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The Theory of Superphosphate Solubilisation.
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The Theory of Superphosphate Disintegration.

1. The manufacture of super-phosphates is one of the oldest branches of the chemical large-scale industries. One might assume that the reactions occurring during the manufacture of super-phosphate have been known in all their details for a long time. In most technologies this manufacture is represented as a simple technical process, which does not create any particular difficulties, and which does not present chemical problems. The change from 'tricalcium-phosphate' to 'monocalcium-phosphate' and calcium sulfate, appeared to be such a simple reaction, that it was not considered worth while to pay too much attention to it. Research, however, especially during the last twenty years, has shown that superphosphate is a complicated substance, during the manufacture of which a wealth of reactions occur, and also, in parts, other reaction components are formed than has been assumed throughout decades.
11. For the manufacture of superphosphate, finely ground rock phosphate is mixed with sulfuric acid. The purpose of this procedure is the conversion of the not easily soluble, and for plant roots, not absorptive phosphoric acid^{o)} in the rock phosphate into an easily soluble form, i.e. monocalcium phosphate. Superphosphate is a mixture of several solid and one liquid phase. The former consist mainly of monocalcium phosphate and calcium sulfate. The liquid phase, in accordance with the starting conditions, represents a more or less concentrated and - with monocalcium phosphate - saturated solution of phosphoric acid. Since the greater part of the monocalcium phosphate is present in gel form, we are justified to mention also a dispersed phase.

The phosphoric acid is bound in the rock phosphate in a complex form, which is called apatite, i.e. as hydroxyl apatite, or as fluor apatite, or as a combination of both. This kind of combination is the most stable of all phosphoric acid compounds, and an energetic attack is therefore necessary in order to break it up.

111. This stability in the last resort is also the reason why any attempts to obtain dicalcium phosphate through a direct method, have not, so far, been successful, although this was the aim of many manufacturers, and has been tried often enough. The available experimental data in respect of the equilibrium in the system $\text{CaO-P}_2\text{O}_5 - \text{H}_2\text{O} (\text{SO}_3)$ are insufficient to determine all conditions

for the limited ranges of existence of mono- and dicalcium phosphate. Also lacking is an accurate investigation of the problem, to what extent the formation of dicalcium phosphate is a matter of the speed of reaction or the equilibrium.

The conversion of rock phosphate by means of sulfuric acid is an exothermically proceeding heterogeneous reaction, during which a solid phase, i.e. the rock sulphate, is reactive to a liquid phase of the sulfuric acid. It has been established that it is characteristic for a heterogeneous reaction to proceed along the phase boundary; this applies to the case under investigation, at least in so far as it concerns the direct attack of the sulfuric acid on the apatite.

The granules of the ground rock phosphate may be approximated as spheres. The ratio surface: contents of such spheres can roughly be expressed as $r^2:r^3$. Thus at the commencement of the reaction there exists a limited surface for a great quantity of sulfuric acid, which is sufficient for the conversion of the total rock phosphate into monocalcium phosphate.

The quantity of the sulfuric acid to be used can be determined by calculation. The rock phosphate naturally contain mainly calcium phosphate, and in addition in varying quantities, calcium carbonate, calcium and magnesium silicates, sulfates, calcium fluoride, silicic acid and also iron and aluminium, either in oxide form or bound in phosphoric acid or silicic acid, and small quantities of organic substance. To be accurate, it should also be mentioned that, in addition, a number of other elements are present, mostly in minute quantities. These are compounds of iodine, chlorine, manganese and alkali. They are of no importance for the conversion of P_2O_5 to the soluble form. The calculation of the required quantity of sulfuric acid can be effected by establishing the requisite stoichiometrical formula for the forming of monocalcium phosphate. In this connection it should be remembered, that a small part of the phosphates must be converted into the phosphoric acid, in order to guarantee the existence of the monocalcium phosphates. In so far as the compounds which are present in the rock phosphate as impurities, react to sulfuric acid, they must be considered in the calculation.

For a long time the superphosphate industry has used in their manufacture considerably larger quantities of sulfuric acid than were established theoretically through calculations. Quantitatively the values were at approximately 20% in excess. One reason for this was that, in parts, up to 30% of the calcium phosphate was converted into free phosphoric acid. Secondly, the excess consumption could be explained by unsuitable or faulty mixers which did not guarantee homogeneous combination of the two reaction components.

Finally the accurate dosage of ground phosphate and acid is of an importance which should not be underestimated. The manufacture of superphosphate is based of the course of a chemical reaction. Therefore, quite definite stoichiometrical ratios must be adhered to, i.e. per time interval a quite definite quantity of phosphate must be always followed by an equivalent quantity of acid. While the accurate dosage of sulfuric acid can be effected comparatively easily, the even and accurate weighing out and apportioning of ground phosphate presents great difficulties, as everybody with practical experience in this matter knows. The undesirable running of the ground phosphate, which may assume such proportions that it spreads like a liquid, or electrostatic charges may always cause time and again unforeseen trouble and inaccuracies.

The results of an inaccurate dosage can be determined very nicely experimentally by taking dissolving samples in vertical direction in intervals of 10-20 cm from a dissolving vessel. Fluctuations up to 20% of the degree of conversion obtained in each case will be quite frequent. The analysis made at the delivery of the daily output

of freshly made superphosphate, represents only a mean value, which shows inaccurate dosage in extreme cases only. Rock phosphate, which has not been converted owing to lack of sulfuric acid, is lost for ever. Likewise if the superphosphate is poured in heaps there won't be any subsequent conversion, since the pouring is not accompanied by a simultaneous supply of acid. The reason for this is that a diffusion of the free phosphoric acid, even if present in varying concentration in the layers of a heap of superphosphate, does not take place within the available storage time from granule to granule. The problem of accurate dosing can therefore not be taken seriously enough. Here are sources of losses as the extent of which will cause unpleasant surprise when the analytical results obtained are evaluated arithmetically. In addition to the aforementioned reasons fluctuations in the degree of conversion may also be caused through incomplete mixture.

In modern installations, where both homogeneous mixing and accurate dosage is guaranteed, acid consumption approximates very closely the theoretically determined values.

In the "Manufacture of the Superphosphate"¹⁾ all compounds present in a rock phosphate have been taken into consideration in the calculation of the acid. It is, however, stated that the quantity of sulfuric acid necessary for satisfactory conversion cannot be evaluated by means of chemical formulae. This discrepancy between theory and practice previously can probably, to a large extent, be traced to the insufficiency of the apparatus available.

