during 1967, and its main objective, apart from determining the operating characteristics of the process, was to determine the effect of a 700 fold increase in reactor volume on crystal size and P_2O_5 extraction efficiency. The plant was intended to be temporary only and was incorporated into an existing phosphoric acid plant site at the West Norfolk Fertilisers factory at King's Lynn. Up to the time of the final closure of the factory and the curtailment of all manufacturing operations, the new hemihydrate process was in operation for three months producing 50% w/w P_2O_5 acid directly in the reaction system.

Sufficient information has been obtained on plant operation and results to allow the design of commercially sized plants.

Materials of Construction

A very large programme of corrosion testing was planned and put into operation for this project. Tests were designed to determine corrosion and erosion rates under static and dynamic conditions using a wide range of metallic, rubber and plastic materials.

Apart from the higher grade alloys all the metallic materials tested were unsatisfactory in 50% P_2O_5 acid slurries at temperatures approaching 100°C. Cast alloys of the type 54 Ni 23 Cr 6 Mo are suitable for expendable items such as pump casings and impellers, some of the cheaper hardened castings of the type SNi 26 Cr 1.5 Mo were also found to be suitable for this duty.

Plastics such as polypropylene and high density polyethylene are satisfactory provided erosion conditions are not too severe. These materials are suitable for fittings and also for pipework on certain duties. Rubbers such as chlorbutyl and Hypalon are also suitable but a good deal of variation in resistance properties was found depending on the choice of manufacturer. Mild steel pipework lined with chlorbutyl rubber is satisfactory for handling reaction slurry and concentrated acid, and Hypalon is suitable for armoured hose for use of the filter.

Agitators may be fabricated from mild steel or stainless steel lined with butyl rubber. As an added protection, polypropylene wear strips may be incorporated into the design.

On the filter which is exposed to concentrated acid intermittently, it is possible to use lower grade alloy steels such as 317 E.L.C. or E.W.4.A. For longer service, however, it is preferable to use higher grade alloys such as Osborn's W.J., H.V.9 or Uranus B.6 i.e. 25 Ni, 21 Cr, 4.5 Mo.

Reaction vessels should be constructed of mild steel, lined with butyl or neoprene rubber and carbon brick. Fittings may be in polypropylene or butyl rubber lined, mild steel.

Plant design

The design of the reaction system was based on the pilot plant results and was primarily intended for use with Morocco rock. Two reaction vessels only with a filter feed tank were used and all of these were fabricated from "Celmar", which is a polypropylene laminate reinforced with fibreglass. The main reasons for this choice of material were the fabrication time and cost. It would also have been extremely difficult to install lined, mild steel reactors as the bulk of the fabrication would have had to be carried out in situ in a very confined area adjacent to a working plant.

The reaction vessels (total working volume 108 m^3) were increased in size from the pilot plant capacities according to the P_2O_5 output required, at the same time maintaining geometric similarity. Agitation of the reaction slurry was provided by six bladed 45° angled turbines operating at the same power per unit volume ratio as the pilot plant. The filter feed tank had a four bladed 45° angled turbine operating at a lower power per unit volume than the main reaction vessels. All the agitator blades and shafts were fabricated in mild steel covered with a loose polypropylene liner. Pumps used for transporting concentrated acid or slurry were made in cast alloy of the type 5 Ni 36 Cr 1.5 Mo. The existing rock feeding system was modified to allow coarse phosphate rock to be fed into the first reaction vessel. In addition a rock screening unit was added to scalp off particles in the feed greater than 2 mm.

A simplified flow diagram of the King's Lynn plant is shown in Figure 6. Coarse rock is fed to the first reactor together with slurry which is recycled from the second reactor. The reaction slurry flows by gravity to the second vessel where sulphuric acid and wash acid from the filter are normally added, before overflowing to a filter feed tank. Filtration of the reaction slurry was effected by means of an existing Prayon filter and associated equipment. "Dry" hemihydrate filter cake was discharged via a hopper and conveyor to a bunker from where it was finally transferred by lorry for disposal to a diamed gravel pit. The Prayon filter had 12 pans fabricated from HV7 alloy steel and these had an effective area under vacuum of 12.3 m^2 .

Results

The 40 tonnes/day P_2O_5 plant was operated under the same process conditions as the pilot plant with the following main objectives:

- (a) To determine the effect of a 700 fold increase in reactor volume on crystal size and extraction efficiency.
- (b) To locate difficulties in operation, particularly in the movement of hemihydrate slurries at temperatures above 80°C and in the operation of a standard, commercially available filter.
- (c) To assess the degree of scaling in pipelines and the general corrosion and erosion properties of the concentrated acid slurries.
- (d) To determine any difficulties in the disposal of "dry" hemihydrate filter cake.

P_2O_5 Extraction and Filtration Efficiencies

The pilot plant results showed that using different agitation conditions there were no significant differences in "lattice" P_2O_5 losses when operating at mixing times * from 5 to 11 seconds in the first reaction vessel.

* Mixing times were determined using models which simulated the hydrodynamic behaviour of both the pilot plant and the 40 tonnes/day P_2O_5 plant.

In the case of the 40 tonnes/day plant, however, the mixing time is of the order of 32 seconds and it was considered that some change in P_2O_5 losses may be possible due to the much slower rate of mixing.

In Figure 7 the insoluble P_2O_5 losses obtained on the 40 tonnes/day P_2O_5 are compared with the correlation found from the pilot plant results. Although the spread of data obtained on the larger plant is slightly more than found on the pilot plant, the points fall about the correlation curve and no significant differences can be detected compared with the pilot plant results. The increased scatter of the King's Lynn results was due to fluctuations in sulphate levels which were caused by the manual control of the slurry recycle. This is discussed later under the section "Operation".

