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TECHNICAL MEETINGS

Spain, 24th - 27th September 1957

Session I - In the Chair, Mr. H. Stevenius-Nielsen

The CHAIRMAN: As President of the Technical Committee, I have the great honour to open this technical meeting, which is the ninth in the history of our Association.

First of all, I should like to say that it was a very good idea of our Spanish members to have invited us here, and, in particular, I should like to thank Mr. Iglesias Saenz, because I feel he is the father of this idea. I would also thank S.A.I.QUI very much for the splendid arrangements they have made for us, and for the splendid reception we have received here in Madrid.

You know that in the preparation of such a meeting, it is always very difficult to get the papers in time. We have received many of the papers on time and I thank not only those authors but the others also. However, I regret to say that we received some of the papers so late that it has been impossible to translate them in time for all the members. Therefore, I wish to apologise if some of our members have not got all the papers, or at any rate have only received them during the last few days. Of course, we of the Technical Committee and the London office have the responsibility, but I would say that the authors also share part of that responsibility.

Our staff in London,have done some very hard work in preparing for this meeting and we thank them very much. But it would have been impossible for them to do this work if it had not been for some of our members, technical people, who helped them by translating and by checking all the technical terms. Here I should very much like to thank Mr. Brook, Mr. Dee, Mr. Sherwin, Mr. Schwehr, Mr. Procter and Mr. Craven of the United Kingdom for their very useful help, and Mr. Cocteau and Mr. Ardouin and Mlle. Foin of France.

Last, but not least, I very much want to thank my friend Dr. Raistrick, for the wonderful work he has done in preparation for this meeting. I am sure we are going to have some very interesting discussions.

We now have the first paper of this morning's section, and it is by Dr. Scheel.

PAPER 914 : Fluo-carbonate apatite as the main constituent of most phosphate rocks, by Dr. K.C. Scheel.

Dr. K.C. SCHEEL (Germany) : I have no special observations to make in regard to my paper, but if you have any questions would you please ask them ?

Dr. B. RAISTRICK (United Kingdom) : Mr. Chairman, Ladies and Gentlemen, the calcium phosphates play a very important part in many life processes, in scientific studies and in technological industries, and our own, of course, is one of these. We all buy calcium phosphate in some form and then we sell it again in a chemically and physically improved form.

The chemistry of the calcium phosphates happens to be extremely complex and difficult, and no part of it is more baffling or is the source of more controversy than the subject of the so-called carbonate apatites about which Dr. Scheel has written the first paper of our conference.

Dr. Scheel's approach to the problem has been to use the very powerful combination of chemical and X-ray methods. Even though these methods really are powerful, in my opinion they are not quite powerful enough, mainly for one reason, about which I should like to say a few words.

The apatite structure is a very stable one. It was first elucidated by Naray-Szabo and determined with exactitude by Beevers and McIntyre. But unfortunately, at least from the point of view of simplicity, the structure is able to accommodate other ions to some extent as alternatives to the calcium, the phosphate and the fluorine which are present in pure fluor apatite. For example, hydroxyl ion and chlorine ion can replace part of the fluorine; strontium can replace some of the calcium, and carbonate groups and water molecules have been described at various times as replacing both phosphate and/or fluorine. Finally, there are those workers who claim that some of the spaces in the structure do not need to be filled at all, and so we have the concept of defect structures involving, for example, a statistical absence of calcium from structural positions.

It seems certain that, because of some of these replacements and absences, the apatites consist of families of solid solutions, the properties of which vary in a continuous manner as a function of the chemical composition. It is for this reason, which we might call non-stoichiometry, that even the powerful techniques used by Dr. Scheel still leave us in a state of uncertainty.

Now I would like to suggest that discussion of Dr. Scheel's paper could be directed most fruitfully, not towards the details of his work, but towards its importance to producers and users of phosphate rock. I personally do not agree with all the scientific details of his paper, but these scientific aspects are mainly in another paper by Dr. Scheel which is not before the meeting today, and so it is the technological significance of his work which I would like to recommend to your attention.

Carbonate in phosphate rock is of importance to fertiliser manufacturers for two main reasons. It is important to manufacturers of elemental phosphorus for two quite different reasons, but I will not go into that now. To the fertiliser manufacturer it has a good feature and a bad feature. The good point is that it facilitates attack by sulphuric acid on the rock, permitting the acid to penetrate the rock, helping to stir the reaction mixture and giving a superphosphate of good physical properties. But, as we all know, some of the purer fluorapatites are relatively poor for superphosphate manufacture because of the difficulty of attacking them.

The bad point about carbonate, of course, is that, no matter whether it is in the rock as calcite or in the apatite structure as a replacement for PO_4 or fluorine, it must be associated stoichiometrically, or almost so, with an equivalent amount of calcium ions and thus be a means of neutralising sulphuric acid in a purposeless way. Later in the conference we have a paper from Professor Talmi describing one means of avoiding the waste of acid, i.e. by calcination.

I very much enjoyed reading Dr. Scheel's most interesting paper and I hope that we may hear from him, and from others too, more of the use to which his findings can be put for the benefit of our industry.

The CHAIRMAN : Does anyone else wish to speak ?

Mr. T. CESCA (Italy) : I should like to refer to a congress held in Munster and to the papers which were given there. I think it would be useful if Dr. Scheel could see those papers.

Mr. F. FAUVARQUE (France) : On Page 4 of your paper, you speak of incorporating calcium fluoride into the apatite structure and you think that the calcium fluoride, as is the case with calcite, is contained in the structure of the apatite.

In the paper which I have written and which I shall speak about shortly, I succeeded in determining the free calcium fluoride by considering the molecular ratio of free calcium fluoride and tricalcium phosphate, and almost arrived at the ratio of three molecules of tricalcium phosphate to one molecule of calcium fluoride. I should like to ask Dr. Scheel what he thinks of the presence of calcium fluoride in the apatite.

Dr. B. RAISTRICK (United Kingdom) : I should like to ask Dr. Scheel to say something more about the calcium carbonate contained in fluorapatite. I think it is likely that some or much of the calcium carbonate is held in solid solution as very small particles of calcium carbonate in the apatite. Would Dr. Scheel like to offer an opinion on this point ?

Dr. K.C. SCHEEL (Germany) : According to your opinion, Dr. Raistrick, the calcium carbonate is a solution in the apatite complex, or did I not understand you in the right way ?