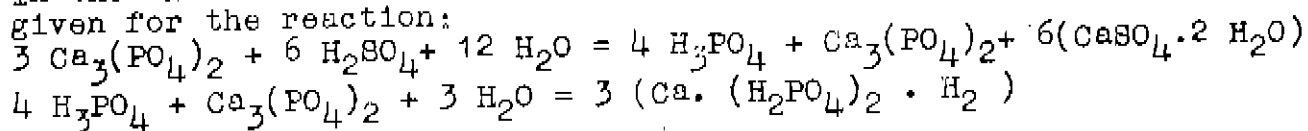
For the calculation of an industrial working quantity of sulfuric acid it is not necessary to consider all compounds which may be present in very small quantities. It will be sufficient to dose the sulfuric acid in such a way that all alkaline earths, after deducting those quantities of acid necessary for the formation of monocalcium phosphate, can be converted into sulfate. A dissolving trial, if possible at the place of manufacture, will easily help in the determining of any small corrections which might be necessary.

To make understanding easier, here is an example. The analysis of a Morocco phosphate in the dry state showed 33.5% P_2O_5 and 51.4% CaO . For the formation of the monocalcium phosphate 13.22% of the CaO are required. Thus another 38.32% CaO must be bound to sulfuric acid. For this purpose 67.02% sulfuric acid (100%) are required. Calculated on sulfuric acid of 58°Bé we obtain a value of 89.5%. Such a quantity of sulfuric acid will enable satisfactory conversion of Morocco phosphate without any difficulties.

This method of calculation of acid ignores the fact that the rock phosphate contains some CaO which is already bound with SO_3 and that a small quantity of the rock phosphate will not be converted; further that a part of the phosphates should be converted into phosphoric acid. This method is, therefore, intended as one of approximation, which however suffices to furnish useful data for a dissolving trial.

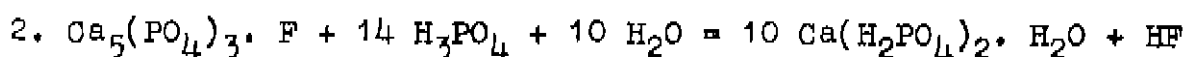
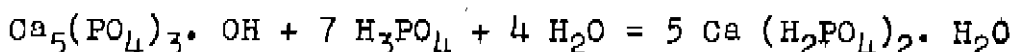
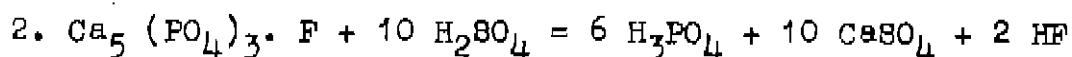
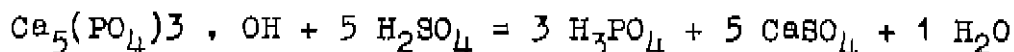
The reaction between rock phosphate and sulfuric acid to monocalcium phosphate proceeds in two steps. During the first, the sulfuric acid converts with the requisite proportion of phosphate to phosphoric acid and calcium sulfate. The latter during the second step reacts with the remainder of the rock phosphate by forming monocalcium phosphate. This reaction sequence is explained through the fact that it is a reaction within a heterogeneous system.

In the "Manufacture of the Superphosphate" the following equations are given for the reaction:



1) Vieweg & Sohn VDDF 1926 page 86.

Since the rock phosphates are not tricalcium phosphate, but hydroxyl - or fluor apatite, and the result is likewise not calcium sulfate, but anhydrous calcium sulfate, the formulae for the reaction should read:



Let us consider the first reaction. As already mentioned, this is a heterogeneous reaction with a change on one phase boundary only, i.e. the surface of the apatite granules. It proceeds strongly exothermic, i.e. by releasing of considerable heat. If ground rock phosphate with a temperature of 15°C is mixed with sulfuric acid having 30°C, then the reaction mixture in an industrial plant will be heated to a temperature of 120°C.

The chronological sequence of the reaction may differ greatly. Efforts should be made to render the conversion rapid and complete. If there are delays, incomplete disintegrations are obtained. The reaction cake does not harden completely, and in certain circumstances a greasy, and in exceptional cases even a liquid mass is the result.

When rock phosphate and sulfuric acid are brought together, the sulfuric acid attacks the surface of the phosphate granules. The apatite granules are thus split up at their surface under formation of various intermediate products. To these should be counted the Di and mono-calcium phosphates as intermediates. It is obvious that further sulfuric acid will always react with the partner possessing best reaction capacity, i.e. in this case with the intermediate products formed under formation of phosphoric acid, before unaffected apatite is attacked further.

Which are now the factors to influence the reaction?

Since the reaction proceeds strongly exothermic, its complete sequence i.e. the nearest possible obtaining of the right hand side of the equation, can be influenced favourably by removal of heat. This is in fact true. Already in the laboratory it can easily be shown that the use of cold sulfuric acid results in considerably better conversion than the same experiment conducted with hot sulfuric acid of say 100°C. In the latter case, apart from unattacked rock phosphate, unused sulfuric acid can be found and it takes a long time, often days and weeks, until complete conversion has occurred. Under working conditions this experience is reflected in the continuous demand on the part of old experienced hands not to let the temperature of acid to be used for the reaction, exceed 30°.

It is however, questionable if the comparatively small temperature difference alone can be taken to have such a tremendous effect. Of greater importance, should be rather that with the rise in temperature in a secondary way the colloid-chemical processes going on are affected unfavourably, i.e. the depositing of monocalcium phosphate and of calcium sulfate.

However, much as a quick conversion may be desirable for working reasons on the one hand, it is equally desirable, on the other hand, to achieve at the same time the greatest possible removal of water, in order to obtain a product with the smallest possible water content. In the first place the removal of water increases the P₂O₅ content of the end product, and secondly, and this is of particular importance, the mechanical properties of the superphosphates improve proportionately to the decrease of the water contents. It does not require further explanation that an increase in temperature is favourable for the evaporation of

water. With this statement, however, we are placing ourselves once more between Scylla and Charybdis; in one instance a decrease in temperature is favourable for a rapid and complete conversion; in the other instance an increase in temperature is desirable for the equally important and required evaporation of water.

In practice a method has been evolved which can be considered as a compromise solution between the two divergent demands. It is based on the use of an acid not exceeding 30°C.

As a further expedient to increase the evaporation of water the carbonate contents of the phosphates was generally considered. In the superphosphate industry it has probably been customary for decades, to convey the reaction material from the mixing containers quickly into the reaction chambers, in order to effect as completely as possible decomposition of the carbonates in these chambers. The freed carbonic acid caused the phosphate paste, now in the process of setting, to loosen in a honey comb or sponge like fashion. This loosening naturally favoured increased removal of water. For these reasons carbonates were occasionally admixed to phosphates deficient in carbonates. These methods however did not become general practice as they were uneconomical.