Using three wash stages on the filter the free acid P_2O_5 washing losses obtained at King's Lynn were the same as those expected from the pilot plant results. On the 40 tonnes/day plant the free acid P_2O_5 losses varied between 0.6 to 0.7% w/w on the dry hemihydrate compared with a range of 0.2 to 0.8% w/w found on the pilot plant. When producing 50% w/w P_2O_5 acid and using three wash stages the filter is operating in an unstable region and this accounts for the variable results obtained. Using four wash stages the free acid P_2O_5 losses fall to 0.1% w/w in the dry hemihydrate and the filter is outside the unstable region. When producing 45% P_2O_5 acid or a lower concentration, it is not so critical whether three or four wash stages are used. In this case the efficiency falls by about 0.25% by the use of three instead of four wash stages.

Neglecting mechanical losses, the efficiencies for the hemihydrate process for different P_2O_5 product acid concentrations are as follows:-

<u>Product Acid</u>	<u>Efficiency Based on Total P_2O_5 Losses</u>
<u>% w/w P_2O_5</u>	<u>In Discharged Hemihydrate %</u>
40	97.0
45	96.4
50	94.0
55	88.6

Crystal Size and Filtration

For the same total reaction volume per unit P_2O_5 produced, the hemihydrate crystals were smaller on the 40 tonnes/day plant than found on the pilot plant, although the basic shapes of the crystals were the same. For example, the specific surface areas of the pilot plant crystals ranged from 600 to 800 cm^2/g , whereas, at King's Lynn, values of 1100/1200 cm^2/g were obtained. It was found on the 40 tonnes/day plant that reducing the rock feed to 75% to the design figure caused the specific surface area of the crystals to fall within the normal range found in the pilot plant. This was contrary to pilot plant results which showed the specific surface area of the crystals to be insensitive to throughput over a wide range.

Subsequent work at Levington has confirmed that the reason for this discrepancy was the presence of an "aerated" slurry in the case of the King's Lynn plant.

The Prayen filter used had sufficient area to cope adequately with a rock feed of 85% of design. It was not possible to exceed this throughput because of cooling limitations.

Product Acid Composition

The following main differences were found between the compositions of 50% w/w P_2O_5 acids produced from the hemihydrate and a typical gypsum process:

<u>Analyse of 50% w/w P_2O_5 (Solid Free)</u>		
	<u>Hemihydrate Process</u>	<u>Typical Gypsum Process</u>
Fe_2O_3	0.35	0.42
Al_2O_3	0.10	0.44
SO_4	1.8 - 2.0	4.0
F	1.0	0.3
Solids	1.5	4 to 8

In the hemihydrate process the higher concentration of P_2O_5 in the reaction system depresses the solubility of calcium and aluminium in the product acid and this is responsible for the substantial reduction in solids content of the filtered acid and the precipitation of the bulk of the aluminium with the hemihydrate. The fluorine will always be higher in the hemihydrate process unless provision is made to include a fluorine stripper, mainly because less water is evaporated per ton P_2O_5 produced than in the gypsum process.

As the hemihydrate process acid contains less impurities it will produce more concentrated products on ammoniation compared to gypsum process acid. There will also be less reversion to water insoluble P_2O_5 because of the much lower aluminium content.

Plant Operation

From the beginning of the project it was realised that the period of operation at King's Lynn was limited and to this end the design basis throughout was one of minimum cost. Instrumentation was kept as simple as possible and, apart from the control of acid levels in the filter seal tanks, all operations were manual. This was a disadvantage in the case of the control of the recycle slurry flow, as frequent adjustments to the control valves were found to be necessary. The provision of a flow controller would have greatly simplified operation and this would have improved the sulphate control and reduced the variability in process results. On a permanent installation the fitting of a flow controller would be essential. In general the control of a hemihydrate process was found to be no more difficult than that of a gypsum process.

If, however, the operating conditions are allowed to move well away from the control points then the resulting effects are greater in the case of the hemihydrate process.

An important advantage of the hemihydrate process which was found during plant operation was that very little scaling occurred in slurry pipelines and pumps. Also, when the reaction vessels were drained and washed out, there was little build-up of scale on the agitators and reactor walls. In 50% P_2O_5 acid the solubility of calcium sulphate is much lower than in 30% P_2O_5 acid and this accounts for the reduced scaling obtained in the hemihydrate process compared to a gypsum process.

At the temperature of the process when producing 50% P_2O_5 acid the concentration of silicon tetrafluoride in the cooling air was high and this led to silica blockages in parts of the air extract ducting. This problem was overcome by fitting water spray jets at intervals along the ducting prior to the gas scrubber.

The air cooling system installed at King's Lynn gave only sufficient cooling for a rock feed of 85% of design and never allowed a comfortable margin to compensate for variations in the flow of return acid and filter wash water. It was not possible in the time available to modify this system to provide higher air velocities. As the rate of heat transfer was lower than anticipated using air cooling, the use of evaporative cooling is preferred for the hemihydrate process.

At no time during the operation of the plant was there any indication of the formation of anhydrite or gypsum in the reaction slurry. This was in spite of the fact that for short periods the reaction temperatures were as low as 65°C and as high as 115°C. There were also no signs of any hydration and hardening of the hemihydrate filter cake during the filtration and washing cycles provided the filter cloths were adequately cleaned each filter cycle.

