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MANUFACTURE OF WET - PROCESS PHOSPHORIC ACID.

The possibility of making 45% P₂O₅ phosphoric acid by the gypsum process.

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INTRODUCTION.

The direct manufacture of highly concentrated industrial acids has always presented a major problem to manufacturers. The problems associated with the manufacture of the main mineral acids, e.g. sulphuric, nitric and hydrochloric acids have in the main been solved. By comparison the production of wet process phosphoric acid does not compare favourably, although it is non-volatile.

The first phosphoric acids produced, by recognised industrial processes, had concentrations less than 20% P₂O₅ and in fact they were often limited between 15% and 18% P₂O₅. Improvements in these strengths were effected in very slow stages only; firstly 21% was made and then 25% and nowadays the largest amount of phosphoric acid produced still has a concentration lower than 30% P₂O₅.

Manufacturers who have made the greatest progress in this field are now beginning to produce an acid containing 32% P₂O₅, but they appear to consider that this strength represents a limit which it is not economical to improve on.

A process introduced by Mr. Nordengren and his colleagues gives a highly concentrated acid containing 40-45% P₂O₅ which is unquestionably an advantage. This acid is obtained, however, by the anhydrite process which uses techniques which differ from those used in conventional processes. In fact the obstacle which must be overcome is the hydration of calcium sulphate formed during the manufacture of phosphoric acid.

In conventional processes, where the acid produced has a concentration equal to or lower than 32% P₂O₅ the calcium sulphate is in the form of the dihydrate or gypsum. Above this concentration, notwithstanding the increasing difficulties of manufacture, it is desirable to have conditions under which the semi-hydrate or anhydrite is formed. Thereby, highly significant quantities of water are liberated at exactly the time when the balance of water becomes difficult to regulate. In order to emphasise this aspect, we would point out that the quantity of water existing in the form of water of crystallisation in gypsum represents 55% of the total amount of water admitted in the manufacture of 32% P₂O₅ acid from 75% Moroccan rock phosphate and 78% sulphuric acid. Naturally this relationship increases as high concentrations of phosphoric acid are obtained and the concentrated sulphuric acid offers no real advantage.

We have, however, tried to obtain highly concentrated phosphoric acids without leaving the phase which covers the formation of gypsum. The particular methods which have been applied are described in the following section and show that these enabled us to develop this study and obtain some interesting results.

II. BACKGROUND.

1. Theoretical data.

Several diagrams have been published giving the state of hydration of calcium sulphate with phosphoric acid, taking into account the P_2O_5 concentration and the working temperature. The diagrams drawn up by M. Lehrecke based on experiments by Van't Hoff show the direct relationship between the crystalline forms of calcium sulphate and the vapour pressure of the water of crystallisation and indicate the margin which is of practical significance. These diagrams are reproduced in the appendix. They show that if it is required to obtain calcium sulphate in the form of gypsum a 32% acid may only be produced at a temperature less than $88^{\circ}C.$, a 35% acid at a temperature of less than $75^{\circ}C.$, a 40% acid at a temperature less than $60^{\circ}C.$, a 45% acid at a temperature less than $40^{\circ}C.$ and a 50% acid at a temperature less than $0^{\circ}C.$ It should be noted that these diagrams do not take into account the quantity of sulphuric acid and the various impurities present in an industrial acid, all of which must play a part in limiting the possibility of raising the temperature at the same concentrations of P_2O_5 . Other diagrams obtained from work carried out under the direction of M. Sanfourche at present in charge of the Chemical Products Laboratory, Compagnie de Saint-Gobain, indicated much more favourable prospects

Again tests were made with pure phosphoric acid to which small amounts of pure sulphuric acid were or were not added. The curves which correspond to the equilibrium obtained using only phosphoric acid are shown (as a dotted line) on the same diagram as the previous curves.

It can be seen that the two curves showing the transformation of gypsum to the semi-hydrate are close together in the presence of a partially concentrated phosphoric acid and become wider apart as the concentration is increased. However, the curves taken from the Sanfourche determinations leave a more extended area to the gypsum. Hence, it was possible to work at temperatures above $80^{\circ}C.$ for 35% acid, above $75^{\circ}C.$ for 40% acid, above $65^{\circ}C.$ for 45% acid and above $50^{\circ}C.$ for 50% acid.