Dr. B. RAISTRICK (United Kingdom) : In our laboratory, we have done similar work to your own, Dr. Scheel, and we have come to the conclusion that sometimes the calcium carbonate in a carbonate apatite of this kind is present as particles which are too small to be identified and characterised by X-ray methods. The X-ray method is extremely powerful, but it fails when the particles concerned are smaller than 100 angstroms cubed. Our results can only be explained on the hypothesis - and it is a hypothesis - that the calcium carbonate, and sometimes calcium fluoride, is present in the sample as particles which are smaller than 100 angstroms linear dimension.

Dr. K.C. SCHEEL (Germany) : I should like to refer to the remark by Mr. Cesca. I myself have also had various communications on that subject from people who were attending the meetings at Munster.

With regard to the point of Dr. Raistrick, I should refer to the extraction methods which have been carried out, and in the case of these very small particles of calcite they were able to find out by the extraction method that these particles are actually in existence. I have gone as far as three, four, five and six extractions to make quite sure that this is the case.

With regard to the remark by Mr. Fauvarque and, having read the report by Mr. Fauvarque, I have again made an attempt to investigate by the X-ray diagrams the presence of fluorspar. Unfortunately, these diagrams are no longer at my disposal. I have been in correspondence with the lady with whom I collaborate.

Unfortunately she is ill at present, but I propose to go further into that question.

The CHAIRMAN : Now we have had the different statements from the members and the answers from Dr. Scheel. I think we can regard this discussion as finished.

We will now move on to the next paper on the Agenda, by Mr. Fauvarque.

PAPER 901 : The use of physical methods for studying and analysing phosphatic fertilisers, by F. Fauvarque.

Mr. F. FAUVARQUE (France) : I have nothing important to add to my paper. I could make a remark on something which I have borrowed from the graphs which Dr. Scheel has published in his paper (Figure 2 where he shows the X-ray diffraction spectra of synthetic fluorapatites in a Constantine phosphate. You will notice that Dr. Scheel has shown three bands : the 120 band, the 102 band and the 002 band, being the three main bands of the apatites. On certain spectra on the same line, in the same column, you will see a small supplementary band which Dr. Scheel has not indicated as being part of the fluorapatite. This is probably the quartz band, the band which we used for determining the silica present in the form of quartz in the apatites. I do not know if Dr. Scheel agrees with me.

Dr. K.C. SCHEEL (Germany) : It is well known that there is a lot of quartz in Constantine phosphate and we have also identified the band.

Dr. W. THIESSENHUSEN (Germany) : I rather regret that the discussion on the paper by Mr. Fauvarque has already started, because I intended making a short introduction beforehand. I should like to refer to the very general title of the paper itself, namely the value of the physical properties.

Physical methods of analysing are a very great aid in determining the contents of fertilisers, particularly where chemical methods are either not sufficient or, to a certain extent, fail altogether. There are determinations which can be carried out with great accuracy. Also there are X-ray methods, which are very valuable in determining the various contents of rock phosphate, particularly SiO_2 and fluorine.

As far as superphosphate is concerned, it is very important, and it is a great help, to be able to decide whether calcium is present in the form of anhydrite or semi-hydrate.

As far as the compound fertilisers are concerned, the conversion of potassium chlorides into sulphates and nitrates is determined quantitatively. By means of infra-red spectrography it was possible to determine the amount of insecticide contained in fertilisers, after the fertiliser had been stored for some time, and to determine the organic additions.

All these various determinations are not only of a theoretical value, but are of very great importance for the manufacturer and for the practical man, and they should be pursued in that manner. I hope that the physical methods of determinations will be increasingly used in all the various laboratories of factories. Thank you, Mr. Fauvarque, for your paper and I wish to open the discussion.

Mr. G. ALBENNE (France) : I should like to say a few words about syngenites of which Mr. Fauvarque spoke.

We have carried out many experiments on this subject and, in addition to the monocalcium syngenite to which Mr. Fauvarque referred, we have found pentacalcium syngenite. When both sulphate of ammonia and potassium sulphate are present, simultaneous crystallisation occurs which is shown by the misplacement of the characteristic ammonium or potassium syngenite bands. It follows that the solubility of potassium or of nitrogen is the solubility of ammonium or potassium syngenite. From the agricultural point of view, this is of no importance, for as fast as plants absorb fertilising elements, new solutions are formed; but from the analytical point of view, it creates a difficulty, because the official methods of analysis are based on salts, either chlorine, ammonium sulphate or potassium sulphate. If we use the official methods without due care, we shall obtain contents which are weak both in ammonium and in potassium. In my opinion, the authorities must be persuaded to take into account these new analytical methods, for example, for ammonium by omitting water extraction and distilling directly in an Aubin apparatus; and, for potassium, instead of making pure water extractions, making them in hydrochloric acid.

Mr. F. FAUVARQUE (France) : Our work on syngenites began precisely because we observed differences in certain cases in the determinations of nitrogen or potassium in fertilisers. The problem was to know if there was not a formation either of syngenite or of mixed compounds. In certain cases, for example, we found enormous differences of 10 to 15% in the determination of ammoniacal nitrogen.

Mr. P. FLEURY (France) : I should like to comment on the part of Mr. Fauvarque's paper which deals with the exchange reaction between ammonium nitrate and potassium salts.

A number of years ago, our attention was drawn to this point by agronomists who were anxious to know if the ammonium nitrate contained in fertilisers did, in fact, change into potassium nitrate - although this is not, indeed, of great importance from the agricultural point of view. In particular, a paper was presented to the Académie d'Agriculture by Boischot and Hébert, in which they spoke of an extraction method using ethyl alcohol as solvent, which enabled them to prove that this reaction was far from being complete. Following this work, we carried out a study, part of which was done with the aid of X-ray diffraction techniques, and partly using the perfected technique of Boischot. The physical method indicated in every case that the transformation of ammonium nitrate and potassium chloride in compound or mixed fertilisers was complete, i.e. only potassium nitrate and the corresponding quantity of ammonium chloride was left. On the other hand, when using the solvent method, we were able, especially with the higher alcohols of the aliphatic series, to find products in which the ammonium nitrate was still fairly soluble, although the potassium salts were not soluble at all. When we treated mixtures and compound fertilisers with these solvents, we found in every case some free ammonium nitrate which could be isolated in crystallised form. Whatever the proportions of potassium and of ammonium, however, we were almost always able to show that about four fifths of the ammonium nitrate undergoes the double decomposition reaction, and that this reaction can even take place in reverse, that is, if potassium nitrate and ammonium chloride are mixed they form ammonium nitrate again.