One problem which was encountered was the disposal of cloth wash water which contained a higher proportion of solids than was expected. Early attempts to dispose of this water directly failed due to settling, transformation to gypsum and build-up. It was found essential to pump the cloth washings away at high linear velocities to a holding tank of sufficient volume to allow transformation to gypsum to occur. Once transformation had taken place then the slurry could be pumped as effluent in the normal manner. This arrangement operated very well at King's Lynn even though the pipeline from the filter to the transformation tank was over 400 yds. long.

There was no indication of any filter cloth blinding during two months operation. Filter cloths installed at the start of commissioning were giving the same filtration rates as cloths fitted near the time of the plant shut down.

Given adequate cloth washing per cycle and a weekly maintenance wash then cloth life in the hemihydrate process is expected to be longer than in a conventional gypsum process.

The acid fumes liberated from the filtration and concentrated acid wash stages were found to be considerable when producing 50% P_2O_5 acid, and it was found necessary to fit a fume extract hood over approximately 50% of the filter area to avoid this trouble. Fuming was also troublesome above the open product acid storage tanks and acid seal tanks and fume extracts would be needed on a permanent plant.

Over the whole period of operation of the King's Lynn filter there were no delays due to difficulties in the final removal of hemihydrate by lorry. Under normal operating conditions the discharged hemihydrate was still friable after standing for twenty four hours. That setting which did occur was due to the carry-over of part of the cake wash water which passed down the conveyor and fell on to a small section of the heap, producing a localised "set". Using a modern filter, water spillage from this source would be negligible. An alternative cake disposal system would be to slurry the hemihydrate with water, transform to gypsum and pump to effluent in the normal manner used in a gypsum process.

6.0 FEATURES AND ECONOMICS OF NEW PROCESS

Fisons new hemihydrate process is more economic than a conventional gypsum process because no evaporation stage is required and grinding is limited to the crushing of oversize materials greater than 2 mm. There is normally, therefore, a significant reduction in investment costs. The actual savings in operating costs will largely depend on the price given to steam. If this is assumed to represent the value $\frac{1}{2}$ of the electricity which could be produced from the steam, then the hemihydrate process gives savings in operating costs of 26 shillings per ton P_2O_5 as 50% acid compared with a gypsum process.

The main process features and advantages may be summarised as follows:-

- (a) The process is capable of producing acid of 50% P_2O_5 concentration directly without the need for evaporation.
- (b) A coarse phosphate rock is processed, and it is only necessary to grind materials which will not pass a 1/16" screen.
- (c) The phosphoric acid produced has substantially lower aluminium sulphate and solids contents but a higher fluorine content than is usual with the dihydrate process.

* Cost of 20 p.s.i.g. steam	= 4.6 shillings/1000 lb
Cost of 200 p.s.i.g. steam	= 7.8 shillings/1000 lb

- (d) The process is flexible in that acid of any concentration between 40 and 50% P_2O_5 can be produced without plant modification.
- (e) Only one filter is required and this should provide four wash stages when producing 50% P_2O_5 acid.
- (f) The King's Lynn plant was operated on Morocco rock only. Other phosphate rocks have been processed on the Levington pilot plant. Generally, sedimentary rocks give similar results to Morocco rock provided the iron and aluminium contents are not high. Rocks such as Florida, which have high iron and aluminium contents, give higher P_2O_5 losses but the results obtained varied with rock source and % B.P.L. value. Igneous rocks such as Kola give large crystals but a higher rock P_2O_5 loss unless the plant is designed specifically for Kola rock.
- (g) The process has been operated successfully as a small commercial sized plant and no serious problems were found with respect to corrosion and erosion of materials of construction and it is considered that these should present no limitations on the process. There were also no signs of scaling of pipelines handling concentrated acid slurry.
- (h) The hemihydrate produced is stable both in the reaction system and on the filter and, provided equipment is suitably designed and adequate fluid linear velocities are provided, the disposal of hemihydrate either as "dry" or "wet" discharge presents no difficulties.

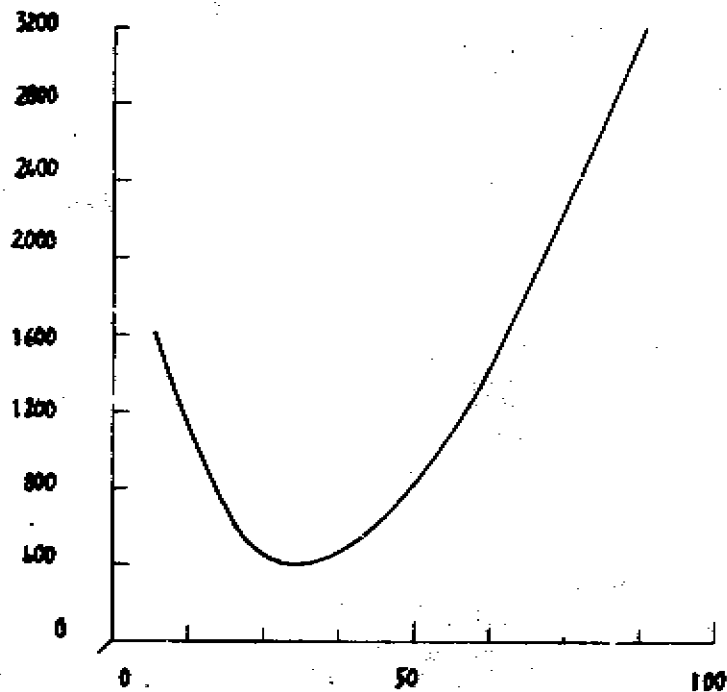
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FIGURE 1 : VARIATION OF SPECIFIC SURFACE AREA OF HEMIHYDRATE WITH PRODUCT ACID P2O5

VARIATION DE LA SURFACE SPECIFIQUE DE L'HEMIHYDRATE EN FONCTION DE LA CONCENTRATION EN P2O5 DE L'ACIDE MARCHAND

Specific surface area of hemihydrate; cm^2/g .
Surface spécifique de l'hémihydrate; cm^2/g .