The reason for these differences is the very slow attainment of the equilibria in the presence of phosphoric acid.

More recent works (A.A. Taperova, M.N. Chouelghina) tend to conclude that the final form of calcium sulphate in phosphoric acid solutions, even when the concentrations are low, is always anhydrite but that at the beginning firstly semi-hydrate and then the gypsum is formed. In addition the time taken to convert the gypsum into anhydrite is extremely long - of the order of several months or years.

We do not aim to develop our studies on a purely theoretical level where a great deal of work has already been done, but to carry out research into the possibilities of working with higher concentrations in industry.

Thereby, we have tried to produce increasingly concentrated acid in relationship to the lowering of the temperature, firstly in order to maintain a temperature at which, as shown by the Lehrecke diagrams, gypsum would be formed and then by progressively raising the temperature until it was nearly up to the Sanfourche curve. The duration of the test was sufficiently long for us to be unaffected by every change which time may have brought and also we did not have the disadvantage of actual manufacture. In all

cases we verified the hydration state of the calcium sulphate. Examples of our working conditions are given in the attached diagrams.

2. Practical Possibilities.

It was fortunately possible for us to develop this work as we had at our disposal from the beginning two essential advantages.

(a) On the industrial side - we had as a starting point a manufacturing process, the purpose of which was to make phosphoric acid at 32% P₂O₅, using a patented technique of reaction in a "unique system" which, following numerous tests, we have recently been able to bring into industrial operation. These brought out the fact that this method was the most logical and became increasingly advantageous as more difficult manufacturing conditions arose, the most important of which were connected with the use of a more concentrated acid.

It is now well known that the production of phosphoric acid is a very delicate operation and must, therefore, take place under extremely precise conditions if regular production and high yields are to be obtained. As the P₂O₅ concentration increases the working conditions must become stricter and the limits of possible variation in the amount of sulphuric acid narrower. In addition the reaction is more likely to become "blocked", crystallisation less favourable etc. It is, therefore, necessary to operate under the best conditions in order to obtain the best results. A badly designed plant will produce acid of low concentration with a satisfactory yield, but will not be able to do this for acids of high concentrations.

The "unique system" process concentrates on continuous production with all its advantages and includes internal recirculation of the reaction slurry. The raw materials are added to the mass of slurry (instantaneous dilution in the mass) and also are added at a point where final reaction occurs (best conditions for attack and crystallisation). These points of addition can be chosen with accuracy (system of vertical and horizontal feeds as applied in industry) and hence the greatest possible regularity and homogeneity of reactions and their products can be obtained.

There are also considerable advantages with the "unique system" in regard to the investment costs of the installation and in the works development, although these are outside the scope of this paper. We would emphasise, however, that in addition to the advantages noted above the great flexibility of the process and the ease with which conditions can be reproduced have greatly assisted our study.

(b) On the experimental side - For some years we have been faced with the problem of how to utilise our plant for the treatment of phosphates of differing analysis and from varying sources. In order that we should be able to answer questions arising from the use of these phosphates we attempted to carry out an experiment which reproduces as closely as possible the manufacturing conditions we would encounter for all the proposed samples of phosphate. This development and results are described in another paper of the I.S.M.A. Conference in this session called:-

"Influence of the Origin and Characteristics of Phosphate Rock upon the Manufacture of Phosphoric Acid by the Wet Process"

The preliminary test gave, from the beginning, unexpected results. The test was improved as we gained experience and as our knowledge of the industrial use of widely different phosphate increased. It became a particularly valuable means of

investigating each of the operating conditions chosen as a variable, and was not limited to studying phosphates. The application of this experimental method to the production of highly concentrated phosphoric acid was found to be one of the most interesting.

We shall not describe here all the operating conditions and the data taken from the test, as these have been described in our paper referred to above. We would, however, point out that some of the data has been expressed differently and included in this paper.

Filtration Speed Expressed in kilograms of P₂O₅ filtered in Hours and square metres of the filter surface and not in volume of acid (litre or cubic metre) which for a variable concentration has only a comparative value.