I should like Mr. Fauvarque to say what he thinks of this variation between the physical and the chemical methods.

Mr. F. FAUVARQUE (France) : Extraction methods using solvents are well-known. Naturally we tried them before studying the reaction by X-ray diffraction. We used light and heavy alcohols, acetones and other products without obtaining a figure giving the total reaction.

A number of years ago we also used another method, namely, measuring the temperature of solution of nitrate/chloride mixtures. There also we found an intermediate solution temperature between that of ammonium nitrate and that of potassium chloride.

But these methods, either of solution temperature or of extraction by solvents, modify the point of ammonium nitrate equilibrium towards that of potassium nitrate, while the X-ray diffraction method leaves the mixture of crystals in the same state as they are in the fertiliser, without risking a change in the equilibrium. This, I think, is the principal reason for a difference between the chemical method and the X-ray diffraction method. I favour X-ray diffraction.

Mr. P. FLEURY (France) : We have thought of this objection and, with a carefully chosen solvent, we have proved that in fact the mixtures do not change at all, because probably the salts do not dissociate enough for there to be a reaction.

Dr. B. RAISTRICK (United Kingdom) : In paragraph 2 of Section 2 on calcium sulphate, Mr. Fauvarque discusses the double crystal between gypsum and dicalcium phosphate. It is our experience that the bands of diffraction are not identical.

Now the type of content of phosphate in gypsum is very important, not merely in the case which is mentioned here, but also in the case of phosphoric acid manufacture. We have done a little wor on this problem and we find that phosphate ions can replace sulphat ions in solid solution in gypsum and that 5 per cent replacement can quite easily not only be identified but actually determined. I believe that by refined X-ray methods - which is the method we have used - as low as 2 per cent replacement of SO_4 ~~in~~ gypsum by HPO_4 could be identified.

Mr. F. FAUVARQUE (France) : I am ~~in~~ complete agreement, but the Philips Norelco apparatus has not sufficient separating power to show a small modification in the lattice, a slight extension in the bands. It is necessary to use a monochromateur for determinin the sulphate, and we are unable to do this at present. With our Philips apparatus we have used an indirect method, which consists in determining the anhydrite and the semi-hydrate, since we were unable to determine the gypsum directly, because of the limited separating power of our apparatus.

The CHAIRMAN : I think we can close this interesting discussion and pass to the next item on the Agenda.

PAPER 913 : Analytical Control in the Manufacture of Fertilisers, by E.W. Schwehr.

Mr. E.W. SCHWEHR (United Kingdom) : Mr. Chairman, Gentlemen, in writing this paper, I wished to put before you the type of problem facing the chemist who is charged with the responsibility of carrying out production control work in the factory. In the paper, I have reviewed the principles on which he must work and have suggested the type and object of tests necessary for the control of the manufacture of single superphosphate, phosphoric acid, triple superphosphate and granular compounds. In some cases I have indicated the extent of variation of analysis which may occur in manufacture and I have indicated the effect of such variations on th analysis of the end product.

I have suggested the use of quality control charts as being both a method of indicating to management and operators alike the consistency of analysis of the materials they are producing and also of continually summarising the analytical results available. In the case of the manufacture of granular compounds, I have shown the basis on which such charts can be drawn up and interpreted.

The CHAIRMAN : I now ask Mr. Fleury to say a few words.

Mr. P. FLEURY (France) : Mr. Chairman, Gentlemen, to open the discussion on the paper given by Mr. Schwehr presents a great difficulty and that is to limit the discussion. This subject and the developments connected with it are so vast that a complete discussion session of our meetings would hardly be sufficient to exhaust it.

Also it is not my intention, in the brief time that I am allowed, to mention all the points in this paper which could be the subject of an interesting discussion. I prefer to draw your attention to a statement which seems to me to be somewhat surprising.

In two other papers which will be given later on and which deal with the control of the weight of sacks at delivery, I have found the following :

1) Mr. Moyrand, in paper 900, says at the beginning : "A surplus weight of 100 gr. per 50 kg. bag", i.e. an error of .2%, "can seriously affect the bagging operation when dealing with 50,000 metric tons of product per year and can cause a loss of 100 metric tons of fertiliser"; or a loss of 1½ million frs. "for an average compound fertiliser."

2) Mr. Angus, in Paper 909, page 2, confirms that an error of .1% overweight per 50 kg. bag gives a loss of £5000 on 200,000 tons of fertiliser and that the accuracy demanded by United Kingdom law is ± 0.5% for weighing apparatus.

We all agree, I think, that a customer who receives sacks weighing 1% less than the guaranteed weight will consider himself wronged and make a claim to the company. But a deficit in the weight of the sack or in the content of the fertiliser, certainly constitutes an equivalent loss to the customer who buys a certain weight of nutrient.

This is why, in France, no tolerances are legally admitted in the guaranteed content of fertilisers. In order to avoid trouble, we are obliged to keep slightly above .. and we have just seen that this is very costly. The tolerances in England, however, seem to be out of proportion with the accuracy required for weight. The errors allowed on the content, Mr. Schwehr tells us, are in the case of superphosphate ± 5% of the amount stated, and for compound fertilisers above a content of 8% fertilising elements, the allowed tolerance reaches 10% of the stated content, or 20 times more than the error allowed in the weight.

Indeed, the precision which analytical control can reach is a little higher than this latter figure, but in the example given by Mr. Schwehr on Page 12, Table III, this accuracy still does not exceed 4% with potassium, and it seems difficult, taking into account the variation of the content as the granule size differs, consistently to do better.

This variation between the accuracy of the weight and that of the content shows us the need for perfecting control methods in manufacture and a more precise regulation of the composition of fertilisers, especially of compound granulated fertilisers.

I believe, in fact, that it is not only in accuracy of sampling and analysis methods that we must look for the remedy for this state of affairs, but also by multiplying control and regulation methods in the works. I am thinking in particular of the manufacture of phosphoric acid, where, if the apparatus for introducing raw materials, the re-cycling and washing liquids, and the control of important factors in the reaction are sufficiently numerous and accurate, the analytical checks themselves can, without risk, be spaced out.