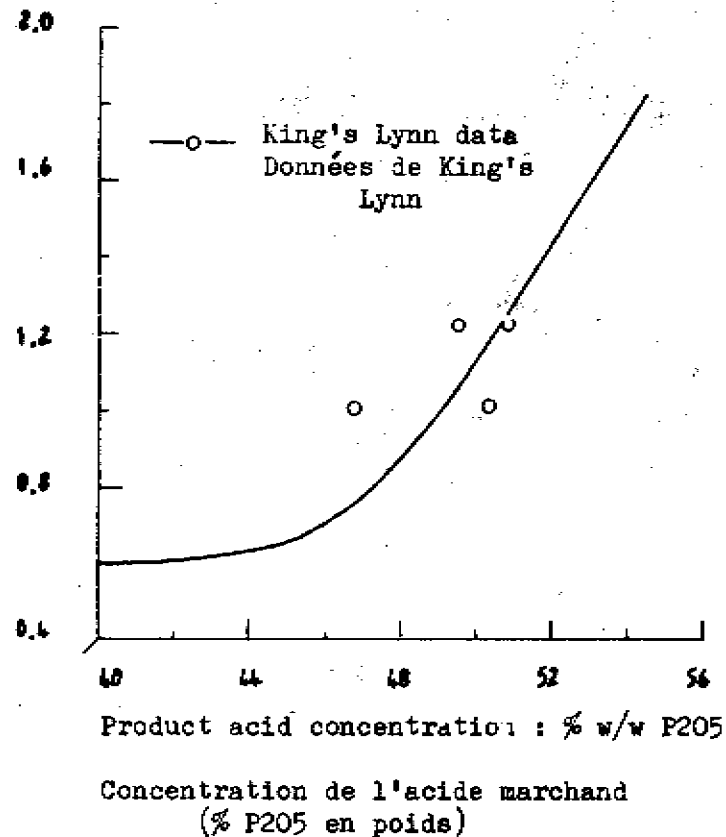


Calcium precipitated in first stage :
% of total
Calcium précipité au 1er étage :
% du total

Lattice P2O5 : % w/w on dry hemihydrate
P2O5 syncristallisé; % de l'hémihydrate sec

FIGURE 2 : VARIATION OF LATTICE P2O5 LOSS WITH PRODUCT ACID P2O5

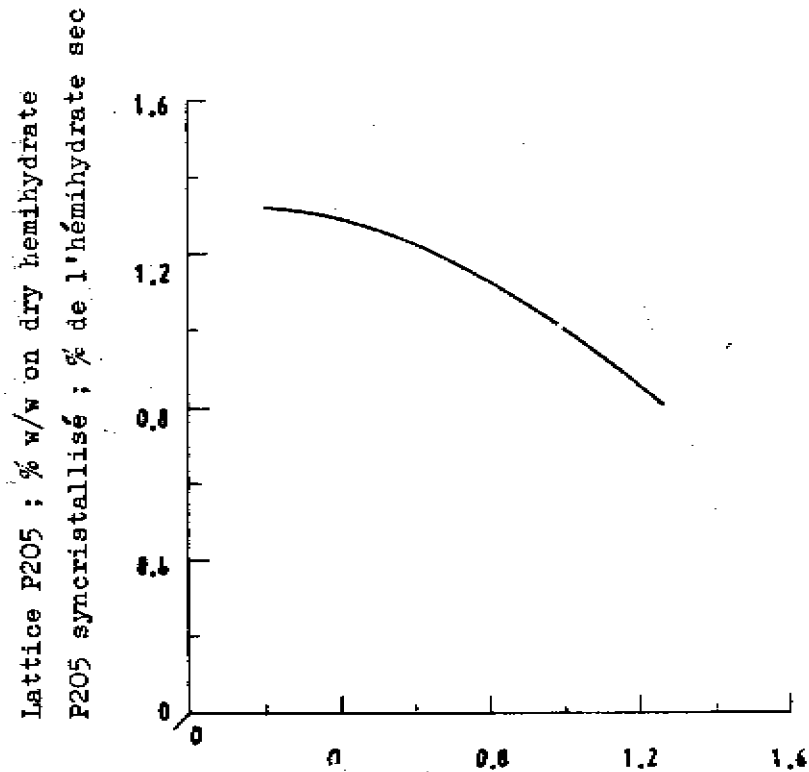
VARIATION DES PERTES DE P2O5 PAR SYNCRISTALLISATION EN FONCTION DE LA CONCENTRATION DE L'ACIDE MARCHAND



Product acid concentration : % w/w P2O5
Concentration de l'acide marchand
(% P2O5 en poids)

