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AN ACCOUNT OF TWENTY MONTHS OF PHOSPHORIC ACID
MANUFACTURE BY A NEW AND ORIGINAL PROCESS.

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1. INTRODUCTION

Since the Second World War, the phosphoric acid production process by the sulphuric acidulation of phosphate rock, causing crystallization of calcium sulphate as gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), has been the subject of a very spectacular development. Practically the whole of world phosphoric acid production by the wet process is achieved by this process.

In 1960, our Company decided to re-examine thoroughly the various physical and chemical aspects of this process (called hereinafter "classical dihydrate process") and arrived at the conclusion that it had practically reached its economic limits.

The lowering of production costs, in our opinion, could be achieved only by technological improvements and by an increase of the unit capacities of the production plants. Consequently, we applied ourselves to these two factors as a matter of priority. At the same time, we assembled a research team for a detailed study of the problem of the attack of phosphate rock in the sulphuric-phosphoric medium.

In fact, the classical dihydrate process presents, even now, a few considerable weaknesses. The first is the limited extraction recovery of the P_2O_5 contained in the phosphate rock. This is mainly due to the fact that gypsum, when forming in phosphoric acid and in the presence of free sulphuric acid, coprecipitates dicalcium phosphate in its crystal lattice.

This phenomenon is ascribable to the very similar geometrical sizes of the ionic SO_4 and HPO_4 groups, which can easily take one another's place in the gypsum crystal lattice. As these ions are always present in the phosphate attack reaction medium, coprecipitation seems inevitable. It is nevertheless possible, by control of operating conditions, to reduce the content of the so-called syncrystallized P_2O_5 . Practically speaking, we have been limited in this procedure, as its cost is too high with respect to the economic advantage obtained.

Another weakness of the classical dihydrate process is the crystalline shape of the gypsum obtained; this normally takes the form of quite long and wide but thin crystals. This type of crystal yields on filtration cakes with a stratified structure of poor porosity, which are rather wet and offer quite a strong resistance

to the passage of the filtration liquids. It should be noted, however, that certain kinds of gypsum, such as Florida and Togo, are exceptions to this rule, due to a phenomenon of crystal association.

Finally, the classical dihydrate process is not suitable for producing very concentrated phosphoric acids. It is normally used to make an acid of 30 to 32% P_2O_5 . Although the manufacture of a much more concentrated acid is possible, in practice there are a series of difficulties which render the process uneconomic in most cases.

We have learnt from technical literature that some other processes have been developed in the hope of obtaining more favourable results.

In certain processes, calcium sulphate is crystallized as hemihydrate or anhydrate. This procedure permits a higher P_2O_5 concentration to be obtained. However, in the past, these processes have had no lasting success as this advantage could not compensate for the difficulties in operation.

Other, more recent processes have endeavoured to attack the phosphate rock with a view to the formation of hemihydrate first and the subsequent transformation of this into gypsum. These processes, commonly called "hemihydrate-gypsum processes" actually obtain a considerable reduction of the syncrystallized P_2O_5 content, but to achieve this, they are compelled to accept a high SO_2 content in the product acid. Moreover, rehydration of hemihydrate into gypsum is a rather slow reaction, particularly with some types of phosphate rock.

2. ACCOUNT OF THE PROCESS

2.1. Gypsum purification tests

The first aim assigned by our Company to the research team constituted in 1960 was the problem of purifying the residual gypsum obtained at the end of the classical dihydrate process.

As already stated above, this gypsum contains an important part of the syncrystallized P_2O_5 which cannot be removed by washing with hot or cold water or with diluted acids or bases.

The research work has shown that it is possible to recrystallize the gypsum into hemihydrate or anhydrite by operating with hot sulphuric-phosphoric acid solutions, at ambient pressure or under higher pressures.

This work leads to important conclusions. When recrystallization of gypsum into hemihydrate is effected in the presence of a considerable sulphuric acid concentration, syncrystallization of P_2O_5 in the hemihydrate lattice becomes practically nil. Moreover, it has been found that recrystallization of gypsum into alpha hemihydrate, when once started and in the presence of hemihydrate crystals formed, is a rapid and easily controlled operation giving large crystals which can be very easily filtered and washed.

The shape of these alpha hemihydrate crystals (orthorhombic crystallization system) may vary from that of a hexagonal prism to that of a regular polyhedron, passing through that of sets of prisms radiating from the same centre and thus forming structures called "entanglements, hedgehogs" according to the number and the length of these prisms. The cakes obtained are more or less porous and their specific surface can be influenced by means of the concentration ratios of sulphuric and phosphoric acids.

The study of gypsum re-crystallization into hemihydrate has investigated a considerable number of phosphate rocks and it has been found that the type of crystallization obtained is invariably the one defined above. Invariably also, the hemihydrate obtained is very stable, i.e. in the course of time and in the medium in which it forms, its shape is maintained and its crystallization water content does not vary. It is possible to keep a suspension of hemihydrate crystals for several hours in the stirred medium in which they formed, without affecting the filterability in the least. The crystals can be washed with cold water and handled while wet with no large amount of rehydration taking place. If the hemihydrate is crystallized in the form of the regular polyhedrons mentioned above, the filtration cakes formed will be particularly dense and their moisture content low, often even less than 10%. It is very easy to clear such cakes by simple washing using a small amount of water.