It has been long established that the simplest method for the reduction of the water contents in superphosphates, was to use a sulfuric acid in excess of 54°Bé. In spite of this, this aim was not reached until comparatively recently.

Owing to the evaporation of water and the expulsion of the carbonic acid the end product obtained is lighter than the sum of the quantities of rock phosphate and sulfuric acid originally introduced. This difference in weight is called shrinkage. It requires an increase of the P₂O₅ contents of the superphosphate, as compared with the mere arithmetical result, which is obtained from the addition of the weights of the two initial components.

If we consider the reaction equation between rock phosphate and sulfuric acid, then we have on the right hand side phosphoric acid and calcium sulfate. In order to prevent the formation of an unstable equilibrium, and rather to enforce a completest possible reaction sequence towards the right hand side of the equation, it is necessary to upset any possible formation of an equilibrium continuously. This can be effected by causing the calcium sulfate, which is forming, to crystallize out continuously. If this crystallization does not take place, the reaction comes to a standstill, and in addition to undecomposed apatite, unused sulfuric acid will be found. This phenomenon is known from the practice to every super-phosphate chemist, and is dreaded. In such a case the mixture is said to be 'overstirred'. It occurred particularly easily when rock phosphate was mixed with a strong sulfuric acid. (F1)

In an explanation regarding the incomplete reaction Schucht 3 & 4) states that the attack of sulfuric acid on the phosphate granules would be slowed down by a superficial layer of gypsum. Quite apart from the fact that not 'Plaster of Paris' but calcium sulfate is formed, this assumption of Schucht does not explain either the varying behaviour of stronger and weaker sulfuric acid during the disintegration.

F1) A further form of 'overstirring' could also occur if the thixotropic properties of the superphosphate (which increase the weaker the sulfuric acid is) are ignored.

3) "Manufacture of the Superphosphate" Vieweg & Sohn 1909 page 372.
4) " " " " " " 1926 " " 69.

Against Schucht's statement speaks also the fact that the solubility of calcium sulfate increases with increasing concentration of the sulfuric acid. Thus for instance approximately 70 mg calcium sulfate will dissolve in 100 g of 100% sulfuric acid, if this acid is available in a concentration of 50 Be.

On the other hand the same quantity of sulfuric acid in a concentration of 59 Be will dissolve approximately 160 mg calcium sulfate.

Buggiech and Meppen ⁵⁾ investigated the dissolving of rock phosphate in diluted solutions. 2.5 g rock phosphate (727 mg P_2O_5) with 2.45 g sulfuric acid (54.7% SO_3) are shaken in 700 cm water for 30 minutes, after which a disintegration of 86.4% was registered. The same quantity of rock phosphate shaken with 14.72 g phosphoric acid (18.9% P_2O_5) resulted in a conversion of 79.3%. If, instead of water, a superphosphate solution was used - obtained through shaking 20g superphosphate 18% in 1 liter water - then the conversion decreased to 41.8% after 30 minutes. If for the phosphoric acid treatment a monocalcium phosphate solution was used instead of water, the former containing 3.322 mg P_2O_5 per liter the conversion obtained after 30 minutes was 47.4%. Should the presence of dissolved calcium sulfate now give rise to the opinion that it would favour the coating of the surface of the phosphate granules with calcium sulfate, then this assumption loses all ground, if there are now only completely soluble particles present in the solution.

Even if the ratios of concentration in these experiments differ from those in the conversion of rock phosphate and sulfuric acid to superphosphate, it is highly probable that in the latter case the reaction products still in solution will have the same effect as in the diluted solutions.

In this connection it should be mentioned that the feasibility of the analytical determination of the superphosphate, and in particular the analytical evaluation of incomplete solubilisation processes in accordance with the official method, might be based on the retarding effect of dissolved calcium sulfate on the reaction sulfuric acid-rock phosphate and of dissolved monocalcium phosphate on the reaction phosphoric acid-rock phosphate. Owing to the dissolution of the salts there is no change in the original reaction state during the shaking with water. Suitable test series can easily be conducted.

Probably in order to eliminate the trouble encountered during the reaction - as discussed in the foregoing - it has been suggested from several quarters, to divide the process into two steps. In accordance with these suggestions, one method would be to add the quantity of sulfuric acid necessary for complete conversion to the rock phosphate in two chronologically separated operations, or - to use a different method - to proportion the sulfuric acid in such a way that in the first place all rock phosphate is converted into phosphoric acid, or even increase the quantity of sulfuric acid used in excess of the amount required for the formation of phosphoric acid.

The irregularities during the reaction are doubtless dependent on the ratio of the surface of the phosphate to sulfuric acid. If there is a large phosphate surface, then the reaction will take place so quickly that there won't be any formation of solutions supersaturated with calcium sulfate.

It is certain that the acid concentrations prevalent in each case are also of some importance in this connection.

⁵⁾ Unpublished paper.

If the shortest possible reaction period is to be obtained while using, at the same time, a strong sulfuric acid, then it follows in the light of the foregoing, that the largest possible reaction surface should be presented to the sulfuric acid. This can be effected through fine powderisation of the rock phosphates. For this purpose it is of importance to get the residue by means of a sieve DIN 1171 of 0.15 mm mesh as close to 0 as possible. As approximation guide it may be mentioned, that a powderisation of the phosphate to a residue of 10% by means of sieve DIN of 0.15 mm mesh permits use with sulfuric acid up to 58° C. This however results to a superphosphate having approximately 8% of water only. A further condition for employing this method is the use of intensive mixers.

One exception from this approximation rule is Kola apatite. This is pure fluor apatite. Quite apart from the fact that it is much more difficult to destroy the structure of fluor apatite than that of hydroxyl apatite, there is an additional factor in this particular case to be noted, e.g. with flotation Kola apatite it must be assumed that size of granule = size of crystal. All other commercial rock phosphates on the other hand have a micro-crystalline structure. The ratio size of crystal = to size of granule is bound to result in a substantial surface reduction. In fact this is shown through the behaviour of Kola apatite to sulfuric acid. Owing to the slowness of reaction of Kola apatite it is therefore favourable when using it, to employ sulfuric acid of higher temperature than is usually suitable and necessary.

Previously it had been customary to effect mixing in the shortest possible time, and to convey the mixture obtained, to the reaction chamber, as quickly as possible. This working method was determined by the apparatus available in older type installations. Since mixing of the reaction components was effected in mixing containers, the mixture commenced to set in the latter during a too long time of stay. In addition it was found necessary to convey the mixture to the reaction chambers also in a, thinly liquid state, especially if the chambers were large dimensioned, in order to spread it evenly all across the width. In the last resort these requirements are bound up with the desire to obtain a high rate of water evaporation, and to eliminate disturbing influences resulting from the thixotropic behaviour of superphosphate. When using strong sulfuric acid, water evaporation is relegated more and more into the background. But also the thixotropic characteristics of superphosphate can now be rendered neutral to a large extent in modern installations through methods of an exactly opposite nature.