FIGURE 3 : VARIATION OF LATTICE P2O5 LOSS WITH SO₄/CaO RATIO

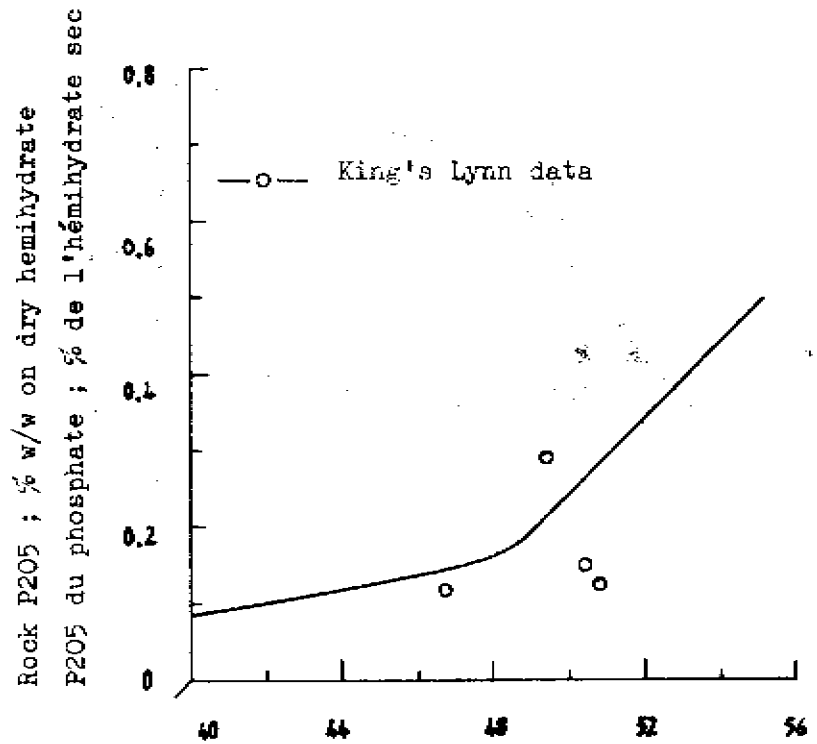
VARIATION DES PERTES DE P2O5 PAR SYNCRISTALLISATION EN FONCTION DU RAPPORT SO₄/CaO



SO₄/CaO fed to first stage
Rap. r. SO₄/CaO à l'entrée du premier stage

FIGURE 4 : VARIATION OF ROCK P2O5 LOSS WITH PRODUCT ACID P2O5

VARIATION DES PERTES DE P2O5 LU MINÉRIEL PHOSPHATE EN FONCTION DE LA CONCENTRATION EN P2O5 DE L'ACIDE MARCHAND

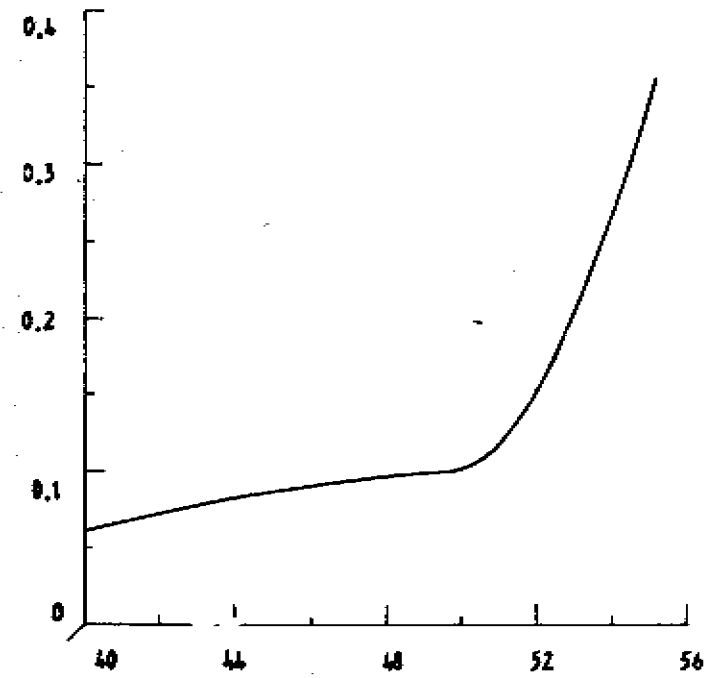


Product acid concentration; % w/w P₂O₅
Concentration de l'acide marchand
% P₂O₅

FIGURE 5 : VARIATION OF FREE ACID WASH LOSSES WITH PRODUCT ACID P2O5

VARIATION DES PERTES D'ACIDE LIBRE DE LAVAGE EN FONCTION DE LA CONCENTRATION EN P2O5 DE L'ACIDE MARCHAND

Free acid P2O5 ; % w/w on dry hemihydrate
P2O5 de l'acide libre ; % de l'hémihydrate sec