To sum up, it may be stated that re-crystallization of gypsum into hemihydrate in a phosphoric-sulphuric acid medium at strong H_2SO_4 concentration is a quick operation which easily yields large crystals that develop well in three dimensions and, consequently, are easy to filter and to wash. The crystals obtained contain very little syncrystallized P_2O_5 and are very stable, i.e. they evolve only very slowly towards the formation of anhydrite and, on the other hand, when washed with cold water, they change only very slowly into gypsum.

2.2 Tests of the gypsum-hemihydrate process

It seemed promising to us to incorporate this re-crystallization of gypsum into hemihydrate in a phosphate rock acidulation process, in order to profit by these particularly advantageous characteristics. This has given birth to the idea of our new process which we shall call the gypsum hemihydrate process. Thus, we made experiments from 1963 onwards, first in the laboratory, then in a pilot plant, in order to perfect the process.

As indicated by its name, the gypsum-hemihydrate process first involves attacking the phosphate rock to transform it into gypsum and phosphoric acid. This is effected according to the well-known standards and conditions peculiar to the classical dihydrate processes. Thus, we apply in this part the principle of re-circulation and cooling of the digested slurry.

At the end of the acidulation, the slurry is fed to a filter or to a static or dynamic settler with a view to thickening it

and drawing off the volume of phosphoric acid corresponding to the production.

The thickened slurry is then fed to the re-crystallization section where an important fraction of the sulphuric acid necessary for phosphate attack is added. This acid is added in the most concentrated form possible in order to make use of its dilution heat. It is, in fact, necessary to supply at this point the heat necessary for the endothermic reaction - gypsum less water = hemihydrate; and the heat needed to reach the required temperature of the re-crystallization medium. If necessary, additional calories are fed by steam injection. It only remains to filter the magma in order to separate and wash the hemihydrate, and to recirculate the diluted mixed acids to phosphate rock attack so as to provoke gypsum crystallization.

2.3 Production of concentrated acid

Thus, the process is designed to crystallize gypsum during phosphate rock digestion and simultaneously produce commercial acid. To this end, it is possible to operate in accordance with the standards of the classical dihydrate process and to produce a phosphoric acid of normal concentration for the process (30 to 32% of P_2O_5) and a well crystallized gypsum.

However, very quickly, it was found that good crystallization of the gypsum is not a necessary condition for good re-crystallization into hemihydrate. When phosphoric acid concentration is increased, the other conditions remaining equal, while keeping the total SO_3 level in the acid rather low, there is a movement towards the formation of a perfectly digested but almost infiltrable gypsum slurry. However, by keeping a suitable solids concentration, it will always be possible to separate the product acid by static or dynamic decantation.

The thickened slurry will then be re-crystallized into hemihydrate without any particular difficulty.

Thus, the gypsum-hemihydrate process can produce a phosphoric acid with higher concentration than the classical dihydrate process. The concentration which is economically possible varies according to the phosphate. It depends above all on the stability of the gypsum formed, i.e. on its resistance to the transformation into hemihydrate.

2.4. Determination of the general conditions for sound operation

There are several requirements which must be met by the gypsum contained in the slurry resulting from the first acidulation if it is to be transformed into hemihydrate with suitable crystallization. It is necessary above all that the gypsum formed should not contain too many alpha hemihydrate nucleus crystals. If the content of nucleus crystals is too high, the average size of the hemihydrate crystals formed grows ever smaller and the filterability and washability are affected. Neither should the gypsum slurry contain too much undigested phosphate rock. There is a danger that this may disturb re-crystallization by forming too many nucleus crystals, or that it may escape

the attack of the re-crystallization acid, thus giving a hemihydrate with a too high P_2O_5 content.

These are the main outlines of the process. Its industrial application and its evolution will now be described.

3. PRACTICAL APPLICATION

3.1 Introduction

After the laboratory and pilot plant tests had brought out the advantages of the new process and determined the operating conditions, we took the decision, two years ago, to transpose it to the industrial scale to meet the technological problems, the solution of which is decisive for the economic future of any process.

3.2 Equipment utilised

To this end, we re-instated the first classical wet process plant of our company into service after having made the necessary adaptations to it, which in fact were not very considerable. The reaction volume was split into two unequal fractions; the first and largest was assigned to the primary reaction - gypsum phase - whereas the second one was given over to the re-crystallization of gypsum into hemihydrate. The slurry cooling and recirculation equipment is part of the first section; a centrifugal separator was installed between the two sections to separate out the acid produced. As to the filtration section, it required only some minor fitting up.

3.3. Results obtained and adjustments made

3.3.1 Primary attack

The phosphate primary attack gave very satisfactory results from the beginning. As the obtaining of a better quality acid more concentrated in its P_2O_5 content and less rich in free sulphuric acid is the aim, this section had to be run under conditions different from the classical process. Among others, it was necessary to reduce the solids percentage in order that the slurry should remain sufficiently fluid. The concentration of the sulphuric acid used has been considerably raised and the repartition of the acids revised in order to take into account the new operating conditions.