Amount Retained The volume of acid retained in the case expressed as percentage of the volume of the solid (Replaces the rate of drying because of considerations analogous to the previous ones).

Note:- In this case the lowest values are the most desirable.

Impurity Index. This is only of limited value and is, therefore, not given throughout.

This work, which is still continuing, may be subdivided at present into three main sections:-

The first experiments on concentrations in the region of 35% P₂O₅.

Exploration of high concentrations in the region of 35 to 45% P₂O₅.

Improvement of operating conditions at higher concentrations.

III. INITIAL EXPERIMENTS - DEVELOPMENT FROM 32% TO 35% P₂O₅

It was found that major difficulties were encountered when the peak of industrial concentrations were exceeded by passing from 32% to 35% P₂O₅. Unexpected variations occurred during the experiments and it was not known what adjustments should be made in order to compensate the errors. At one time we had reached the practical limit of manufacture, at least by the gypsum process. It is probable that this was due to the same difficulties that had, up to now, been unsurmountable obstacles in the development of the manufacture of high concentrations of phosphoric acid. These difficulties were overcome by progressive improvements enabling the manufacturing characteristics for 32% acid to be applied to 35% acid and hence its industrial manufacture envisaged. It has since been possible to apply the same methods for higher concentrations and thus avoid similar obstacles. The principle development of this work was as follows:-

The experiment dealing with the manufacture of 32% P₂O₅ was governed in particular, by the following conditions. It will be seen, however, that these are modified in the course of the paper:-

Reaction of Moroccan phosphate	75%	-	Unground
Temperature of Reaction		-	700C.
Duration		-	6 hours.
Sulphuric acid content in the liquid phase		-	22g. per litre.

The direct application of these conditions to the manufacture of a 35% P₂O₅ acid was unsuccessful. The phenomenon which we call "blocking of reaction" occurred, resulting in the phosphate no longer being attacked and as a result the sulphuric acid content continually increased as more raw materials were added. As the blocking of the reaction is itself the result of too high a sulphuric acid content, particularly with the given conditions of concentration and temperature, it is seen that, once begun, this phenomenon gives rise to a chain reaction. This can only be stopped by suspending the addition of raw materials and waiting until the attack on the phosphate has progressed sufficiently to result in a lowering of the sulphuric acid content below the danger point or "content limit". It is possible to try to accelerate the regression of this phenomenon either by adding phosphate, although this itself ceases to dissolve in the mixture practically instantaneously, or by changing the condition of the mixture. This latter course can be effected by lowering the temperature, changing the dilution, lowering the sulphuric acid content, returning phosphoric acid etc. None of these steps is very effective and in industrial production would interrupt manufacture. In addition, the onset of the phenomenon should be prevented by working with a significant safety margin for each condition affecting the phenomenon. In this particular case the limit of sulphuric acid content was in the region of 20-22 g. per litre, which was less than the content originally anticipated, and hence explains why it was possible to carry out manufacture.

In a second series of experiments we worked with a lower sulphuric acid content in the liquid phase i.e. 20g. per litre H₂SO₄, 15g. per litre H₂SO₄ and 10g. per litre H₂SO₄. Manufacture was thereby possible but the margin of safety was too small, particularly with 20g. and 15g. per litre. In addition there was a significant lowering of the results as compared with those achieved in the manufacture of 32% acid:-

The reaction efficiency dropped from 98 to 97, 97.6 and 96.8% respectively.

The crystals were smaller and "R" greater; 2 to 4, 3 and 2.5

The filtration speed fell from 840 to 520, 495 and 450 kg. P₂O₅ per hour per square metre.

The amount retained increased from 120 to 192, 190 and 212%.

The washing efficiency decreased from 97.9 to 92.8, 93.2 and 91.8%

The reaction time was then increased from six hours to 7½ hours and then to 9 hours.

The sulphuric acid content in the liquid phase was increased to 22g. per litre thereby:-

The sulphuric acid content limit was increased from 22 to 25 and 27g. per litre.

The reaction efficiency approached the experiment values of 97.9 and 97.75%

The crystallisation was improved - shorter and thicker crystals ("R" = 2.5-3).