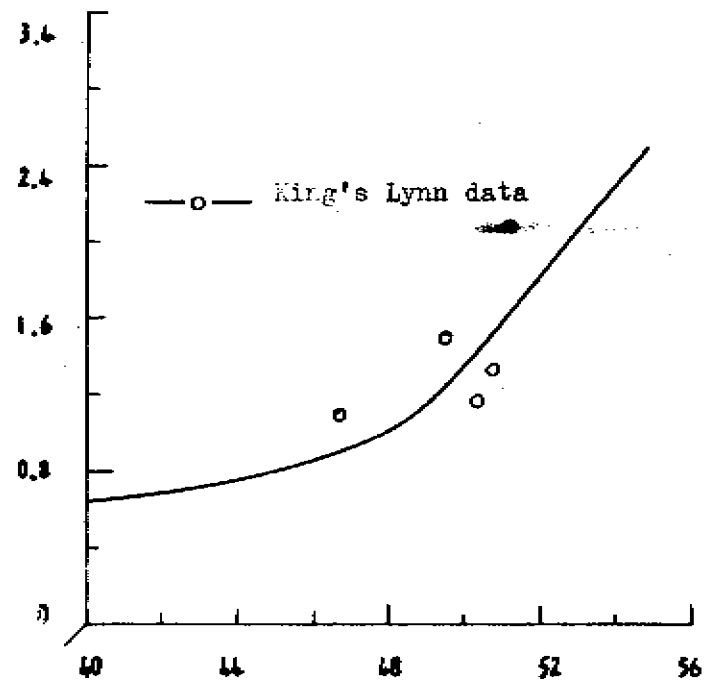


Product acid concentration ; % w/w P2O5
Concentration de l'acide marchand % P2O5

FIGURE 7 : VARIATION OF INSOLUBLE P2O5 LOSSES WITH PRODUCT ACID P2O5

VARIATION DES PERTES DE P2O5 INSOLUBLE EN FONCTION DE LA CONCENTRATION EN P2O5 DE L'ACIDE MARCHAND

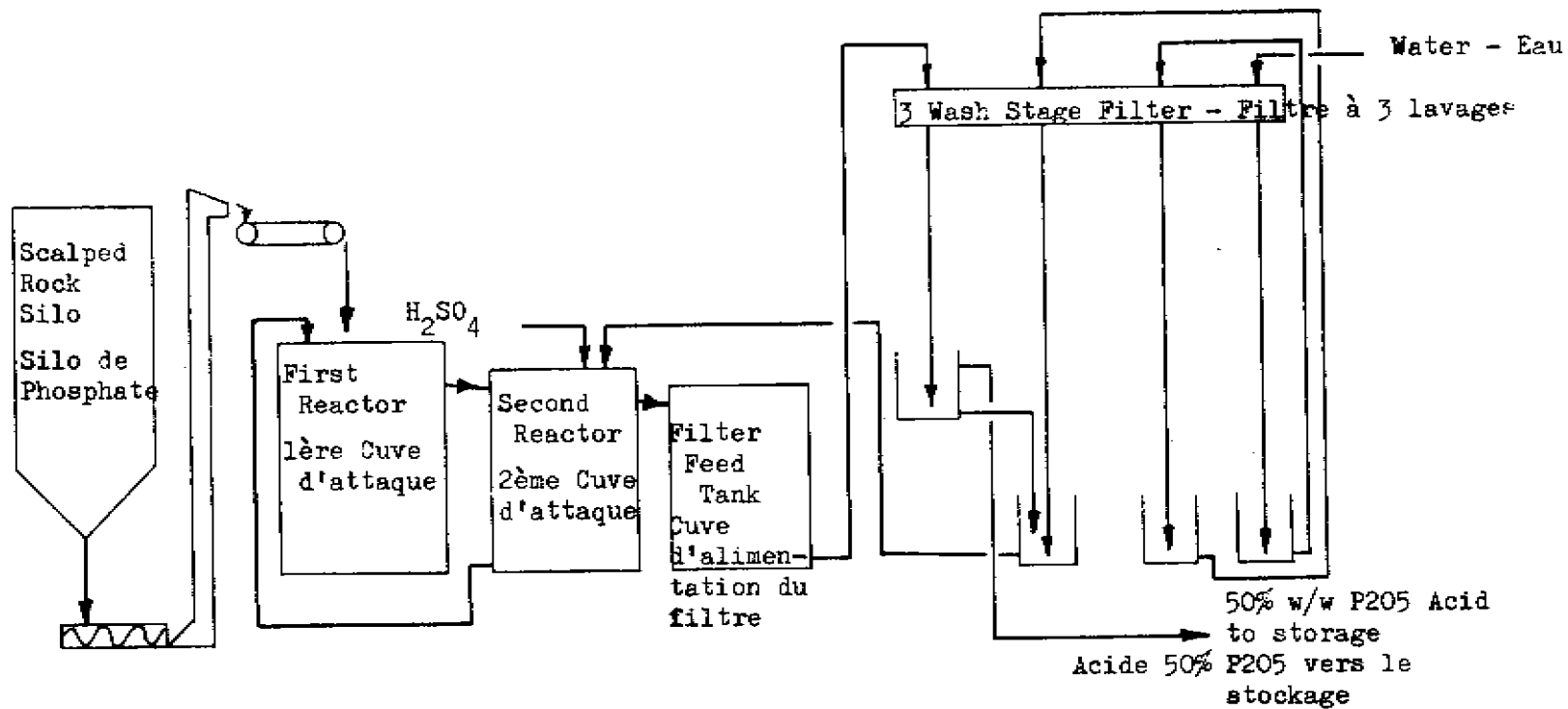
Insoluble P2O5 ; % w/w on dry hemihydrate
P2O5 insoluble ; % de l'hémihydrate sec