In addition to improved apparatus equipment the most important factor in the developing of superphosphate in respect of improved quality should have been the fine grinding. ^{F1)} It is likewise of great importance for the degree of disintegration, the extent and speed of the after-disintegration and thus for the final yield. It is possible to obtain within a few minutes a completely reacted superphosphate of sandy nature, if only fine grinding has been effected to a sufficiently high degree.

Limitations in this respect should be determined through economic factors only, as the increase in power requirements for the grinding assumes considerable proportions with increased fineness. A further point is that most existing plants are not equipped technically for a manufacturing process employing such short, reaction periods.

111. Let us consider now the second step of the reaction rock phosphate-sulfuric acid. Let us suppose in this connection, that the process of step 1 has taken place practically quantitatively, and that all sulfuric acid has been converted into phosphoric acid.

F1) Certain improvements requiring a further working process are of independent of this, e.g. drying or mixing with marl etc or granulation.

This phosphoric acid is now to form - with the residual apatite - monocalcium phosphate. In this case also, we have a heterogenous reaction proceeding exothermically. As experience shows, the conversion of phosphoric acid proceeds easier and better than that with sulfuric acid, and the difficulties and complications which could be noticed in the course of the first phase, are hardly noticeable here. From the manufacture of double-superphosphate, i.e. from phosphoric acid, it is known that this reaction proceeds practically trouble-free. The reasons for this can perhaps be found in the fact that in this case one substance only is formed, i.e. monocalcium ~~sulfate~~, and not - as in the sulfuric acid reaction - two substances, i.e. phosphoric acid and calcium sulfate.

If in the case of sulfuric acid reaction the conversion process depends on the precipitation of calcium sulfate, then it depends in the case of phosphoric acid reaction on the precipitation of monocalcium phosphate.

Tschelewetzki and SS. Rubinowa ⁶⁾ investigated the rate of disintegration of the apatite in phosphoric acid in relation to the H-ions concentration, the surface area of the apatite particles and the temperature. They found that the conversion proceeds proportionally to the H-ions concentration and represents a logarithmic function of the reciprocal values of the absolute temperature. The reaction is delayed through the formation of the reaction products having a buffer effect.

The reaction between phosphoric acid and apatite can proceed comparatively quickly. Here also, owing to the heterogenous nature of the reaction, the reaction period depends on the surface available. Thus fine grinding has also a quite favourable effect here in two ways. In the first place surface increase effects a decrease in the reaction period, and secondly a far more thorough conversion is obtained, i.e. an increase in the yield, than in the case of using coarse powder.

Monocalcium phosphate is only stable if phosphoric acid is present. Further details are to be discussed in connection with the treatment of the free acid. It is therefore necessary to proportion the quantity of sulfuric acid employed and thus also that of phosphoric acid in such a way that part of the rock phosphate is converted into free phosphoric acid. Both in order to economise with acid, and in particular to obtain high quality products the endeavour should be to keep the proportion of free acid as small as possible and to approximate it as close as possible to the theoretical value of the equilibrium monocalcium phosphate - phosphoric acid.

In the case of commercial super phosphates this value (theoretical) is assumed at approximately 0.8-1.2% free phosphoric acid. In reality however, the contents of free acid in super phosphates is considerably higher. It was not rare to employ in previous years, a free acid contents of 6-7%. This was done mainly in order to obtain greatest possible conversion by means of using great quantities of sulfuric acid to forestall any decrease in water solubility while the material was being stored in a poured heap. The water content of such a superphosphate was usually near 14%.

The reaction periods, i.e. the time interval between the mixing of the components and the taking away from the reaction chambers should usually have been between 2-4 hours.

When working with modern plant and the use of fine powder and strong sulfuric acid, this picture changes substantially. The total reaction period up to the removal of the super phosphate can easily be reduced to 20 minutes. The products obtained - with a water contents of approximately 8% - show after 14 days a free acid contents of 2.5-3% only. By this means a total yield of 95-97% of water soluble phosphoric acid is obtained. By considering the citrate soluble particles these yields can be increased to 98-99%.

6) Central Gazette 1938 1. 1453.

For many years it was assumed that the setting of the superphosphate paste was due to the setting of the gypsum. This is a fundamental error, as we shall see in the following when the components of the superphosphates will be discussed, since the substance formed is not gypsum, but anhydrate, i.e. water-free calcium sulfate. The solidifying of the superphosphates is thus not due to formation of gypsum, but to the crystallization of calcium sulfate. For this process the forming of monocalcium sulfate is however also of great importance. The thixotropic properties of the superphosphate alone indicate that we have here a colloidal chemical process. Such processes most probably apply also to the solidifying of the primarily liquid superphosphate paste. Stevenius-Nielsen ⁷⁾ states, that monocalcium sulfate most probably precipitates in the form of a gel. It can thus be visualised that the monocalcium sulfate formed during the disintegration with phosphoric acid, will constitute a sol immediately after the reaction in heat, the monocalcium sulfate being in solution in micro-crystalline form. During cooling this sol then changes into a solid gel. Condition for the solidifying, i.e. rapid formation of a gel, is the suitable arrangement of the crystals in conjunction with the adsorption of a water surface. This process is accelerated through heat which is determined at first through the exothermic nature of the disintegration reaction.

If the statements made in the foregoing be true - their experimental verification would be very desirable - then it can be deduced that it is suitable to cool as quickly as possible the superphosphate after commencement of the solidifying process, in order to accelerate the crystallizing processes. This action would then accelerate the conversion of the superphosphate into a solid product.

This has been proved in practice. In addition cooling has also favourable effects on the so-called 'after reaction'.

IV. The manufacturing period, i.e. the time interval between the joining of the components and the removal of the formed superphosphate from the reaction chamber, does not suffice for the full completion of the reaction. At the end of the period of time mentioned above, conversion of the rock phosphate has been effected up to 85-90%. The reaction then proceeds during the storing of the superphosphate in poured heaps, which may take up to 6 weeks. The retarding, or rather the slowing down, of the conversion process might be explained with retarded precipitation of the monocalcium sulfate. The effect of such a slowing down has been already discussed in connection with the reaction with phosphoric acid. Furthermore, there are diffusion processes which take place during the total conversion of these rock phosphate particles which are not yet attacked, and these processes do not proceed easily 'to the very end'.