Before inviting my colleagues to speak in the discussion, I myself should like to put a few questions to Mr. Schwehr on some particular points :

1) Could he indicate what quick method is used by those working phosphoric acid plants to test the quantity of free sulphuric acid present in gypsum slurry where the reaction takes place ? (Page 7. (i) (e))

2) In the manufacture of granulated compound fertilisers, does not Mr. Schwehr think that, in order to check if the flow regulator are working properly, it is also necessary to analyse the mixture before granulation ? In fact, a deficiency in nitroge for example, in the finished fertiliser can arise just as well from an irregularity in the sulphate of ammonia feed, as from the accidental decomposition resulting from a loss of nitrogen in the drier.

3) Finally, there is one point where I am not entirely in agreemen with Mr. Schwehr. He says on Page 3, paragraph A :-

"Never take increments at regular time intervals if they are to be combined to give one sample for analysis. There is always the possibility that the time period chosen will coincide with some periodic fluctuation of the plant, so that a biased sample will be produced."

This risk is, in fact, very minute and, if one tries to avoid i it is very difficult to achieve a system of automatic sampling. But I think that this is a solution that must be adopted wherev possible, for it gives greater security than manual sampling, even when the latter is done by a very conscientious person.

Mr. E.W. SCHWEHR (United Kingdom) : I think a number of Mr. Fleur statements are not mine to answer but should be referred to subsequent papers; I think he will raise the questions again then.

With regard to the limits of variation in France, where they have a minimum, we in England have a maximum and a minimum, and it is as bad for us to give the farmer an excess as it is to give him a deficiency of any one plant food. That, I think, is the main difference between the two countries. From the analytical control point of view, we would much prefer to base our statutory statement on a minimum only. It would be much cheaper in the long run to give a little bit extra, to know that you were never going to come below the lower limits of tolerance.

Going to Mr. Fleury's three questions,

1) We determine the excess free sulphuric acid in the gypsum and phosphoric acid slurries by electrometric titration on the filtrate of the pulp solution and direction metation by using a pH meter. An alternative method is to titrate the slurry with barium chloride solution, using sodium rhodizonate as an external indicator. As soon as excess barium ions are present, a red lake is given on spotting the indicator. We are going to use this method in England fairly soon.

2) The next question Mr. Fleury raised was the desirability of analysing mixed materials before granulation. Because of the rotary granulation system in use in England and because of the differences in analysis of granules of different particle size, it is impossible to do this, since you never know what percentag of each cut (i.e. fines, product, or oversize) you will get at the end of your granulation process, and your feedbacks become rather more difficult to control.

3) Mr. Fleury's last question dealt with sampling. I think most of us here will agree that if we start arguing the merits of different sampling methods we shall never get on to the next paper. I prefer to do everything on a random basis, having spent a very long time chasing a non-existent nitrogen loss at one stage, which was eventually traced to a biased sample.

So I do everything possible to remove the possibility of a biased sample, even going to the extent of issuing randomised time-cards to plant operators which set down the times at which they will take the sample during each shift.

Dr. W. THIESSENHUSEN (Germany) : I should like to ask a question in connection with the size of granules. How is it possible that there is much non-homogeneity of the granules if, before granulation, there was in fact homogeneity ? Is this lack of homogeneity of the various granules permitted by law ? In Germany, the size of granules is absolutely guaranteed. Even if there were a difference in the size of individual granules we would get into trouble with the law.

Mr. E.W. SCHWEHR (United Kingdom) : In the first place, I do not in the brief paragraph explain the granulation system in use in Great Britain. In effect, we are mixing four or five solid materials and we are merely spraying them with water to stick them together to form granules. Each one of the raw materials in the mixture will have different characteristics towards granulation; it depends to some extent upon the particle size of each raw material and upon the proportions in which each one is present in the mixture how homogeneous is the analysis of the individual granules produced. This example I have quoted is probably the worst compound we have produced for non-homogeneity, and I have only used it there as an example of how different it can be.

With regard to the second question as to whether it is permitted by law, the answer is yes, because we sell it. The regulations applying to the sale of fertilisers in Great Britain lay down a method of sampling, and that the sample for analysis shall be drawn from such and such a percentage of the bags in the consignment. The whole sample is then treated, ground up and analysed and the limits are laid down according to the concentration of the fertiliser which is analysed. I think that this approach in the British regulations is considerably more realistic than the approach of the regulations in some of the countries on the Continent. While they, shall we say, fondly imagine that all their granules are of the same analysis, those samples I have seen and analysed, I would suggest, are somewhat similar to our own.

Dr. K.C. SCHEEL (Germany) : I do not quite agree with what Mr. Schwehr says as far as storage is concerned, as the coarser particles are bound to work themselves down in the heap, whilst the finer particles remain in the core. Therefore, in the manufacture of granules, there should be great care taken with regard to granule size.

Mr. E.W. SCHWEHR (United Kingdom) : I do not think there is anything to answer there, Sir.

Mr. C. HEUDIER (France) : I was surprised, as was Dr. Thiessenhusen, at the difference in analysis between small and large fertiliser granules. I think that this is a result essentially of manufacturing processes. I have, myself, never found such great differences, not even between the granulation fines and the finished product. I think that in processes where, for some reason or other, the constituents lose their physical properties of density and fineness, there is much more chance of obtaining homogeneous products, whatever the size of the granules. On the other hand, in granulation with water, there is not sufficient water to cause the constituents to lose their physical properties, and quite obvious variations are found.

I should like to put a question to Mr. Schwehr. It concerns the merchant rather than the manufacturer, but it is of great importance to the latter also. In France, we sell fertilisers based on a guarantee of content, which is stated on the ticket attached to the sack. In Great Britain, do the same conditions of sale exist? Or is the product sold in an analysis carried out on a sample quant of fertiliser?

Mr. E.W. SCHWEHR (United Kingdom): In England we must give to ever customer a statement of the analysis of the material he is buying. That analysis refers to his consignment; if he buys a one hundredweight bag, it refers to that one bag. If he buys five tons, it refers to a hundred bags.

Mr. C. HEUDIER (France): In these conditions, errors can only occu in the final analysis from the sales point of view and not in all t preceding manufacturing processes.

Mr. E.W. SCHWEHR (United Kingdom): Table 3 is, in effect, the finished product.