Product acid concentration ; % w/w P2O5
Concentration de l'acide marchand % P2O5

FIGURE 6 : SIMPLIFIED FLOW DIAGRAM OF 40m.t.p.d. P2O5 PLANT AT KING'S LYNN

SCHEMA SIMPLIFIE D'UN ATELIER DE 40t/j P2O5 A KING'S LYNN



DISCUSSION

MR. ROBINSON: This paper describes the development of a phosphoric acid process capable of producing a 40 - 50% P_2O_5 acid directly without a need for an evaporator stage. A feature of the process is that hemihydrate is produced rather than gypsum and is filtered and washed using conventional filtration equipment. Fisons Ltd. having engaged on the development of this project since 1967, the project has progressed through the laboratory and pilot plant stages to the design and erection of a 40 tpd P_2O_5 plant at King's Lynn in England. The object of this plant was to demonstrate that the process could be operated in a commercial manner and to determine the effect of the 700 fold increase in reaction volume from the pilot plant scale on the P_2O_5 extraction efficiency and hemihydrate crystal size. This plant was commissioned during 1967 and operated using Morocco rock phosphate, producing a 50% acid. This was operated until the final closure of the factory. A paper has previously been published on the laboratory and pilot plant development. The present paper compares the results from the 40 tpd plant with the pilot plant and also reviews the main variables which affect the hemihydrate crystal size and P_2O_5 extraction efficiency. The performance of the King's Lynn plant demonstrated that the process could be successfully operated under commercial conditions. The hemihydrate produced was stable both in the reaction system and during filtration. No trouble was experienced with the final disposal of the hemihydrate. This is achieved at King's Lynn by conveying the filter cake to a bunker then loading it into lorries during the dayshift only. The P_2O_5 extraction efficiencies we obtained on the 40% tpd plant were not significantly different from those of the pilot plant. The crystal size, however, did tend to be smaller on the 40 tpd plant, although the shape of the crystals remained the same. The acid produced had less solid content and also less aluminium content, and there is also far less tendency to scale in the pipelines carrying acid slurry, compared with the normal gypsum process.

In the paper, the figures of the new process and the operating conditions and experience gained at King's Lynn are given. The paper also gives the P_2O_5 extraction efficiencies based on the total losses in the hemihydrate full range of P_2O_5 product acid concentration.

As the hemihydrate process can handle a coarse ground phosphate rock, and no evaporative stage is needed, there is a saving in the investment cost. The saving in operating costs depends to some extent on local factors, but if we assume that the cost of steam is equivalent to the value of electricity which could be produced from the steam, then costings have shown savings of about 26 to 30 shillings per ton of P_2O_5 from the hemihydrate process compared to the gypsum process. The King's Lynn plant was operated only with Morocco phosphate rock. We have tested a variety of other rocks on the pilot plant equipment, including Togo, Kola, and Florida rocks, calcined and uncalcined of different grades and from different sources. Generally the process is influenced to some extent by the nature of the rock source. Some rocks give higher filtration rates than others, and also the P_2O_5 extraction efficiency varies slightly. In some cases there is an advantage in using a modified reaction system compared to the one described in the paper.

MR. Y DE TUNCO (Péchiney-St. Gobain, France): It must be recognised that, compared with the classical gypsum process, the hemihydrate process appears to present numerous difficulties, unless special precautions are taken. These can include a poor reaction yield with a tendency to reaction blockage, the presence of syncrystallized P_2O_5 in the gypsum, sometimes difficult filtration, the more so since one is seeking to improve the yield, considerable corrosion, more extensive scaling and a limited amount of water, since the main aim of this process is to make a concentrated acid which is separated from hemihydrate.

We emphasise these difficulties not to condemn the hemihydrate process but to highlight the importance of the work presented today.

In particular, the details of materials withstanding corrosion are extremely interesting, and we note that you have not hesitated in certain cases to use plastic materials which should have enormous potential development possibilities in the phosphoric acid industry, provided the development is in relation to their quality.

It is undoubtedly the complexity of the problem which led Fisons to work first with a pilot plant and then with a small scale industrial plant. Of course, 40 tpd P_2O_5 was considered 10 years ago to represent quite a substantial production. In view of their experience, I should like to ask the authors whether they consider it indispensable to pass through the stages of the pilot plant and a 40 tpd P_2O_5 plant to extrapolate to present day production capacities of 300 tpd and more. In other words, which of these two stages taught you more, having regard to the economics of the operation.

With regard to the preparation of the slurry, I do not doubt that your process has been well studied and developed, but I would not personally condemn the single, non-compartmental tank. In the field of gypsum, spectacular reversals are not unknown.

Our own studies have shown that it is possible to work with a single tank at a lower temperature for equal concentrations. This presents a definite advantage with regard to the corrosion of the agitators, for example. Nor would I offer outright condemnation of air cooling. Our company has a very considerable experience of this technique in the classical process and we do not understand why it is not suitable for the hemihydrate process, since the quantity of heat to be evaporated is rather less and the temperature of the slurry is somewhat higher. We should be grateful for your comments in this regard.

The process does, indeed, operate with a so-called coarse phosphate rock, but we are talking here of Morocco rock and there is no lack of gypsum plants working with raw or merely screened Morocco rock. With Florida-type phosphates, which are excellent materials, do you consider that you are able to achieve a saving on grinding compared with what is current practice: about 50% passing through 200 mesh?

We understand that you think your 50% P_2O_5 acid is more economic despite the indicated yield than a 30 - 35% P_2O_5 acid obtained by the gypsum process and subsequently concentrated to 50% P_2O_5 . Do you think it would be profitable to add a rehydration to gypsum to improve your yield, and are you planning to pursue your studies in this direction?

MR. ROBINSON: The first question was which stage is the more important in the development of this process? Every stage is important, and each stage depends on the results of the previous stage. The pilot plant was based on the results of the laboratory. If we had tried to do this directly without the laboratory work, we should certainly have had trouble and would have wasted a great deal of time. The 40 tpd plant at King's Lynn was necessary because we did not fancy a scale-up from a smaller pilot plant to something like a 250 tpd plant directly, although we have done this with the gypsum process.

Secondly, regarding the possible use of a single reactor, one main object in developing this process initially was to find ways of growing hemihydrate crystals which would filter and wash satisfactorily. The initial work showed that this could not be achieved using the single reaction stage, and it was necessary to use a multi-stage process in order to get satisfactory crystal growth.

The third question, I think, referred to cooling. There is perhaps some confusion here. In the paper the intention was not to give the impression that air cooling is not possible for the hemihydrate process. Certainly it is. Our objection to it is mainly that it is inefficient, more inefficient than in the gypsum process because the rate of heat transfer from the slurry to the air is much lower due to air and gas in the reaction slurry, so we prefer, for efficient heat removal, to use an evaporative cooler.