Cooling of the hot superphosphate favours crystallizing of the monocalcium sulfate. Accordingly it would be correct to cool the superphosphate leaving the reaction chamber in the hot state. If it is poured on a heap without any further cooling, then it retains a substantial part of its original reaction heat. This however, is equivalent to, a slowing down of the further conversion. This also explains why a sample selected from a freshly poured heap and stored separately, will convert at a much more rapid rate than the total mixture having a higher temperature.

This part of the conversion is generally called the after reaction. In accordance with the grade of phosphate and the manufacturing conditions chosen, the final yield - related to water soluble phosphoric acid - may amount to approximately 98% maximum. By including the citrate soluble particles this figure can still be increased. In conjunction with the after disintegration, setting the poured super-

7) Applied Chemistry 1943, page 176.

phosphates commences. This phenomenon we shall discuss later on.

Generally applicable figures in respect of the extent of the primarily obtained conversion, the duration of the after reaction and the yields obtained finally cannot be given since this is determined from many factors which are due to local conditions. In itself it is possible to accelerate the reaction very considerably. By using very finely ground rock phosphate, and strong sulfuric acid in an intensive mixer, conversions of 90% and more can be obtained after only 30 minutes. The answer to the question whether to employ such a method depends mainly on economic factors.

In order to obtain the highest possible yield, it was customary previously, to use a considerable surplus quantity of sulfuric acid, resulting in 6-7% free phosphoric acid in the final product. Apart from the unnecessarily increased consumption of sulfuric acid such an action has always detrimental effect on the quality. Owing to the continuous demand to improve the mechanical properties of the super phosphate it was necessary to discard such a method. The new method was to work not with an acid surplus, but with a quantity below the required norm, in order to obtain lowest possible figures of free acid and likewise of water.

By this means products were obtained with approximately 90% of the effective P_2O_5 in water soluble form and 10% in citrate soluble form at approximately 3% free acid.

The best conditions for the formation of a highest possible proportion of citrate soluble particles is not yet known. So far comparative investigations of different products from various manufacturers have merely shown that there seems to be a certain relation between the degree of citrate solubility obtained and the concentration of the acid used for the disintegration, in such a way, that the citrate solubility increases with the concentration of the acid. This is understandable and probable. The formation of dicalcium phosphate is, as we know, a secondary reaction, which is dependent on the liquid phase in the superphosphate. In accordance with the concentration these secondary reactions proceed in a different manner. The concentration of this liquid phase, however, is determined through the quantity and the concentration of the originally applied sulfuric acid. In contrast to previous manufacturing conditions this process uses approximately 10% less sulfuric acid for the dissolving process. If the quantity of sulfuric acid employed is reduced further, then there is practically no formation of citrate soluble salts. This too might be explained by a liquid phase of the superphosphate, which in such a state and under such conditions is not suitable any more for secondary reactions.

In so far as the conversion of a part of the phosphoric acid into citrate soluble dicalcium phosphate is officially recognised, the once dreaded so-called decrease of the water solubility in super-phosphate has lost its importance. This process may be the subsequent formation of dicalcium phosphate. This reaction is caused through the hydrolysis of a proportion of the monocalcium phosphate to dicalcium phosphate and free phosphoric acid.

In the 'Manufacture of the superphosphate' ⁸⁾ it is stated, that monocalcium phosphate can change under pressure with surplus tricalcium phosphate to dicalcium phosphate and thus the decrease of the water solubility is favoured accordingly through pressure.

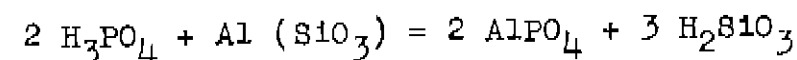
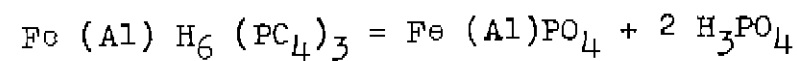
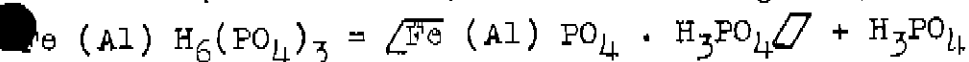
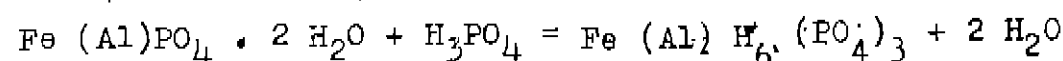
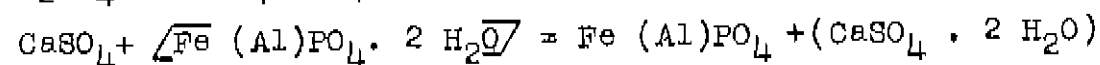
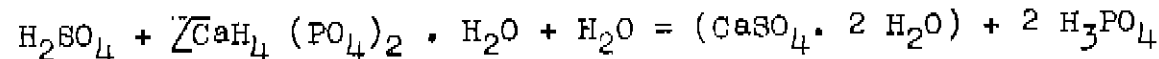
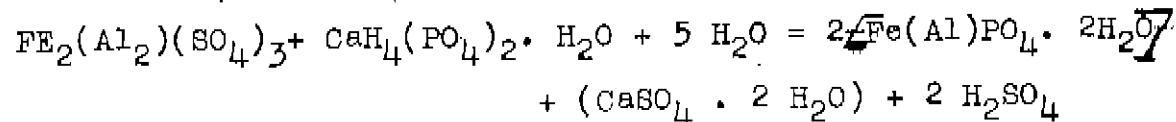
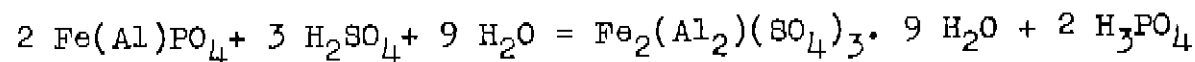
8) VDDF Vieweg & Sohn 1926 page 70.

Since monocalcium phosphate does not form dicalcium phosphate with apatite, such reaction is not likely to be set in motion by pressure which apart from everything else is comparatively low. The only point to be noted would be, that owing to storage pressure the superphosphate particles are brought closer to each other, and that over a longer period of time a change in the liquid phase of a quantitative nature in a heap of superphosphates occurs, in such a way, that at the bottom a concentration takes place. These two phenomena might then favour hydrolysis. As already mentioned, however, there are no exact data. The possibilities for the formation of the dicalcium phosphate will be discussed later on.

A further factor for the decrease in the water solubility are the iron and aluminium compounds present in the rock phosphates. Previously, when rock phosphates were used containing considerable quantities of these substances, this could give rise to serious trouble. It was, therefore, the custom to fix the iron and aluminium oxide contents of the rock phosphates at 2%, and the suppliers of rock phosphates are under a contractual obligation not to exceed this proportion.