3.3.2 Separation of the acid produced

Contrary to what happens in the classical process, the primary attack is carried out only as a function of the properties of the phosphoric acid to be produced, regardless of the gypsum obtained simultaneously. Thus, it is at that moment that the acid produced should be drawn off in order to maximize quality; however the size of the gypsum crystals obtained in practice excludes filtration and the problem has been solved by centrifugal separation. The latter supplies an acid which still contains a little solid material and which is afterwards clarified by static decantation. Abrasion, combined with corrosion, render the working conditions of the centrifugal separator similar to those of the attack tank agitators.

Since the starting-up of the plant, research work into the running conditions and construction materials best suited for this separator has enabled us to satisfactorily solve this problem.

3.3.3 Re-crystallization of gypsum into hemihydrate

In this section, the attack slurry of the gypsum phase, thickened by the drawing off of product phosphoric acid is mixed with sulphuric acid at 66° Bé and heated by steam injection, so as to attain the conditions in which the calcium sulphate dihydrate becomes unstable and is quickly transformed into hemihydrate, while freeing 75% of its crystallization water.

The speed of this transformation on the industrial scale is such that we have had to make some modifications to the existing equipment in order to secure a harmonious development of the very rapidly formed hemihydrate crystals. The main purpose of this stage of the process is to obtain a perfectly crystallized solids phase, this giving it good filterability with satisfactory stability of the hemihydrate.

The vigour of the physical and chemical conditions of the medium is such that practically all the P_2O_5 present in a solid state in the gypsum fed is dissolved and passes into the acid, thus raising the solubilisation efficiency to above 99.5%; consequently, the solid phase is greatly impoverished in P_2O_5 and we find contents of about 0.1% there.

These conditions are, of course, equally difficult for the material of the conversion tank, but with most phosphate rocks, the traditional construction materials of our industry are still quite suitable. For the other cases, we have found solutions which are economically acceptable and technically suitable.

3.3.4 Hemihydrate filtration

At this stage of the process, it only remains to separate out the hemihydrate, the filtered liquors being recycled to primary attack. This operation is carried out in our classical filter which has been slightly adapted for the purpose. So long as the conditions of hemihydrate formation have been well controlled, the hemihydrate will have a much better filter ability than gypsum, which enables us to obtain very advantageous nominal filtration capacities. Then again, the stability of the hemihydrate is also best when the material is in the form of well developed crystals. Under these conditions, even with phosphates which in the classical process give rise to encrustations in the filtration section which are difficult to wash with water, the new process gives excellent results with a water wash of the circuits carried out at a regular interval and a continuous wash of the filtration cells.

As a result of the good physical properties of the cake, it has been possible to reduce the number of washes from three to two, without impairing the degree of exhaustion and without increasing the amount of water necessary for washing, so that the filtration section is in fact simpler than that currently used in the classical process.

The average time of operation of the plant has been 90% of the period of possible operation in the course of the last four months, which value compares favourably with those obtained in many plants utilizing the classical process.

4. CONCLUSIONS

After 20 months of continuous running and adjustment of the plants and of their utilization, we are now able to present a new industrial wet phosphoric acid manufacturing process by sulphuric attack which has the following outstanding advantages as compared with the classical process:

- the P_2O_5 recovery exceeds 99%;
- the phosphoric acid can be obtained at higher P_2O_5 concentration (35 to 38%) and with a lower SO_3 content (2 to 2.5% of the P_2O_5 instead of 6 to 7%);
- the filterability of the calcium sulphate obtained as hemihydrate is better than that of the gypsum;
- the calcium sulphate obtained is purer, which opens up many new markets for it, among others:
- ceiling materials and the production of pre-fabricated sections,
- the cement industry as an admixture to clinker on grinding,
- in the manufacture of clinker coupled with the production of sulphuric acid which can be returned to the process.
- in ammonium sulphate manufacture.

ANALYSES OF THE PRODUCTS OBTAINED IN THE "GYPSUM
HEMIHYDRATE" PHOSPHORIC ACID MANUFACTURING PROCESS

Phosphate Rock utilized: Kola

on dry matter	P ₂ O ₅	:	39.4%
	CaO	:	50.6%
	SO ₃	:	0.07%
	SiO ₂	:	3.1%
	F	:	3.4%

Phosphoric acid:

	P ₂ O ₅	:	36.1%
	CaO	:	0.2%
	SO ₃	:	0.8%
	SiO ₂	:	0.7%
	F	:	2.2%
	Solids	:	0.6%

Calcium sulphate: On cake as discharged from the filter:

total water 20%

On cake dried at 50%: crystallization water 6.1%

On cake calcined at 250°C

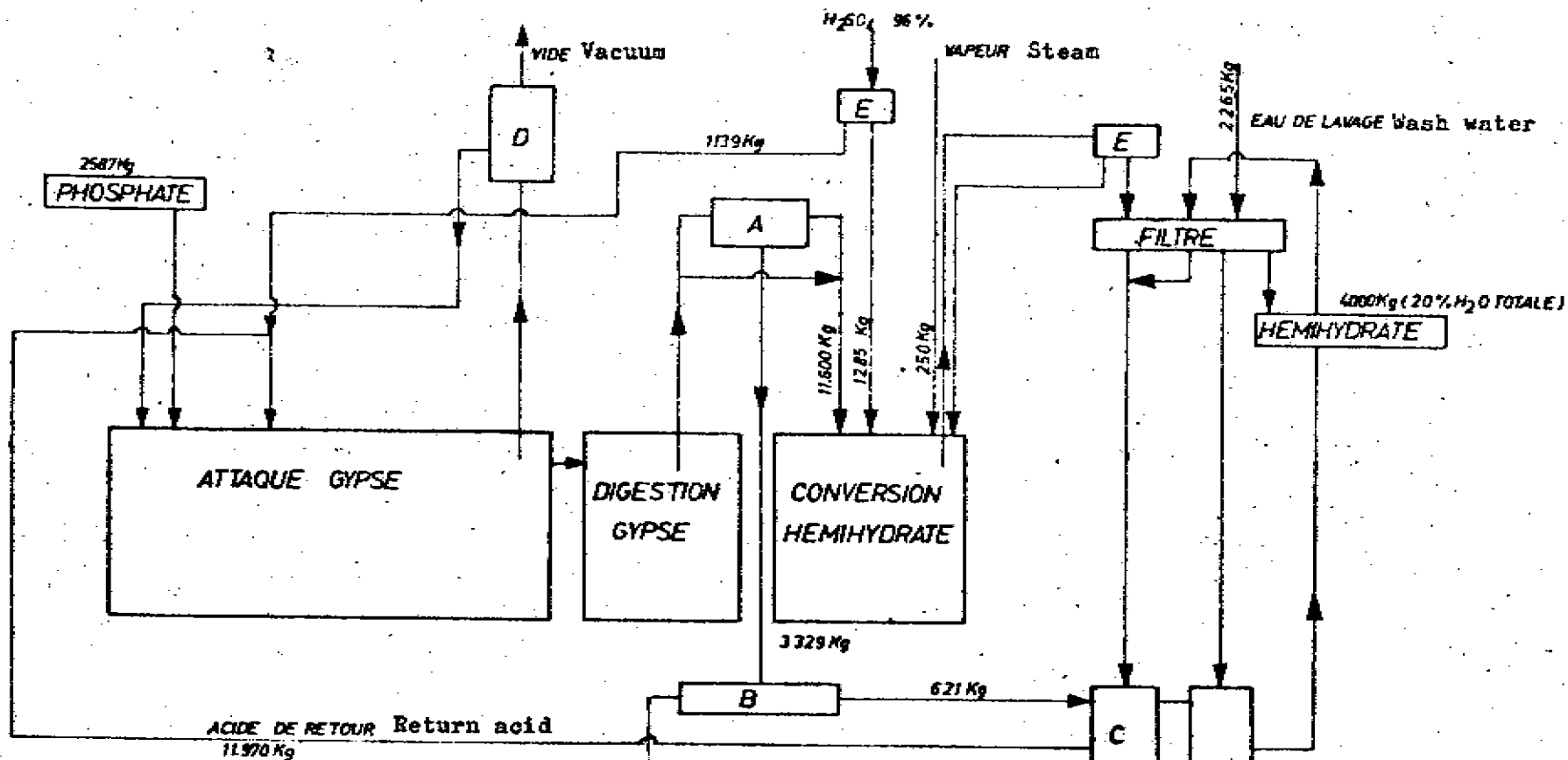
	P ₂ O ₅	:	0.19%
	of which insoluble:	:	0.1%
	CaO	:	39.9%
	SO ₃	:	56.5%
	SiO ₂	:	0.5%
	F	:	0.07%

ANNEXE 1: SHEMA DU PROCEDURE GYPSE HEMIHYDRATE

ELEMENTS DE DEBIT POUR MARCHE AVEC PHOSPHATE KOLA (PAR TONNE DE P₂O₅)

ENGLC. 1 : DIAGRAM OF THE GYPSUM HEMIHYDRATE PROCESS.

THE FLOWS ARE FOR OPERATION WITH KOLA ROCK (PER TON OF P₂O₅)



LEGENDE

A: DECANTEUSE
 B: DECANTEUR STATIQUE
 C: GARDE BAROMETRIQUE
 D: EVAPORATEUR SOUS VIDE
 E: BOITES REPARTITION

A. Settler
 B. Static settler
 C. Barometric seal tank
 D. Evaporator under vacuum
 E. Repartition boxes

DISCUSSION

MR. PAVONET: The paper which Mr. Davister and I have the honour to present describes how, in 1960, our company set up a research group which, whilst attacking the problem of the purification of residual gypsum observed that the re-crystallization of this gypsum to the hemihydrate state in a sulphuric-phosphoric medium gave very good results with regard to solubilisation of the syncrystallized P_2O_5 , speed of re-crystallization and size of the crystals obtained. The paper shows how a phosphoric acid production process was deduced from these experiments and outlines the general operating conditions of this process. Finally, it describes a production unit established at Engis which uses this process and has been in operation for 20 months.