The fourth question related to the grinding of phosphate rock. All the phosphates we have tried in this process have been with coarse-ground rock, including Florida rocks. 50% through 200 mesh was mentioned. A normal grind of phosphate rock is something like 12% through 100 mesh, and this applies to Morocco and Florida rock. Kola rock is much finer as received, and no grinding is necessary in that case.

The final question referred to the possible addition of a crystal transformation stage to gypsum in order to improve the efficiency of the process. We have been working on this for about a year now. The efficiencies of the hemihydrate process can certainly be improved. In fact, efficiencies of up to 98% can be obtained, making 50% acid on Morocco rock. The difficulty is that it is an integrated process, i.e. the process follows the main hemihydrate process. This increases the complexity of the evaporation, and certain aspects of this process have to be investigated. We are not yet in a position to recommend it as an integrated process. Personally, I think this is the final direction which phosphoric acid manufacture will take.

MR. Y. DE TUNCO: With regard to air cooling, you said there was a mixture of slurry and air. This is also exactly the case in the classical gypsum process. Is there any particular problem with hemihydrate?

MR. ROBINSON: It is true that the gypsum in the hemihydrate process is similar. But, because of the high viscosity of the acid, the problem is aggravated. The viscosity of the acid in the hemihydrate process is much higher than in normal gypsum process, and this tends to cause aeration which is not dissipated as quickly as in the gypsum process and the presence of this air reduces the rate of heat transfer. By blowing

air into the slurry you get less heat transfer, because of the presence of the air in the slurry which is worse in the case of the hemihydrate process than in the gypsum process. This is why we prefer to use an evaporative cooler.

MR. PAVONET (Société de Prayon, S.A., Belgium): In your paper you speak of temperatures of 85 to 110° C and of a concentration of between 40 to 50% P₂O₅. What is the correlation between these temperatures and concentrations? Should we understand, for example, that at 40% P₂O₅ one operates at a higher temperature, whilst with a higher P₂O₅ concentration one operates at a lower temperature?

Secondly, when you speak of the comparison between your trials on the pilot scale and your industrial trials, you mention a different mixing time. You say that in the industrial trials the mixing time was about 30 seconds, whilst it was considerably shorter in the pilot plant. We should like to know how one should understand this time expressed in seconds.

MR. ROBINSON: The temperature range given in the paper is the range we have tried on the pilot plant equipment. At King's Lynn, we operated at 100° C, as this was the best temperature as a compromise between several factors. The higher the temperature, the higher the filtration range, the higher the attack rate on the rock phosphate and also the lower the P₂O₅ losses in the hemihydrate. It is an advantage to work at the maximum temperature allowed by the materials of construction. It does not relate to the 40 to 50% P₂O₅ at all.

With regard to the mixing speeds given in the paper, these were determined with plastic models of the pilot plant reactor, using liquids of similar viscosities to the slurry which we use in the pilot plant. We also used models of the King's Lynn reactor using water and the mixing time was determined using indicators to cause a colour. We obtain mixing zones and we measure the disappearance of the colour with time. The times given indicated the vast difference in mixing time between the 40 tpd plant and the pilot plant, and this was one important reason why we built a 40 tpd plant.

MR. VERSTEEGH (Mekog-Albatros N.V., Netherlands): Figure 7 mentions a relation between insoluble P₂O₅ in the hemihydrate. Figures two and four mention lattice and rock P₂O₅ in the hemihydrate. What is the relation between those three types of P₂O₅ ?

MR. ROBINSON: This relationship is given in the paper as an equation. The rock P₂O₅ is that caused by unreacted rock phosphate still present in the hemihydrate. Insoluble P₂O₅ is the sum of the unreacted rock P₂O₅ and the P₂O₅ present as HPO₄ or lattice P₂O₅ as we call it. These are obtained by determining total P₂O₅ and free acid P₂O₅ in the hemihydrate. By subtracting the free acid from the total, one has the insoluble fraction. By determining the rock P₂O₅ and deducting that from the insoluble P₂O₅, one has the lattice P₂O₅.

MR. BAUWENS (Ugine Kuhlmann, France): I think the process is very sensitive to P₂O₅ loss through formation of citrate soluble P₂O₅ or syncrystallized P₂O₅. To avoid this loss, I should imagine that one is obliged to pay very close attention to materials flow, i.e. the proportion of sulphuric acid fed into the first tank. Are there industrial processes

for analytical control of the solution in the first tank?

MR. ROBINSON: The normal control analysis we used in this process was to analyse the slurry being fed to the first reaction stage and here we normally determine the sulphate concentration. The sulphate concentration in the first stage is of the order of 0,1 to 0,2% and this is extremely difficult to determine accurately. We have determined the calcium concentration in the first stage and used this as the control. The main difficulty here is the length of time required to carry out a calcium determination. What is normally done is a control of flow every cycle and a sulphate analysis in the recycle, and this is normally good enough to control the process. This is how we controlled the process at King's Lynn, and it worked quite adequately.

MR. SCHOEMAKERS (Nederlandse Staatsmijnen, Netherlands): Do you think that a direct precipitation of hemihydrate is possible in the nitrophosphate route with the precipitation with ammonium sulphate?

MR. ROBINSON: We have done little in this direction. The main difficulty is the concentration of acids and the temperature to give a stable hemihydrate. The tendency is to get a transformation to gypsum. You need a very high temperature in order to stabilize the hemihydrate.