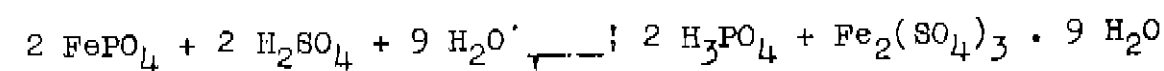
In commercial phosphates the effects of these compounds may therefore be neglected. They may occur in varying compounds, as oxide or as compounds with phosphoric acid or silicic acid. In consequence the attack of the sulfuric acid may vary also, so that by no means the total quantity of iron- and aluminium compounds need necessarily always be converted.

In 'The Manufacture of superphosphate' ⁹⁾ a series of equations are given, representing the sequence of the reaction processes.



There is no experimental data regarding the actual process sequence in accordance with these equations.

It is further stated that in accordance with the conversion



phosphoric is in a position to maintain iron oxide in solution in the form of a soluble compound i.e. sulfate. This certainly might explain to a large extent, why in former years the content of free phosphoric acid in superphosphates was kept comparatively high.

⁹⁾VDDF Vieweg & Sohn 1926 page 197.

Regarding the conversion possibilities of the sesquioxides Stevenius Nielsen¹⁰⁾ is much more cautious. He states that part of the iron- and aluminium compounds are dissolved to sulfates, which in the course of the progressive formation of the monocalcium sulfate are converted into primary iron- and aluminium phosphates. A further dissolution of the iron- and aluminium compounds still remaining in the rock phosphate residue takes place later. The decreasing concentration of free phosphoric acid will cause - according to Stevenius Nielsen - hydrolysis of the dissolved iron- and aluminium phosphates, in such a way¹¹⁾ that these salts will precipitate again in the form of phosphates not soluble in water.

It is also possible that in this process there are merely solutions supersaturated with iron- and aluminium phosphates from which these salts precipitate, if owing to secondary reactions the conditions for the supersaturation are not fulfilled any longer.

In these reactions iron must take first place, as it is attacked easier than the aluminium compounds. It would therefore be more correct if, in the case of phosphate purchases, no common limitation would be stipulated for the contents of iron and aluminium, but separately for both. However now that the water solubility alone is not more the determining factor for the evaluation of a super phosphate, these problems, which formerly could have become pretty important, no longer arouse much interest.

The after reaction then consists of two opposite running reactions. Firstly by means of further attacks on the remaining rock phosphate still intact an increase of the water soluble phosphoric acid is effected, and secondly a reduction in the proportion of water soluble phosphoric acid may occur through formation of the dicalcium phosphate and in certain circumstances also through formation of a dicalcium¹¹⁾ phosphate - calcium sulfate dihydrate crystalline solid solution. We shall revert later on to the possible formation of small quantities of calcium sulfate dihydrate.

A further reduction in water solubility may occur through formation of basic iron- and aluminium phosphates. In general, however, the occurring of additional water soluble phosphoric acid is more substantial than their reduction through the secondary reactions. In the case of normal storage periods no final equilibrium is obtained. Owing to the supersaturations of the solutions and the comparatively close proximity of the stable areas of components the reactions proceed extremely slowly. To this has to be added that, at least during the primary period of the after reaction, a continuous change in the concentration of the liquid phase takes place.

As the last of the reactions to be discussed in this connection we should briefly touch on the expelling of fluorine. The fluorine content varies greatly in accordance with the type of rock phosphate. In Curacao phosphate it amounts to 0.7% and may reach up to 4% in Morocco phosphate, but within one particular type it remains fairly constant. It is a little higher than the stoichiometric ratio of the fluor apatite indicates. In such a case it is likely that the fluorine is present in the form of calcium fluoride. Even if the fluorine content in a rock phosphate does not exceed the proportion necessary for the formation of fluor apatite, part of the fluorine may be present in the form of calcium fluoride, if the rock phosphate concerned is a mixture of fluor and hydroxyl apatite.

10) Journal for Applied Chemistry 1943 pages 177/178.

11) These phosphates may likewise not be soluble in ammonia citrate solution and citric acid.

11) Scheel, Paper read at the International meeting of Superphosphate Chemists at Hamburg, October 1937.

During the conversion of the rock phosphate with sulfuric acid a comparatively small proportion only of the total fluorine contents is expelled, this varying again in accordance with the type of phosphate, from approximately 10-35%. 65-90% are thus not being utilised and are lost, i.e. they remain in the super phosphate.

The fluor yield does not now depend in any way on the proportion of the fluor contents, for by no means the largest quantities of fluorine expelled from the phosphates with highest fluor content. Related to sodium fluosilicate, the yield for instance from Morocco phosphate, having 4% fluorine, amounts to 6-8 kg per ton of produced superphosphate only, while the yields from Constantine- and M'dilla phosphate, having 3.5 - 3.8% fluor, amount to 11-13 kg sodium fluorsilicate.

This varied behaviour of rock phosphate types is in the main probably determined by their crystalline structure and the resulting reactivity. It may also be assumed that apatite bound fluorine and calcium fluoride show different chemical behaviour. A favourable factor for fluorine separation is, among other things, a higher carbon content of the rock phosphate, as for instance in the case of Constantine phosphate.

The fluorine should be separated in the first place as hydrogen fluoride, and should then convert with silicic acid to silicon tetrafluoride. This reaction is desirable since in the superphosphate industry fluor is generally obtained in the form of fluorsilicic acid. If the silicic acid contents of the rock phosphates does not suffice for the conversion of their expelled fluorine constituents to silicon tetrafluoride, then the detrimental effects to the yields may be considerable.

The conditions under which the phosphates are dissolved is also of some importance for the yield. In accordance with several manufacturing observations the extent of the fluorine expulsion increases with the strength of the sulfuric acid used. An acid temperature of 30-35°C has proved to be the most favourable. The differences in apparatus and plant of the various disintegration processes, however, has only a negligible effect on the yield, since even in most modern and continuously working installations no higher fluorine yield can be shown.

VI. The chemical investigation of the super phosphate was applied mainly previously to the determination of the proportion of water soluble and non-soluble phosphate, since the ratio of this value is of determining importance whether the manufacture is an economic proposition. No importance whatsoever was attached, on the other hand, to calcium sulfate, quantitatively the main constituent of superphosphate, amounting to over 50%. This explains that until recently completely wrong views were held in respect of this constituent. For instance the solidifying of the superphosphate paste in the reaction chamber was ascribed to the setting of the gypsum, i.e. the conversion of the calcium sulfate anhydrite to dihydrate. Besides, the experimental verification that in the case of superphosphate we have anhydrite and not dihydrate, is not at all difficult. This makes it appear even more amazing that such a fundamentally wrong assumption as the one regarding the formation of gypsum, could prevail for decades without anybody even thinking of verifying it experimentally.