The CHAIRMAN: The time is rather advanced now, so I think we shall have to close this discussion.

I will ask Mr. Lagerholm to take the floor.

Paper 908 - GRANULATION OF FERTILISERS IN A CONICAL DRUM

by N. Lagerholm

Mr. N.W.G. LAGERHOLM (Sweden): Mr. Chairman, Ladies and Gentlemen, in presenting this paper I have tried to describe the application o a granulation principle which, as far as I know, is new, and certai is new inasmuch as it has been possible for us to obtain patents i most countries of the world. I should think that the apparatus w most resembles the conical granulator is the Teller granulator, bu of course, there are certain essential differences between the two apparatuses.

We have made certain experiments with the Teller granulator i order to compare the results on this conical drum and the granulat Our experience has been that the product obtained from our conical drum is more uniform and the individual granules more spherical th those obtained by using the Teller granulator.

As I mentioned in the paper, we have performed a certain numb experiments and trials with a conical granulator which has a diame of 4 metres. These results are not quite ready for publication, I can give an example of what the product looks like which we have obtained from this large conical granulator.

An experiment was performed with a mixture of potassium chlor and ordinary superphosphate and the capacity during the trial amou to about IO tons per hour. Around 90 per cent of the product was between I mm and 5 mm; 7.5 per cent of the product was excessive size and 2.2 per cent was under I mm. Inside the limits I to 5 m 5.I per cent were between I mm and I.8 mm; 46.I per cent were bet I.8 mm and 3.0 mm; 39.5 per cent were between 3.0 and 4.0 mm; a finally, 9.3 per cent were between 4.0 mm and 5.0 mm.

I should like to state that the 7.5 per cent excessive size originated mainly from the original superphosphate fed into the granulator due to insufficient disintegration. I do not conside that this capacity of IO tons an hour is the maximum obtainable, I should think that the capacity of such a granulator should be somewhere around I5 tons an hour.

Mr. Chairman, I have nothing more to say.

The CHAIRMAN: Please would M. Heudier speak now.

Mr. C. HEUDIER (France): I am particularly happy to open the discussion on this paper, because I am, myself, engaged in granulation and even in auto-granulation of superphosphates. I have not, unfortunately, had the time to study granulation apparatus, but here is a paper where an original plant is described which has remarkable qualities of granulation and selection of the granules formed.

I should like to put one or two questions to Mr. Lagerholm, which I should like him to answer stage by stage.

(to Mr. Lagerholm) You yourself have said, in your note, that the conical drum plays two roles - firstly granulation, and then sorting the grains. Has an attempt been made to study these two functions separately, particularly the sorting, by, for example, introducing well dried, granulated fertiliser into the drum, and measuring the length of time it takes for the different sized grains to pass out of the drum?

Mr. N.W.G. LAGERHOLM (Sweden): We have made no special experiments and trials on this point, but we have a certain amount of experience inasmuch as we know that when we have a fertiliser which is easily plasticised we cannot increase the amount of feed without limit, because when we exceed a load on the drum of about I5 tons an hour we know that, even if the granules plasticise and agglomerate sufficiently, we have exceeded the separating capacity of the drum. I hope that will answer your question.

Mr. C. HEUDIER (France): I suppose that the sorting of the grains of a fertiliser actually in the process of granulation must be fairly rapid, otherwise the grains would become considerably enlarged.

Mr. N.W.G. LAGERHOLM (Sweden): That is quite right. That is a problem because if we have a fertiliser or a fertiliser mixture which has too much liquid phase, which is too fresh, then those granules formed tend to grow excessively. Therefore, if we try to help this phenomenon by increasing the feed, it is impossible because we then exceed the separating capacity of the drum.

Mr. C. HEUDIER (France): At the foot of page 3 of the French text you have defined the capacity of the drum, but there is one sentence which, at least in French, would appear rather optimistic: "During operation, the load on the drum must, within quite narrow limits, equal the capacity of the drum". I understand this to mean that the amount fed into the drum must equal exactly the amount passing out .... What exactly does this sentence mean?

Mr. N.W.G. LAGERHOLM (Sweden): If the feed is less than the agglomerating capacity of the drum, then the granules tend to grow too large. By the load on the drum I mean the amount fed into the drum; by the capacity of the drum I mean, in this instance, the agglomerating capacity.

Mr. R.M. COLLINS (Honorary Member): It has to work at that capacity all the time to give those results.

Mr. N.W.G. LAGERHOLM (Sweden): If you want to change the capacity you have to alter the slant of the drum.

Mr. C. HEUDIER (France): I should like to ask one other question. What is the quantity of superphosphate in the drum at any given time?

Mr. N.W.G. LAGERHOLM (Sweden): In the case of the small granulator I should say it is about 500 kilograms.

Mr. C. HEUDIER (France): Which means that, if one is granulating at the rate of 3 tons an hour, the material remains in the drum for a period of IO minutes.

Mr. N.W.G. LAGERHOLM (Sweden): I should say something like that; perhaps something less.

M. C. HEUDIER (France): And at the rate of I½ tons an hour, it rema in the drum for 20 minutes.

You have shown considerable variations in output which, in your opinion, are due to the age of the superphosphate. You have define the age as being the length of time which elapses after the superphosphate is taken out of the dens. Has it occurred to you that th age of the superphosphate is a variable factor, tying up with the granulation of the super?

Mr. N.W.G. LAGERHOLM (Sweden): Yes.

M. C. HEUDIER (France): I disagree! You are correct in saying "ye if you consider that the granulation of the super commences at the t it is put into the granulator, but I disagree, because the granulati of the super does not commence then, but at the moment when a specia prepared phosphate is brought into contact with a specially prepared sulphuric acid. In these conditions, the age of the superphosphate on leaving the dens does not mean a thing. The superphosphate is capable of granulation during a certain phase of its evolution. It could very well be incapable of granulation after having left the de or, if so desired, it could still be capable of granulation eight da later. I think that all the variations which you have given in the granulating possibilities of your drum are possible only because you have taken this variable factor of the age of the superphosphate whi in my opinion, is not good. You could have obtained much more spectacular results if you had manufactured a super specially for granulation.