The filtration rate remained low; 540 and 525 Kg. P₂O₅ per hour per square metre.

The amount retained improved from 215 to 165 and 159%

The washing efficiency improved from 93 to 94% and 95.1%

It will be seen, therefore, that there is an appreciable improvement, but as yet, in certain cases, it is too small. Also the limits of variation for the sulphuric acid content would be insufficient for industrial manufacture. The temperature was lowered from 75°C. to 65°C. with a reaction time of 9 hours. It is noted that the lowering of temperature resulted in an obvious improvement of all the conditions.

The reaction efficiency fell from 97.95 to 97.7%

The "content limit" of sulphuric acid was increased from 27g. to more than 32g. per litre (limit not determined).

The crystals returned to a normal thickness and form (rather irregular in size from 1.5 to 3).

The filtration speed rose to 680 kg. P₂O₅ per hour per square metre.

The amount retained improved from 165 to 120% (same as trial)

The washing rate improved from 95.1 to 97.4%

The improvements resulting from the reduction in temperature indicated the source of the difficulties encountered - reaction in a mixture which was near the conversion phase from gypsum to semi-hydrate.

The use of ground phosphate brings about a highly significant improvement in results when all other conditions are governed by their basic values. These results are an improvement, in part, to those obtained with a 32% P₂O₅ concentration added to raw phosphate.

The content limit in sulphuric acid rises above 35g. per litre.

The reaction efficiency reached 98.2%

The crystals are thicker and shorter ("R" = 1.75).

Only the speed remains markedly unimproved - 710 kg. P₂O₅ per hour per square metre.

The amount retained improves slightly - 115%

The washing efficiency reaches 98%

Although the grinding of 75% Moroccan rock only causes secondary changes in the characteristics of the manufacture of 32% acid, it is noticeable that it plays such an important part when manufacturing 35% acid. This is similar to conditions described for the "unique system". Under our normal working conditions the manufacture of 32% acid from phosphate rock provides results which are very near to the possible maximum. Therefore, any improvement, whatever its potential, could only have a minor effect on these results. On the other hand if we had to work under more difficult conditions any improvement would be very valuable. The question may be asked - "What is the mechanism governing the influence of the phosphate grinding?" It would seem that we should look for it in the acceleration of the reaction and hence in the acceleration of sulphuric acid consumption, thereby retarding the H₂SO₄ content limit and reducing the risk of blocking the reaction, both of these being prejudicial to a good yield and quality of crystallisation.

Whatever the reason this part of the study has permitted us, not only to overcome the peak concentrations of 32% to 35% P₂O₅, but also it has enabled us to determine the conditions

which permit a 35% acid being produced with yields approaching those obtained with a 32% acid. In addition, for the remainder of the investigation we have at our disposal a certain number of factors which may be classified in order of decreasing effectiveness, viz.

Intense grinding of phosphate.

Modification of the temperature during reaction.

Increase of duration of reaction.

Reduction of the H_2SO_4 content in the liquid phase.

The simultaneous application of these factors when necessary and the possible existence of still undetermined factors, e.g. the rate of recycling the acid, allows us to look forward with optimism to the introduction of higher concentrations in phosphoric acid manufacture.

IV. EXPLORING THE ZONE OF HIGH CONCENTRATIONS 35 to 45% P_2O_5 .

In this series of experiments we have tried throughout to determine the concentration of phosphoric acid which could be obtained without changing the hydration state of the crystalline calcium sulphate. Secondly, we tried to specify the limits of the zone wherein gypsum would be formed under our operative conditions by varying the temperature of the reaction mixture. Finally we have noted each case where the concentration was raised, but have not tried to improve on it. This work is the subject of the following survey.

Following the conclusions of the previous experiments, the operative conditions were laid down at the start. All the possibilities, were however, not used to the maximum, part of these being kept in reserve in case any particular difficulties were encountered.

We worked in all cases with 75% ground phosphate.

The temperature was lowered below the limit value (see below).

The sulphuric acid content was maintained between 20g. and 25g. per litre, whatever its concentration, and not increased in proportion to the P_2O_5 .