MR. FROCHEN (Pierrefitte): As outlined by the authors, the production of wet process phosphoric acid over the last few decades has been carried out almost exclusively with crystallization of calcium sulphate in the dihydrate or gypsum form which has the disadvantage of causing a loss of P_2O_5 syncrystallized with the calcium sulphate. This disadvantage also applies in exactly the same way if crystallization is effected in the hemihydrate form. We know that one way of remedying this defect lies in operating a change of crystallization during manufacture, either from gypsum to hemihydrate or from hemihydrate to gypsum, in both cases in a strong sulphuric medium in order drastically to reduce or suppress conditions favourable to syncrystallization. This re-crystallization can be made either after drawing off product acid and repulping the crystals in a different reaction medium, or without drawing off product acid but simply changing the conditions of the medium - temperature, sulphuric acid concentration, etc.

However, if the theoretical conditions are fairly simple, the practical realization poses various problems, and we can only congratulate the Société de Prayon on having solved them.

My first question to the authors is: What reasons have induced them to adopt the gypsum-hemihydrate method rather than the hemihydrate-gypsum method? Theoretically, in fact, it would seem that this latter method is more promising from various points of view:

1. To achieve a primary crystallization exclusively as gypsum - a condition described by the authors as necessary for good secondary crystallization - one is obliged to maintain conditions of temperature and P_2O_5 concentration which limit the P_2O_5 content of the product acid to about 35%. Crystallization as hemihydrate, on the other hand, permits much higher concentrations which can go well over 40%.

2. In both cases two solid-liquid separations must be carried out. The first is fairly brief, since one does not aim to extract all the P_2O_5 from the cake; but the second is as complete as possible, because it is this separation which determines the yield. Now, for this second separation, necessitating several washes, it is certainly easier to work with gypsum rather than with hemihydrate, even if it is considered stable, for one can never exclude a disturbance of manufacturing conditions, and everyone knows the serious consequences of a re-hydration of hemihydrate on a filter.

3. With the gypsum-hemihydrate method considerable cooling is necessary during phosphate dissolution, followed by re-heating during re-crystallization. This seems a waste of heat, since the hemihydrate-gypsum method requires no heating.

4. With the gypsum-hemihydrate method, the calcium sulphate emerges from the system in the hemihydrate form and thus the amount of water to be provided is less than in the opposite case. Thus, one has less water to carry out the washing of the sulphate cake.

Apart from this long question concerning the principle of the process, I should like the authors to clarify the following points:

1. With the dihydrate process, as is well known, mixed or bristly crystals allow greater filtration speeds than tabular crystals but give rise to greater losses of water soluble P_2O_5 . Is this not also true of the hemihydrate process?

2. In the classical processes the volume of the reaction tanks is conditioned not only by the conditions of the phosphate dissolution and gypsum precipitation, but also by the need to desaturate the acid as much as possible, in order to decrease the risk of later precipitation. Is this the same for the hemihydrate process?

3. The authors explain that by taking the necessary precautions re-crystallization of the hemihydrate in the filter circuits is slight. But in the classical process most of the encrustation is due to fluo-silicates. Is this not so in this new process? Also, is there no encrustation in the centrifugal separator? Finally, could the authors say what percentage of solid material and gypsum emerges from the centrifugal separator?

MR. DAVISTER: Mr. Fröchen's question as to why we did not choose the opposite method of producing our phosphoric acid in a hemihydrate medium, eliminating our calcium sulphate in gypsum form, is obviously very relevant, and the excellent theoretical reasons quoted by Mr. Fröchen are perfectly correct. In fact, about ten years ago we did carry out experiments, reacting phosphate rock in conditions in which the calcium sulphate was obtained as hemihydrate. At that time, we were never able to arrive at anything entirely satisfactory as an industrial process. If the process were transformed, in the sense that the phosphoric acid was first drawn off as Mr. Fröchen suggests, and then the hemihydrate was converted to gypsum, it would present a certain problem, since the re-crystallization of hemihydrate to gypsum is a relatively long operation. This is because it must take place in conditions necessary for the stability of the gypsum - fairly low temperatures and relatively weak concentrations of phosphoric and sulphuric acid - whilst the conversion of gypsum to hemihydrate, in order to eliminate the calcium sulphate from the process, is a reaction which takes place at high temperature with a high acid concentration, producing well formed hemihydrate crystals with exceptional filterability in a very short time. This, together with the advantage of terminating the calcium sulphate treatment in extremely reactive conditions, ensuring almost total solubilisation of the P_2O_5 , is the main reason why we directed our research towards the gypsum-hemihydrate process.

MR. PAVONET: If you choose the hemihydrate method with re-crystallization to gypsum, another reason is also the difficulty of separating product acid after the reaction in hemihydrate. You need a means of separation - either a filter or a decanter - and the problem of separation is certainly much more difficult after a first hemihydrate stage with a weak solution than after a first reaction in gypsum. The advantage of our process is that we can add sulphuric acid to effect the re-crystallization of the gypsum to hemihydrate and, in this combined medium with sulphuric acid at any concentration, it is very easy to eliminate almost entirely the formation of syncrystallized P_2O_5 . On the other hand, if we choose the method of re-crystallization of hemihydrate to gypsum, we should have to suppress or at least avoid exaggerating the sulphuric acid content to prevent this reaction from occurring. In brief, therefore, there are a number of advantages in favour of the opposite process, re-crystallization of the gypsum to hemihydrate.