Let us however discuss the monocalcium phosphate first. First of all the monocalcium phosphate, which formed as a sol, will convert into a gel. A part of this reaction (even more than that) - the final phase of the conversion of the phosphoric acid with the rock phosphate altogether takes place after the pouring of the superphosphate in a heap. The hardening of the fresh superphosphate is caused thereby through storing. The hardening does not depend therefore on the setting of the gypsum, in so far as they are not very considerably in excess of the usual storage periods but the causes are essentially colloid-chemical effecting this process. Finally in addition the micro-crystals may form larger crystals. This process may also cause hardening.

The degree of hardening may vary greatly. It depends first of all on the quantity of the liquid phase in superphosphate. If this proportion is very high, then it will of course cause closer cementing of the primarily loosely poured superphosphate particles, especially under storage pressure. Crystallization from the liquid phase may also occur. The degree of hardening also caused through the colloid-chemical processes just discussed, is determined through the quantity of the liquid phase with regard to its intensity. Hardening may take place to a considerable degree, rendering the use of such a superphosphate difficult.

If it is considered desirable to oppose the hardening process and if possible to eliminate it, then the manufacture of superphosphate must be effected in such way, that the factors causing the hardening are where possible eliminated, or at least kept within small limits. By using strong sulfuric acid the water contents in superphosphates can be decreased considerably. Furthermore care should be taken to conduct the disintegration in such a way that at the time of the storing of the superphosphate the reaction is completed to the greatest possible extent. The further this can be achieved, the less trouble there will be from excess hardening.

Finally the secondary reactions are also of importance for the hardening if only in a subordinate manner. The behaviour of the calcium sulfate will be discussed later on, in detail. We should however recall at this stage the formation of iron- and aluminium phosphate, mainly however the hydrolysis of a part of the monocalcium phosphate and the formation of dicalcium phosphate caused thereby. This reaction will also be discussed later on in connection with the treatment of the liquid phase in superphosphate.

The monocalcium phosphate is not able to attack the apatite present in commercial rock phosphates. This explains why it is not possible to obtain dicalcium phosphate in one single working process respectively in one single reaction sequence. If the quantity of sulfuric acid used is just sufficient for the formation of dicalcium phosphate, then no dicalcium phosphate is obtained, but a quantity of monocalcium phosphate corresponding to the quantity of sulfuric acid used, apart from unattacked apatite. No further conversion takes place of the monocalcium phosphate with this residual apatite.

Against tricalcium phosphate, however, monocalcium phosphate reacts differently. Here a reaction occurs, enabling the formation of dicalcium phosphate from monocalcium phosphate + tricalcium phosphate. Since however tricalcium phosphate does not occur in the rock phosphates, this reaction is of no interest for our present discussion.

Similarly, the monocalcium phosphate is able to convert with bone meal to dicalcium phosphate. This is of interest, as in its structure bone meal is similar to rock phosphates. After all, bone meal - as has been established beyond doubt - is hydroxyl apatite. If this substance should nevertheless behave chemically in a different manner, then this might be explained by the -in contrast to the rock phosphates- extremely fine micro-crystalline structure of the apatite in the bone. This unusually fine structure makes it possible for the monocalcium phosphate to attack.

As mentioned already the super phosphate contains in addition to the mixture of salts, i.e. monocalcium phosphate and calcium sulfate, a liquid constituent, which saturates these two salts and keeps them in parts in solution. This liquid consists of phosphoric acid saturated with monocalcium phosphate, the concentration of which is variable. The different degrees of concentration depend on the initial conditions selected for the disintegration, i.e. quantity and strength of the acid and the obtained change. In standard analysis this constituent can be evaluated by determining the water ^{#1} and the free acid.

#1) In superphosphate water occurs in three different forms; water of constitution, water of crystallization, hygroscopic or free water.

Ordinary superphosphate contains usually 10-14% moisture and 4-5% free phosphoric acid. These figures, however, by no means represent the total moisture contents. If for instance 14% water and 4.3% free acid have been determined in a superphosphate, a contents of 20% of phosphoric acid of 30% concentration can be evaluated from these figures. In addition this acid is then saturated with monocalcium phosphate and calcium sulfate and contains also small quantities of hydrofluoric acid, sulfuric acid and other substances. Since the solubility of these substances depends on the temperature, the moisture contents of the superphosphate is also determined by the temperature. Although there are no accurate investigations of the equilibriums applicable, the moisture contents in the example selected can be approximated at 25-28%. This then is approximately double the value which appeared likely in accordance with the initial figures. This shows that the liquid constituent in the superphosphate is quite considerable and it explains its importance for the mechanical properties.

The usual method of determination of the free acid, i.e. to titrate a watery extract of the superphosphate to be examined with $n/4$ NaOH, cannot be employed in all occurring cases. In particular the values obtained when investigating superphosphates with additions of a basic nature ⁽²⁾ are far too low, i.e. during the shaking conversions occur between the surplus basic constituents and the free acid still present. Conversely too high values are obtained when shaking dried superphosphates, because acid pyrophosphates are hydrolysed. These errors ⁽³⁾ can be avoided by substituting organic solvents such as cyclohexanol or acetone ether mixtures for the water. This method is bound up with the determination of the free water. The usual drying chamber method would also furnish wrong figures, since the removal of the water effects changes in the concentration conditions, ⁽⁴⁾ resulting in secondary reactions with subsequent erroneous evaluations.

By means of such methods it could be established that even with surplus basic additions present in the superphosphate, phosphoric acid could still be found. The correctness of this assertion can be proved as follows :- In a saturated monocalcium phosphate solution partial disintegration takes place through hydrolysis ^(2 and 5) resulting in an equilibrium: $\text{Ca}(\text{H}_2\text{PO}_4)_2 \rightleftharpoons \text{Ca HPO}_4 + \text{H}_2\text{PO}_4$. In basic superphosphates therefore the free phosphoric acid can disappear only then, when sufficient basic additions have been introduced allowing the total monocalcium phosphate originally present to convert into dicalcium phosphate.

From the determination of the ratio of water and free phosphoric acid in the above equation it can further be deduced that in a superphosphate a certain amount of phosphoric acid must be present, as long as there is free water still present, i.e. for every 1% free water at least 0.079% free P_2O_5 . Accordingly a superphosphate containing 14% water should contain in the most favourable case at least another 1.2% free phosphoric acid. In practice such figures cannot be obtained, and if in a superphosphate without basic additions at satisfactory disintegration a figure of 2.5% for the free acid can be obtained, then such a result can be considered very good.