With regard to the granulation of compound fertilisers, there a as many different circumstances as there are formulae of fertilisers because it is the solubility of the constituents, of the potassium s or ammonium salts which are added to the super, which is instrumenta in producing the liquid phase essential to granulation. If you are granulating fertilisers with an ammonium nitrate base, you will appreciate that, from the practical point of view, granulation is impossible, because you will have, almost immediately, a liquid slu which will not granulate. On the other hand, with potassium salts chlorides - there should be no difficulty. With sulphates, it is much drier; the solubility of sulphate is much lower than that of chlorides. The whole question rests on the solubility of the salts and, consequently, it is not possible to generalise.

I do not want to spend more time on this at the moment, as I expect my colleagues will have a number of questions to ask, but I should like to say to M. Lagerholm that it would give me pleasure, after the meeting, to go through his paper with him, word for word.

Mr. L. DIDIER (North Africa): Mr. Lagerholm attaches much importan to the sphericity of the granules. From the agronomical point of view, is it necessary to attach much importance to the shape of the granules, as long as the size is correct?

Mr. N.W.G. LAGERHOLM (Sweden): I think when it comes to spreading granular fertilisers the spherical form of the granule would have a a certain importance. If I understand your question right, you ar asking whether the form of granule will influence the agronomic efficiency. I cannot answer that question.

Mr. L. DIDIER (North Africa): I don't think that is of great importance. It is certain that, with a Teller granulator, as M. Lagerholm has said, the product is less spherical, but I don't think that makes any difference from the agronomic point of view.

With regard to the age of the superphosphate, there, also, I am of the same opinion as M. Heudier; I do not think the importance is as pronounced as is described in your report.

Mr.G. ALBENNE (France): It seems to me that one factor which merits further explanation is the granular state of the superphosphate, before granulation, and the methods which have to be employed in order to obtain this granular state with fresh superphosphate.

Mr. N.W.G. LAGERHOLM (Sweden): Yes, I quite agree. I think it has a very great importance indeed. We have noticed that, when we try to operate a drum without disintegrating, the result is much inferior to the result which we obtain with a disintegrator. I should like to say that I would think it is impossible to obtain good results without disintegration before granulation.

Mr. G. ALBENNE (France): What kind of disintegrator do you use?

Mr. N.W.G. LAGERHOLM (Sweden): We have used a rather primitive apparatus which consists of a vertical axle with a propeller.

Mr. A.I. COLEMAN (United Kingdom): I would like to refer, Mr. Chairman, also to a question that has been raised before in connection with the statement made by the author, that the granulation capacity of the drum must be very close indeed to the output of the plant. This is a matter of some concern when the re-cycle feed is a very large proportion of the production capacity. You have said, of course, that about 7 per cent is over-size and about 2 per cent under-size, but in many English plants I believe that the re-circulation load is as much as 70 per cent of the production capacity.

Naturally there are periods when granulation is good and periods when granulation is bad, and whether granulation is bad because of under-granulation or over-granulation the effect is the same on the re-cycle. Therefore, to some extent, the skill of the granulator man is concerned with how well he can anticipate a previous period of bad granulation.

Therefore, the matter of the output of the granulator equalling the production capacity of the plant is really ignoring the influence of the re-cycle on the plant. One gathers the impression that the granulating and classifying capacity of the conical granulator is too sensitive to permit the normal adjustments in plant operation.

Mr. N.W.G. LAGERHOLM (Sweden): I think you could overcome such a difficulty, if you really had those very large variations, by using, for example, a small amount of water in granulation which gives you another factor. We have noticed that the amount of water necessary, if it is sprayed on effectively, is rather small: it is something like I per cent. Suppose you had your plant constructed in such a way that you always used a superphosphate which was slightly too mature, and then always used a little water to adjust the capacity, I think that would be a possible way of helping that problem.

Mr. A.T. BROOK (United Kingdom): On the subject of conical granulators, this is the first on which we have seen any detail. We naturally compare it with the inclined tube which is our standard method. Bearing in mind the differences in the raw materials, which are considerable, and in the efficiency of granulation expected, the mai point which strikes me is the very low capacity of this drum for its diameter. It prompts me to ask the question, what is wrong with th ordinary inclined tube as a granulator, instead of going to the compilation of conical shapes with their more involved mounting gear and driving gear?

I may perhaps make one comparison with our present practice, where we make a compound similar to the 0-I4-I4 reported by Mr. Lagerholm. In this case we can make this compound in a shell of 6 feet in diameter, at anything up to I5 tons an hour. So I should like to ask the question, what is the point of the conical drum granulator if straightforward granulation in an inclined tube can give perhaps three times the comparative output with, as far as I ca judge, the same degree of granulation efficiency? We would get som thing of the order of 60-70% out of the granulator lying between I½ and 3½ mm. I think that is, very roughly the same order of grading as Mr. Lagerholm's 90% between I and 5 mm. It just raises the poin in my mind as to what advantages you get from the conical drum. I know that in theory the Teller granulator produces a particle size which, when it has reached the optimum, will roll out of the machine but I think it ignores another factor which is that granulation of t raw materials then has to take place at the bottom of the bed, cover by finished granules. Granulation is not so efficient when it is taking place at the bottom of the bed of material as it is when it i freely cascading in a rotary drum.

<u>Mr. N.W.G. LAGERHOLM</u> (Sweden): I should say that one of the point of using a conical granulator would be that you consumed less water in granulation. You have to dry less water, your drying costs decr under the assumption that the separating capacity of these two granu lators are the same. That would be one of the advantages of the conical granulator.

I should like to add that maybe you could do away with drying altogether in certain circumstances.

<u>M. FLEURY</u> (France): I should like to put two questions to M. Lagerh

(I) Has he been able to ascertain whether his machine gives as go results with superphosphates coming from continuous production as wi discontinuous superphosphate production?

(2) Regarding the age of the superphosphate, one important point which he has not mentioned is the temperature. Once through the machines, the super loses heat as it gets older. Surely the temperature must have a definite effect on granulation. Has M. Lagerh studied this effect?

<u>Mr. N.W.G. LAGERHOLM</u> (Sweden): As to the first question, we have continuous plant.

On the second question, I quite agree with you; I think that the temperature does have a certain influence, but I do not think th phenomena which we have experienced can be explained alone by the temperature, because we have done certain experiments where the temperature has been about the same in the two cases. We have been able to increase the feed much more in the case of the fresh superphosphate although the temperature has been the same. I do think it has a certain influence, but not a large enough one to explain these phenomena.