MR. DAVISTER: The arguments presented by my colleague, Mr. Pavonet, are those of a practitioner in the production of phosphoric acid; and having overcome the problems inherent in our process, whilst avoiding those more complicated problems which, we think, are posed by the opposite process, we can tell you that we are now at the stage where 20% of our company's phosphoric acid production can be obtained from this new process continuously, on a day to day basis, according to the firm's manufacturing and sales programme. The process is therefore already in perfect industrial operation, and results are such that by the end of the year it will account for one-third of production.

Coming to Mr. Fröchen's detailed questions, he objected to the fact that during the primary reaction in gypsum phase we cool in order to control the crystallization of the gypsum and that we must consequently re-heat to form the hemihydrate. But the re-heating is only an incidental operation; we do not have to provide a large amount of heat but merely to adjust the temperature of the hemihydrate tank. In general, the addition of sulphuric acid, made at the second stage of the process to convert gypsum to hemihydrate, is made in the form of 66° Bé acid, and the heat of dilution of this acid provides most of the necessary calories.

Another objection of Mr. Fröchen was that, since the calcium sulphate leaves the process in the hemihydrate form, much less water is taken off than if it left the process in the form of gypsum. In fact, only one-quarter of the amount of combined water is taken off. In practice, this has not proved to be a serious disadvantage because, at the same time, filterability and washability of the hemihydrate obtained in the conditions of the process are so much better than that of the classical gypsum obtained by the wet process that we can exhaust it with very small amounts of water. Our water balance is thus perfectly adjusted, and we do not suffer from the fact that the calcium sulphate carries off little combined water. Indeed, this is an advantage if you have to do something with the calcium sulphate, because it is much easier to dry and, if necessary, to calcinate.

With regard to the fact that mixed or bristly crystals give greater filtration speeds and cause greater water soluble P_2O_5 losses, I must say that with the hemihydrate as we obtain it, the problem does not arise this way. Firstly, there is no occluded P_2O_5 , because the final hemihydrate is obtained in very reactive conditions which dissolve it entirely, and

because the maculation of the crystals of hemihydrate occurs very rapidly. The form of these twin crystals which I can only characterise by comparing them to a sphere with multiple facets, is such that it does not permit a retention of the acid phase between the various crystals comprising the filter cake. This is quite different from what happens when maculated gypsum crystals occur in bristly formation.

The following question concerned the volume of the reaction tank which, in the classical process, is conditioned not only by the need to dissolve the phosphate and precipitate the gypsum but also by the need to desaturate the acid as far as possible. Is this the same in the new process? Obviously, yes, but the solid hemihydrate phase is produced in a medium where the sole object is to produce this phase in the form corresponding to the minimum P_2O_5 content. Consequently, the conditions for obtaining the hemihydrate are adjusted so that the desaturation is extremely rapid and thus the operation can proceed at a speed and with a volume determined solely by the need to develop hemihydrate crystals without regard for the problem of supersaturation which is thus automatically resolved.

Are the crystal formation and encrustation in the filter circuit calcium sulphate or fluosilicates? In the new process the encrustations are mostly present as calcium sulphate hemihydrate. Hence the possibility of removing them by washing.

Finally, Mr. Fröchen, may I ask you to clarify your last question concerning the percentage of solid material and gypsum emerging from the centrifugal separator?

MR. FROCHEN: I should like to know the solid/liquid ratio in the slurry emerging from the separator and going to the re-crystallization section.

MR. PAVONET: The gypsum slurry enters a decanter for separation with a solid content of about 30% and is separated in a thickened phase containing about 60% of solid material, with product acid also containing a few per cent of solid material and thus requiring clarification by decantation.

MR. O. JENSEN (A/S Dansk Svovlsyre- og Superphosphat-Fabrik, Denmark):

1. Can you give me an estimate of the investment costs for a plant working according to the gypsum-hemihydrate process compared with a plant with the same capacity working according to the classical process?

2. It is said in your paper that the product acid from the centrifugal separator is not so clean as the acid from a Frayon-filter. You mention that the subsequent cleaning is done by static decantation. Could we hear a little bit more about how this is done, since an effective purification of the 30% acid is not a very easy process?

3. What materials are used in the centrifugal separator and how long a lifetime do you reckon that this important equipment will have?

4. You obviously have made an improvement of the classical process in respect of the higher P_2O_5 efficiency, the lower SO_3 -content in the acid

and the purer calcium sulphate by partly changing to the hemihydrate process, but it seems to me that you have gone into the difficulties of the latter without obtaining the full advantage of the stronger acid, which the hemihydrate process can give. Could we have your comments on this point?

MR. DAVISTER:

1. With regard to the levels of investment for a classical dihydrate process and for this new process, various estimates made in recent months for factories of various capacities have shown that investment is of the same order of magnitude in both cases. The possible difference between the two processes is more influenced by local conditions than by the actual process.