It is surprising that calcium sulfate, the main constituent of superphosphate, has received attention during the last few years only, considering that the problem of the formation of gypsum is of great importance for the improvement in quality of superphosphate.

⁽²⁾ Meppen & Scheel, Journal 'Applied Chemistry' 1937, page 811

⁽³⁾ Lehrecke Journal 'Applied Chemistry' 49, 620/1936.

⁽⁴⁾ Hill and Jacob, Journal of the Association of Official Agricultural Chemists, Menasha, Wisconsin, USA. volume 17 1934, page 487.

⁽⁵⁾ Basset, Journal Inorganic Chemistry 59, 1 (1908).

Calcium sulfate may occur as gypsum $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ as semihydrate $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ (Plaster of Paris) and as anhydrite. Semihydrate can be obtained by the action of nitric acid 1.4 on gypsum or through heating of gypsum in air heated to over 107°C . This is the conversion point from gypsum to semihydrate. At this temperature hydrated water removal to semihydrate occurs. If heated further the crystal water is given off zeolitically, i.e. while the crystal lattice is maintained. A conversion to anhydrite occurs only at heating to 500°C . According to Van't Hoff and Balarew 2 modifications can be distinguished for the anhydrite, one capable of reaction and one less capable of reaction. The first modification can be obtained through the dehydration of dihydrate. It is called soluble anhydrite; the second, which is the one less capable of reaction, is a type of mineral anhydrite known as non-soluble anhydrite.

Contrary to older views calcium sulfate occurs in superphosphate nearly exclusively as anhydrite.^{18,17,18)} This is of pigment-like fineness, the grain size in the different superphosphates varies and may depend on the method of manufacture. The superphosphate anhydrite corresponds to the soluble anhydrite of Van't Hoff. Since the difference between the latter and mineral anhydrite is the speed of reaction only, it can be assumed that we do not have different modifications in this case, but that the capability to different reactions can be explained by the different sizes of the grains.

In ordinary superphosphates with 3% free phosphoric acid and over, practically no hydration of the anhydrite to dihydrate occurs even during long storage periods. Only in very old samples of superphosphate containing less than 3% of free phosphoric acid and in specially neutralised super phosphates greater quantities of dihydrate can be identified¹⁹⁾.

Semihydrate occurs in superphosphates in very small quantities only^{F1)}. It may originate during the formation of the anhydrite in the course of passing through an intermediate stage. On the other hand it may occur in wet phosphoric acid manufacturing methods. It is interesting to note, that in this case the semihydrate is of the type which hydrates only very slowly²⁰⁾. This slow capability to hydrate is probably caused by a larger crystal size than occurs usually in semihydrates.

In order to explain the behaviour of the anhydrite in superphosphate, this problem was investigated scientifically before the War by Scheel. In this connection it has been necessary to refer to investigations which have not yet been largely published.

If the anhydrite is to hydrate in the superphosphate, then it should extract the water necessary for this process from the liquid phase of the superphosphate, i.e. from a phosphoric acid. This would mean an increase in the concentration of the phosphoric acid. If formation of dihydrate does occur at all, then it can take place only so long, until the phosphoric acid - owing to the extraction of water - has reached such a concentration that its vapour pressure equals that of the dihydrate crystals. This point should be of notable interest both for the manufacture of superphosphate and the obtaining of phosphoric acid by the wet method.

16) Krugel and Retter 'Superphosphates' 1950 page 57.

17) Lehrecke, Tekn, Tidekr. 1935, Afd. Kemi 11 and 12.

18) Hill and Henricks. Ind. Engng. Chem. 28,440 (1936).

19) Scheel, lecture at the International Chemists Congress at Hamburg, 1937.

F1) This semihydrate may also be the cause of the presence of negligible quantities of dihydrate in the superphosphate.

20) Lehrecke: Patenter Kemiska, Landskrona.

In a paper by D'Ans and Hofer with regard to the system $\text{CaSO}_4 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ the boundary concentration of the phosphoric acid, at which di-hydrate is just still stable at 25°C , is stated as amounting to approximately 45%.

If treated with water, mineral anhydrite reacts only very slowly with a starting period extending over days and weeks. Then all of a sudden an increase in the formation of the hydrates occurs. The behaviour of the anhydrite from the superphosphate differs from the former in quality only. To quote some figures: Anhydrite from superphosphate has absorbed after 10 days approximately 17% of the crystal water necessary for the total formation of dihydrate, and after 30 days hydration is nearly completed. By comparison mineral anhydrite has absorbed approximately $1/3$ of its crystal water only after 110 days.

If hydration of anhydrite is effected in phosphoric acid of varying concentration, we have the notable result that a phosphoric acid of approximately 10% accelerates the hydration. If the concentration of such an acid rises to approximately 24%, the water absorption of the anhydrite is greatly retarded. At a phosphoric acid concentration of 44% it comes completely to a standstill, without being equivalent to a complete reaching of the equilibrium.

The experiment to determine and to establish the equilibrium between $\text{CaSO}_4 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$, may be attempted instead from the anhydrite direction likewise in analogous form over semihydrate or dihydrate. The work done in this direction has however not been completed. Up to now accurate results have been prevented through very long reaction periods, supersaturations and similar disturbing factors.

Calcium sulfate - dihydrate, which crystallizes from phosphoric acid, always contains some phosphate. This is determined through a mixed crystal formation between the calcium sulfate-dihydrate and the isomorphous dicalcium phosphate - dihydrate. In a phosphate solution of calcium sulfate the following equilibrium exists: $\text{CaSO}_4 + \text{H}_3\text{PO}_4 \rightleftharpoons$

$\text{CaHPO}_4 + \text{H}_2\text{SO}_4$; This however has been moved greatly to the left. The separation of the dicalcium phosphate - dihydrate is favoured through its lesser solubility as compared with calcium sulfate-dihydrate

The determination of this mixed crystal is very elucidating, since it explains why in the phosphoric acid processes, in the course of which calcium sulfate is always precipitated as gypsum, this gypsum always contains a phosphoric acid content which cannot be washed out.

To summarize the results known so far we can say this:-
In phosphoric acid concentrations up to approximately 45%, the solubility of the dihydrate is smaller than that of the anhydrite. In this case the dihydrate is then the solid phase. Over this concentration, however, anhydrite is less soluble and therefore stable. Of course the difference in solubility within the existing range of the anhydrite and likewise just before are very small. Hydrating of the anhydrite and conversely the dehydrating of the dihydrate must be divided into two part processes: Firstly the disintegration of the metastable solid phase up to the saturation of the solution, and then the separation from the solution of the stable solid phase forming, whereby the former is supersaturated. The rate of the conversion is therefore influenced by the rate of dissolution, the solubility itself and the rate of separation.

Hönningen-Rh., 17th March 1955.