<u>Mr. R.M. COLLINS</u> (Honorary Member): Mr. Chairman, Mr. Lagerholm, you

mentioned that your most successful trials were made with a superphosphate containing a mixture of pebble rock and that you believe that was because of the rather higher free acidity when the superphosphate was fresh. Do I assume that you think that that would follow with almost any granulation process using fresh superphosphate straight from the den, or do you think that this is something quite peculiar to your own very interesting process?

Mr. N.W.G. LAGERHOLM (Sweden): No, I do not think it is unique for this process, because it is a question of just agglomerating the material with an addition of a minimum amount of water, or no water at all.

Mr. R.M. COLLINS (Honorary Member): In other words, part of Mr. Heudier's observation that you could make a suitable superphosphate for granulation at any age is, in fact, met by this. Obviously you want to granulate straight from the den to save handling costs, and you have, in fact, used a mixture which you find gives you a suitable superphosphate for ready granulation?

Mr. N.W.G. LAGERHOLM (Sweden): Yes.

Mr. P. FLAMENT (France): Actually, it is a question of a machine which granulates without drying, but, in certain cases, the author says he was obliged to dry. I should like to know whether he dried in the granulator itself, or in some other machine, and what precautions were taken to avoid agglomeration of the granules.

Mr. N.W.G. LAGERHOLM (Sweden): We have not dried any of our products. In some cases drying would have been necessary because the granules were weak, but we have not yet started to study their drying.

Paper 936 - GRINDING OF GRANULATED FERTILISERS IN A PHILLIPS COFFEE MILL - by Dr. G. Behnen

Mr. A.T. BROOK (United Kingdom): Mr. Chairman, Gentlemen, I think the opening comments on Dr. Behnen's paper should be in proportion to the length of the paper! With your permission, I would just make one or two remarks which I think are appropriate.

I feel, in reading the paper, that Dr. Behnen's need to use this mill perhaps arose from lack of any other suitable apparatus, and I would point out that we have found, in our laboratories, a satisfactory mill in the Christie Norris No. 8. This is a small rotating blade type of mill, as distinct from a swinging hammer type, and has a rotor rather like a simple centrifugal pump. The granules are broken by impact upon the blades, which are rotating at high speed.

Just as a point of interest, this mill will run without replacement of the rotor for about ten times the number of estimations which Dr. Behnen has quoted for this coffee mill. Probably that is because the materials of construction in the Christie Norris mill are designed for breaking hard materials, whereas the rotor in Dr. Behnen's mill was presumably designed for breaking only coffee beans.

The CHAIRMAN: Then I will close this first session of our meeting and thank all the authors for their very interesting papers. I thank the openers for the interest they have shown, for working out their brief opening statements, and I thank the delegates who have taken part in the discussion.

(The Meeting adjourned)

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TECHNICAL MEETINGS

Spain, 24th - 27th September I957

Session II - In the Chair, Dr. B. Raistrick

THE CHAIRMAN: Ladies and Gentlemen, I think we should start our afternoon meeting now.

We have a very interesting set of papers this afternoon. They are mainly concerned with the attack of acid on phosphate rock. The first paper is going to be presented by Professor Talmi (Israel).

PAPER 905: The use of termally beneficicated (Calcined) Rock in Superphosphate Manufacture, by E.R. Herman, Y. Kosirovski, S. Stern and A. Talmi (Israel).

Prof. A. TALMI (Israel): I should like first to refer to three points in the English and French texts of our paper. You will find on page 2 of the English text that the section "Experimental" starts with the following sentences: "Two series of experiments were made. In the first one mechanically beneficiated, calcined, Moroccan and Florida phosphates were reacted with sulphuric acid".

I do not think this formulation is clear and it might mislead, because we carried out no experiments with calcined Morocco or Florida phosphates. I think a better formulation of this sentence would be: "In the first one mechanically beneficiated Israel rock, calcined Israel, rock and Moroccan and Florida phosphates were reacted with sulphuric acid".

Then there is a small error on page 5, Table 3, of the English text. The headings of the fourth, fifth and sixth columns are missing and should be "Calcined Rock". In the French translation the heading has subsisted.

Finally, in the French text on the first page, the sixth line from the bottom, as a result, I think, of wishful thinking on the part of the translator or the typist, there is a small error. It reads, "......... et demande 2 tonnes d'acide sulfurique de moins par tonne d'anhydride phosphorique". That would be beautiful if it were true. Unfortunately, the words "de moins" should read "ou moins".

I should like to add that, although the experimental procedure that we used in this research work was relatively primitive - nothing to compare with the wonderful work reported by Nunn and Dee at the previous meeting of ISMA - we feel confident that we could feed Israeli calcined rock into our existing Kuhlmann installation without any change. The calcined rock of Israel has proved no less reactive than the non-calcined. This was, in fact, the object of the work reported to you here.

There is the question, what are the factors determining the reactivity of the various phosphate rocks? We do not feel that we have thrown any light on this very important question, but in a pap which you are going to discuss this very afternoon, by Dee, Nunn an Sharples, I think this very, very important question is discussed admirably.

The CHAIRMAN: Now I shall ask Mr. Coleman to open the discussion.

Mr. A.I. COLEMAN, (United Kingdom): Mr. Chairman, Gentlemen, I should like to preface my remarks by saying that I feel that the authors are to be congratulated on having chosen not only a novel subject, but also upon the clear exposition of the methods they hav used for utilising the chemical deficiencies of their rather special rock in order to make it a more economic working proposition.

I should like to turn now to page 4, Table 1, in which are give the analyses of the various types of rock used in the experiments, and in particular of the thermally beneficiated rock of Oron. In the column entitled "Moisture content" there are figures given rang from 0.1 to 0.2 per cent. I hope Professor Talmi may be able to explain this fact a little futher, because on the face of things these rocks have been heated to red heat and presumably should contain no moisture content.

I would conjecture somewhat here that perhaps the process of separation has resulted in a change in the chemical form with which the calcium is combined. Originally it is present as calcium carbonate. It is converted substantially to calcium oxide, and I conjecture that perhaps in the separation process there is a conversion to the hydroxide which would permit 0.1 to 0.2 per cent of free moisture to be present. In asking this question, I assume th were there to be any absorption of atmospheric moisture after calcination, it would be absorbed as calcium hydroxide.