2. The acid clarification after its separation on the centrifuge is an operation carried out by static decantation in very easy conditions.

3. With regard to the construction materials used for the centrifugal separator and its useful life, this is the kind of question which, in the case of a process still in the course of development, one is never very certain of answering adequately. The materials which are normally used - stainless steels with 20% chrome, 25% nickel and 4-5% molybdenum, classical in the normal phosphoric acid industry - afford operating lives of several years without problems for certain parts of the machine, whilst for others considered as the wearing parts, this kind of material may need a replacement or at least a repair after six months' service. Other materials, however, now tried for longer than six months, are continuing to give satisfactory service, and in this case I cannot honestly tell you what their life will be. I hope it will be as long as possible.

4. I think you mean by this that the process is too difficult and not sufficiently rewarding. I think it is only difficult on paper, for the experience acquired with a plant in continuous daily operation has convinced us that it operates exactly in the same conditions of flexibility as a classical process. It is, of course, a fact that the grade of product acid is between 35 and 38% P_2O_5 . But, on the other hand, not only can we derive the economic benefit of an excellent P_2O_5 yield and very good P_2O_5 recovery, but also the residual calcium sulphate hemihydrate is so low in P_2O_5 that it constitutes an easily usable raw material for a variety of uses which we have listed in our paper.

MR. MORAILLON (Péchiney Saint-Gobain):

1. What is the production capacity of the pilot plant?

2. What is the maximum production capacity in tonnes of P_2O_5 /day of a centrifugal separator?

3. What is the approximate price of a separator constructed from an appropriate material?

4. With regard to the filtration of the final hemihydrate on a Prayon filter, what is the approximate production capacity per m^2 of useful surface area and for what thickness of cake?

5. What are the problems relating to stoppages in the re-crystallisation tanks.

6. I should like to have the author's comments on the following points : In my view the process has two main advantages - the very high P_2O_5 yield and the purity of the calcium sulphate. However, it seems to me that the increase in P_2O_5 concentration is not very significant, since one is speaking of 36% P_2O_5 with Kola phosphate, which can be obtained with a classical gypsum process.

MR. PAVONET: The price of a separator with a basket of 400 cm. diameter and suitable for a plant of about 50 tpd P_2O_5 is of the order of B.Frs. 1-1.2 million in suitable materials.

MR. DAVISTER: The capacity of the pilot plant is now 50 tpd P_2O_5 and has varied generally during the last few months between 40 and 55 tpd P_2O_5 , according to the objects of the research involving its use.

Secondly, you ask what is the maximum possible capacity with a single centrifugal separator? Centrifugal separators exist for a capacity of at least 200 tpd P_2O_5 . Of course, we have no experience yet of this, and this figure is obtained by extrapolation from the separator which is currently giving 50 tpd P_2O_5 . We think that the limit of 200 tpd can be increased by at least 25%.

Next, what is the production capacity expressed as tonnes of P_2O_5 per m^2 of filter? Despite the double crystallization of the calcium sulphate, the influence of the original phosphate rock continues to affect this figure, but for the poorer phosphates this capacity would be a minimum of 6 tonnes P_2O_5 per m^2 of filter surface, whilst for the better phosphates one could state a figure of 10 tonnes P_2O_5 per m^2 of filter surface, both figures being very conservative.

Another question relates to the behaviour of the hemihydrate tank during plant stoppages. Obviously, a plant is made to operate and not to be stopped. We all know that, from time to time, one must carry out plant maintenance. In these conditions the calcium sulphate hemihydrate in the tank is stable for 6-10 hours. The conditions of the medium must be adjusted to ensure conservation of the hemihydrate, in order to avoid either a more extensive dehydration to the anhydrite stage or a re-hydration to gypsum. If these precautions are taken, stoppages of 24 hours or so cause no difficulty.

Finally, the last point is, I think, more a reproach than a question: Why do we not make a higher grade of acid? A higher grade can be obtained in equilibrium with calcium sulphate dihydrate, but it is not a question here of laboratory trials which we have made. If this was the case, we could have aimed for the last possible percent of concentration. We are dealing with the regular, continuous operating conditions of an industrial plant and we do not consider that it is possible to operate in industrial, economic conditions to the limit permitted by an equilibrium. One must take account of a certain safety margin between actual operating conditions and limiting conditions, in order to allow the operator to be sure of his production without constantly seeking performance. Of course, the grade being what it is, there is the cost of concentration. But if one compares a classical dihydrate process, such as one finds in dozens throughout the world, operated intensively with a product acid grade of 30-31%, even

32% P₂O₅, the amount of water to be evaporated to concentrate this acid to the usual commercial grade of 54% P₂O₅ is, with this new process, reduced to two-thirds of what it was before. Thus a plant of 200 tpd can be expanded to 300 tpd with this process, without any alteration in the concentration section.

DR. E. SACHER (Osterreichische Stickstoffwerke, A.G., Austria): It is stated in the paper that the size of the gypsum crystals effectively excludes any filtration and that only centrifugal separation is possible. What is the size of these crystals?