Duration of the reaction was, however, extended to 6 hours (this time represents the average period which the phosphate spends in the mixture which is being reacted, and should not be confused with the duration of the test which was of the order of 30 hours for each of the variations studied). Similarly the acid recycling rate was such that the proportion of solids in per cent by weight of reaction slurry was constant. This was unfavourable in trials of high concentrations.

The order of the variations were as follows:-

The concentration was brought in stages from 35% to 45%,
: 35 - 37.5 - 40 - 42.5 - 45% P_2O_5

The temperature was at first dropped to a level such that the working conditions were within the zone, specified by the Lehrecke diagrams, where gypsum is formed. Following this the temperature was raised until it approached the conversion curve based on the findings of Sanfourche.

The following variables were studied:-

(a) 32% phosphoric acid (control experiment)	T ^o 75 - 80 - 85°C.
35% P ₂ O ₅	T ^o 65 - 75 - 80°C.
37.5% P ₂ O ₅	T ^o 60 - 65 - 70°C.
40% "	T ^o 55 - 60 - 65°C.
42.5% "	T ^o 50 - 55 - 60°C.
45% "	T ^o 40 - 50 - 60°C.

No irregularity or "blocking" was noted in experiments using high concentrations under these conditions. When these appeared with concentrations of 32% and 35% P₂O₅ at temperatures of 80 - 85°C, they occurred exactly in the same zone where the Lehrecke and Sanfourch curves tended to come together, our working conditions being nearer the higher curve. It was verified that in all cases the calcium sulphate in the reaction slurry was in the form of gypsun. Moreover physical measurements were confirmed by raw materials balances and the absence of discontinuity in the development of the experiment.

The results of the manufacturing experiments are summed up in the following table. The data given is limited to an intermediate temperature except for the control experiment (32% P₂O₅) where the temperature was 75°C.

<u>P₂O₅ Concentration %</u>	<u>32</u>	<u>35</u>	<u>37.5</u>	<u>40</u>	<u>42.5</u>	<u>45</u>
<u>Temperature</u>	<u>75°</u>	<u>75°</u>	<u>65°</u>	<u>60°</u>	<u>55°</u>	<u>50°</u>
<u>Reaction efficiency</u>	<u>98.25</u>	<u>98.2</u>	<u>97.5</u>	<u>96.8</u>	<u>96.0</u>	<u>95.6</u>
<u>Residue H₂SO₄ % Ph.</u>	85.6	85.5	84.5	83.9	84.6	83.2
<u>% P₂O₅ attacked</u>	259.2	259.0	257.9	258.0	262.3	259.1
<u>Crystals (L) (μ)</u>	100-200	50-200	50-100	25-80	20-75	15-75
<u>R (L/l)</u>	<u>2</u>	<u>2</u>	<u>2.5</u>	<u>3</u>	<u>3.5</u>	<u>4</u>
<u>Filtration speed</u> (P ₂ O ₅ per hr. per sq. metre).	<u>815</u>	<u>710</u>	<u>515</u>	<u>300</u>	<u>235</u>	<u>105</u>
<u>Amount Retained</u>	100	115	160	170	167	155
<u>Washing Efficiency</u>	<u>98.15</u>	<u>98.0</u>	<u>97.4</u>	<u>94.9</u>	<u>92.0</u>	<u>86.6</u>
<u>Phos. Acid made °Be</u>	37.0	39.9	42.4	44.75	47.55	51.2
<u>P₂O₅ %</u>	21.9	34.9	37.3	40.1	42.45	45.45
<u>H₂SO₄ %</u>	1.65	1.65	1.75	1.5	1.3	1.15
<u>Distribution of Flourine</u>						
<u>CaSO₄ Slurry</u>	45.0	46.5	-	45.0	41.0	43.9
<u>Acid</u>	45.5	44.5	41.1	39.8	38.4	31.2
<u>Liberated</u>	<u>9.5</u>	<u>9.0</u>	-	<u>15.2</u>	<u>20.6</u>	<u>24.9</u>

The manufacturing characteristics showed a continued marked deterioration as the concentration was raised.

The reaction efficiency was progressively lowered and was no longer within the acceptable limits.

The crystals became thinner and they became more uniform.