Secondly, what type of centrifugal separators do you use? You spoke just now of a diameter of only 400 cm. without indicating the type.

Thirdly, how does resistance to wear of the various pieces - you have indicated an average of 6 months - vary according to the SiO₂ content of the gypsum?

MR. PAVONET: The size and, in particular, the thickness of these crystals depend on the concentration desired and attained. The higher this concentration, e.g. up to 40%, the more difficult becomes the formation of the gypsum crystals. In our normal conditions (36% P₂O₅), measurement of crystal lengths and widths are not particularly different from those observed with 32% P₂O₅, although the thickness of the crystals is distinctly less, and thus the sedimentation is also much reduced. The speed of sedimentation and, in particular, the speed of filtration, is, however, considerably slowed down.

The centrifugal separators have a conical and a cylindrical section, and the centrifugal forces used vary between 600 and about 1000 G.

Now, with regard to wear, Mr. Davister has spoken of various pieces resisting up to six months. Very probably this does, in fact, depend on the SiO₂ content of the gypsum, but our industrial operation has used only Kola phosphates up to now, and so we cannot yet say to what extent this is true.

MR. GLIKIN (Simon Carves Chemical Co., U.K.): The authors have shown that it is possible to adapt an existing phosphoric acid process to improve efficiency whilst retaining the advantage of reliability gained from many years' experience with the conventional dihydrate process. By intermediate removal of product acid the process appears to have gained in flexibility since crystallization of CaSO₄ can take place in a solution where there is a high excess of sulphuric acid thus preventing uptake of HPO₄ ions into the CaSO₄ crystal. Also the filtration section of the plant is rather less dependent on the operation of the reaction section than is the case with a conventional process. However, these two sections of the plant are still interlinked - recycle phosphoric acid returning from the filter to the attack tank. Have the authors considered feeding to the evaporators this dilute recycle acid, then returning the more concentrated acid to the primary attack tank, and removing product acid of a higher concentration?

Advantages would appear to be as follows:

1. This system virtually completely separates the re-crystallization and filtration stages from the attack stage. The control of the process is thus simplified.
2. A greater quantity of higher concentration return acid can be fed to the attack tank and this will produce a higher liquid/solid ratio and should therefore make it possible to produce a rather higher concentration product acid. It should also be possible to operate this section of the plant at a lower temperature and thereby increase the life of the equipment.
3. The concentration equipment is used in the most economic way. This is because it is easier to remove water from acid of lower concentration than from more concentrated acid. For example concentrating 20% P₂O₅ acid to 25% would require very much simpler and smaller equipment than if the same amount of water is removed from acid of 35% concentration. (It may be necessary to partially neutralise the excess sulphuric acid in the return phosphoric acid).

MR. DAVISTER: If I understand Mr. Glikin, he suggests that we should reconcentrate the sulpho-phosphoric acid at the filter stage before returning it to the attack tank. But I must say that to achieve the results quoted in the text, we have no problem with our water balance because we can use very concentrated sulphuric acid. The only considerable quantity of water introduced into the process is that used to wash the hemihydrate cake on the filter. And here again we have a cake which filters and washes very well, thus limiting the amount of water required. We could, of course, always draw off water from the system to work at higher temperature, but then we should reach a limit. This comes back to what I said just now to Mr. Morillon: We do not wish to operate the process at the extreme limit of what can be achieved in a laboratory or even in a pilot plant. We want to operate it in industrial conditions with a certain margin in relation to the limit in which the gypsum or the dihydrate calcium sulphate is stable. Thus, at least in present circumstances, there is no great interest for us in drawing off water from the process. Of course, if one did do so, one would have a certain independence as between the attack section and the filtration section. But I think one would have to pay a high price, because, as Mr. Glikin says, it is easier from the thermo-dynamic point of view to evaporate water from a weak acid than from a concentrated acid; but, on the other hand, it is certain that a sulpho-phosphoric acid such as we use at P₂O₅ concentrations of, say, 20% is a very corrosive product, and I fear that the small calorie gain from working in a dilute medium would be very largely offset by difficulties caused by encrustation arising from the concentration of an acid at this grade.

MR. PAVONET: Our experience of corrosion problems does not differ particularly from those encountered with the classical dihydrate process, as far as our reaction to make gypsum is concerned. In brief, therefore, we have never encountered any particular corrosion problem. Of course, we know there are sometimes difficulties with certain types of phosphate and one is then obliged to change materials. Our stainless steels with

a base of 20% chrome, 28% nickel and about 4.5 - 5% molybdenum hold up fairly well in these conditions, but if extreme corrosion problems exist, one must sometimes use rubberised constructions to overcome them. We have encountered more serious corrosion problems in the re-crystallization section, i.e. in the transformation of gypsum to hemihydrate, where the sulphuric medium is distinctly more concentrated; and we have already mentioned something about this.

As far as the filter is concerned, we have had no particular problems. We think that Carpenter 20 is a very suitable material for most phosphates, even in the re-crystallization section. With Togo rock, in any case, we have certainly encountered special corrosion difficulties also in the hemihydrate section. Plastic linings should be used. They stand up very well and are perfectly feasible in the operating conditions we have chosen.