There was at first a rapid deterioration in the removal of liquor from the cake which afterwards progressed steadily at a favourable rate. It was above all the filtration speed and the washing efficiency which were most seriously affected.

It must, however, be pointed out that the filtration speed only represents the passage of "strong" acid fractions and that this variant is considerably reduced by the passage of solutions which are being continually diluted by washing. Therefore, the results which may be attained can be appreciably lower than those obtained here with the same speeds.

Further to washing, this was done in our experiments without recycling the partially concentrated acid. It is certain that in order to obtain a highly concentrated acid, several washings must be used: two washes up to 35%, three for 35 to 40% and four above 40%.

It is noticeable that the fraction of the fluorine liberated from the acid increases with higher concentrations, but that the amount retained in the cake is not influenced to a very large extent. Also, we would emphasise that the raising of the temperature within the limits studied would lead to a slight improvement in the reaction efficiency and filtration speed, but this change may be unfavourable for the washing stage. The conclusions reached in this part of the paper may be summarised as follows:-

It is not impossible to obtain concentrated phosphoric acid from the gypsum process.

The concentration can be as great as 45% or more, the limit not having been reached.

The manufacturing characteristics are on the other hand unfavourably influenced to a high degree by concentration. Therefore, from the results obtained industrial production above concentration of 35% cannot be envisaged.

It is possible to discover more favourable conditions? We have at our disposal significant possibilities:-

Increase in duration of reaction.

Increase in recycling rate.

Raising of temperature
Raising of H₂SO₄ content } No limits have yet been established.

More intense grinding of phosphate (the fineness of phosphate used was lower than 60% through a 200 mesh (0.08mm)).

Research into practicable improvements is the subject of the last part of this paper.

V. IMPROVEMENT OF OPERATING CONDITIONS WITH A HIGH CONCENTRATION.

This final phase of our study had, at least on an experimental scale, to be decisive. At the time of writing, this phase is only just beginning. However, the results obtained are already sufficiently interesting and, as they bring with them prospects of final success, merit mention.

The work will have to be carried out in the following manner:-

Firstly, research into the operating conditions and the interpretation of the action of the principle factors for a normal concentration. Following this, the development of tests required to calculate the results when using different concentrations.

The concentration of 40% P₂O₅ was chosen for the first stage of the trials. This, it will be noted, is already high in comparison with the actual manufacturing conditions and is the average of the zone explored.

The reaction temperature was raised to 70°C. and then to 75°C. (prior to this it was 55 - 60 - 65). No trends towards the irregularities in the reaction were observed even at 70°C. and the calcium sulphate was always in the form of gypsum. There was little improvement in manufacturing characteristics. It affected the reaction efficiency which increased from 97.1% at 70°C. to 97.15% at 75°C. The filtration speed was increased from 300 kg. P₂O₅ per hour per square metre to 320 kg. and then fell off to 305 kg.

The acid recycling rate was increased to make the proportion of solids expressed as a percentage of the volume of the reaction slurry equal to that of the reference experiment:-

The solids content expressed in percentage by weight dropped from 36.5 to 35%.

The temperature was maintained at 70°C.

The effect of this was favourable but improvements remained limited.

The reaction efficiency increased from 97.1 to 97.25%

The crystal size increased 25 - 80 to 50 - 100 and the ratio decreased from 3 to 2.5

The filtration speed noticeably improved from 320 to 385 kg. P₂O₅ per hour per square metre.

The reaction time was increased to 9 hours.

The solids content by weight remained at 33%

The reaction temperature remained at 70°C.

There was a marked improvement in comparison with results obtained in the first experiment using 40% P₂O₅ (see IV). The reaction efficiency increased from 96.8 to 97.9.

The crystals were of normal size (as for 32 - 35% acid).

The filtration speed rose from 300 to 575 kg. P₂O₅ per hour per square metre.

The washing efficiency increased from 94.9 - 95.5%.

It can be seen that an improvement in the results may still be affected. The last operating conditions which were used showed that reaction characteristics can be obtained approaching those of experiments with 32% P₂O₅. The filtration performance remained inferior, but to a certain extent this is inevitable; this is because of the higher viscosity of the acid at that filtration speed. The concentration of P₂O₅ in the cake makes it necessary to have systematic washings..... but the differences with the 32% acid are not greater than those found with the best working conditions using concentrations between 25 and 32%. Also the values obtained in this instance makes it possible to envisage industrial production.

The work will be continued as previously indicated for higher concentrations.

CONCLUSIONS.

We are not yet in a position to say that we can manufacture economically a 45% phosphoric acid directly by the gypsum process. We have, however, proved that this production is not theoretically impossible. We have specified the development of the properties and performance of manufacture with increased concentrations in addition to the steps to be taken when encountering known set backs.

The process which is theoretically open to development can only be perfected as our knowledge and the technical developments at our disposal improve. We think that in the near future it will be possible to look back at our present concentrations in the same way as we now look at the earlier stages of the manufacture of phosphoric acid.

We shall be satisfied if, through this paper, we have contributed to progress in new technical possibilities.

SUMMARY.

The production of highly concentrated phosphoric acid has always been one of the major problems of manufacturers.

This problem has not been solved adequately because, in spite of the urgent demand for highly concentrated phosphoric acid, the largest proportion of phosphoric acid produced by the wet process has a concentration of less than 30% P_2O_5 ; the maximum concentrations obtained by the gypsum process are in the neighbourhood of 32% P_2O_5 .

The causes for this limitation of attainable concentration are twofold:-

1. The theoretical diagram of the state of hydration of sulphate of lime appears to indicate that high concentrations cannot be reached without the formation of a semi-hydrate or anyhydrite; as compared with gypsum, this results in a very unfavourable moisture equilibrium which is contrary to the aim pursued.
2. The conditions for realising this aim are getting more intricate, the process tends to become unstable and the conditions of manufacture deteriorate proportionately to the increase in concentration.

We have undertaken to investigate the possibilities of obtaining a highly concentrated acid and to determine the limits which are theoretically attainable and economically advantageous.

In this connection we have the following important factors in our favour:-

1. Theoretical data which lead us to expect, under certain conditions, a larger zone of stability for gypsum than it has been admitted generally,
2. The most logical process of industrial production in a "single vessel" which becomes economically more attractive, the more difficult, theoretically speaking, the operating conditions tend to be.
3. Methods of investigation reproducing on a small scale the exact and perfectly co-ordinated conditions of industrial manufacture, especially concerning the study of phosphates of different origin (subject of our first paper).

We divided the paper in its present form into three sections:-

1. Increase in the limit of industrial concentration from 32 to 35% P_2O_5 .
2. Use of the operating zone attainable during the gypsum phase (35 to 45%)
3. Improvement of the conditions for obtaining a high concentration
 1. During the initial stage of this experiment we have, at first, encountered serious difficulties in manufacture, the same difficulties explaining, very likely, the limitation of the concentration to 32% P_2O_5 when produced on an industrial scale. We have learned to overcome these difficulties and to determine the variables which permit to obtain a high concentration: crushing of phosphate, increase in duration of attack and of re-cycling phosphoric acid, lowering of temperature, maintenance of H_2SO_4 content of the liquid phase within definite limits.....²...⁴ The application of a certain number of these variables, enables one to obtain 35% of P_2O_5 with an output equal to that of a 32% acid.
 2. Based on the first results we succeeded in attaining a concentration of 45% P_2O_5 in successive stages without modifying the state of crystallisation of sulphate of lime which remains in the form of gypsum. This concentration, however, is not a limit which could go beyond 50% P_2O_5 .

In contradistinction to this, the conditions of manufacture and output deteriorate in no uncertain manner as the concentration increases. That is the reason why we proceeded directly to the third section of this paper seeing that the possibilities of a practical manufacture remain our primary aim.

3. Our endeavour to improve operating conditions focused, at first on an acid with a concentration of 40% P_2O_5 . By bringing into simultaneous play favourable variables, the investigation of the adapted operating conditions enabled us to improve very considerably the first results obtained by that concentration, opening up new possibilities of improvement.

The trials conducted since writing this report, have, in fact, provided very favourable results permitting the consideration of the carrying out of these experiments on an industrial scale.

In another paper we have started to study in detail the zone of stability of gypsum under our operating conditions.