In column 4 of the same Table, given the percentage of carbon dioxide on the dry basis, there is still reported to be 1.3 per ce of carbon dioxide. It seems possible to me that this carbon diox may be of several sources. Perhaps the efficiency of the thermal decomposition is not 100 per cent, perhaps some carbon dioxide has been absorbed in the recarbonation process and perhaps some carbon dioxide is also present in other chemical combinations.

The authors have not referred to other possible effects of the thermal process. For example, no reference has been made to orga matter present in the original rock and presumably the calcination treatment would result in its complete removal. I also wonder whether there are any other thermal decompositions of, for example complex chemicals such as fluorides during this calcination proces at such a high temperature. It would appear that the calcination treatment may also have resulted in some benefit were this rock to be used for making phosphoric acid. The combination of low - perhaps no - organic content and very low carbon dioxide would presumably be of assistance in the reaction process.

I should now like to refer to really some conjectures as to t what extent the principles of this rather special case may be of general application. The saving of 1 ton of sulphuric acid for every ton of P_2O_5 obviously justifies the very high capital and operating cost of the installation which the authors report under construction.

Most phosphate deposits in the world yield some low-grade ores and the question of the beneficiation of these ores is one which i becoming increasingly important as more fertilisers are made from phosphoric acid and less are made from superphosphate.

Would it be possible for Professor Talmi to say what would be the minimum calcium carbonate content of an Oron rock which would justify the very high capital and operating costs envisaged in the installation to which he has referred? I must confess to having had no knowledge of the type of plant which is to be installed, but normally when several hundred tons of material are heated to near red heat one has in mind lime kilns which are 200 feet long and 8 or 10 feet in diameter, with brick lining and so on.

As a slight corollary on the last question, would Professor Talmi feel that low-grade rock from a North African source imported into Israel justifies the capital and operating costs of the thermal beneficiation process which he has described?

The CHAIRMAN: Thank you Mr. Coleman. Would you like to reply now, Professor Talmi?

Professor A. TALMI (Israel): I am grateful to Mr. Coleman for his questions which will help me to clarify a few points not explained in the paper.

The thermal beneficiation consists mainly of two stages: the first stage is the calcination, that is to say the decomposition, of limestone into lime and carbon dioxide. There is no difficulty whatsoever about this stage. I will come to this later.

The second stage is the stage of removing the lime. This is easier said than done. It happens - and it depends on the nature of the phosphate - that the lime just does not want to get out. If the lime stays there, although the P_2O_5 percentage has risen, the acid consumption per unit of P_2O_5 is the same as that for uncalcined rock.

An important part of the lime removal is lime hydration. The lime is converted into calcium hydroxide, thereby undergoing physical disintegration into a very minute particle size, and this is the secret of its elimination. Therefore, Mr. Coleman was right in saying that the humidity which was reported for the calcined rock is a result of the hydration of the lime to convert it into calcium hydroxide.

Regarding the CO_2 percentage reported in Table 1, these calcined rocks which are mentioned in Table 1 are the product of first calcination experiments on a large scale. The calcination was not quite complete and there was also some re-carbonation, as Mr. Coleman guessed. But from later experiments we are quite confident that the calcined product will not contain more than 0.7 per cent of CO_2. Even this CO_2, or a large part of it could be removed, but it is not worth while.

Again Mr. Coleman was right when he said that the organic materials in the rock will be destroyed during the calcination. They are in effect destroyed, there is no appreciable amount of organic material in the thermally beneficiated rock. I am sure that many of you know how important it is to eliminate organic material from phosphate rocks.

The question as to whether calcined or thermally beneficiated rock would be suitable not only for single superphosphate, but also for phosphoric acid and triple superphosphate manufacture, has been investigated in our laboratory and the preliminary results are encouraging. We are sure, or, say, 95 per cent sure, that the calcined rock is very suitable for the manufacture of wet process phosphoric acid and it is equally suitable for the manufacture of triple superphosphate. Of course, when a complicated material like phosphate rock is calcined at a high temperature many chemical and physical changes take place: not only does the limestone decompose, not only is the organic material destroyed, but many other less important changes take place. For instance, some of the aluminium oxide of the clay content, although it is not much, in the presence of much calcium oxide is converted into calcium aluminate. It is possible that some free silica, if present, is converted, but only to a very small extent, into calcium silicate. We have noticed no loss at this temperature of the fluorine content, at least, not an appreciable loss.

Regarding the furnaces in which the calcination could be carrie out, there is really a large choice. The mechanical furnace of th Herreshof type has proved satisfactory. The sintering grate of th type manufactured by Lurgi has given very good results, but we do not need such complicated furnaces because the ordinary rotary kiln has proved a good apparatus of calcination. We have even tried fluidised beds. A pilot plant using a fluidised bed has given ver good decomposition of the limestone, so that there are really many possibilities. Economic factors, such as the prices of fuel, of transportation, of investment charges, etc., determine the type of furnace to be chosen.

Mr. Coleman asked me about calcination of North African phospha There are people present here who have done this, or are doing this and I think it is better if they tell us what their experience with the North African phosphate has been.

Finally, as regards the economical evaluation of the process, w have not calculated what would be the minimum CO_2 content of the ro to justify calcination because we are blessed with a considerable CO_2 content in all our phosphate deposits. But we have certainly established beyond any doubt the economic advisability of the therm beneficiation process in the case of our own phosphate.

Dr. K.C. SCHEEL (Germany): Dr. Talmi's results confirmed my conception of the structure of carbonate-fluorapatite. The structure is shown to be not simple; if it were, the method of thermal enrichment would give a product of 42% P_2O_5 content, in practice only 35% P_2O_5 is achieved.

Prof. A. TALMI (Israel): I would like to say in this connection th phosphate rock is a very complicated thing and apart from calcium oxide, P_2O_5 and fluorine, it contains a lot of other substances. crucial problem for us has been how these substances would behave during the separation of the lime. Would they follow the lime or would they remain in the phosphate? The people who wanted to use this process to get good lime wished, of course, that the impuriti would remain in the phosphate, but this was not the object of the process. We wanted the impurities to go with the lime and fortun ly the greater part of the impurities are eliminated with the lime Still, some impurities remain behaind and, therefore, our product not pure apatite. But in the cases where the rock really consist of apatite and calcium carbonate we got very good results. We ha even in one exceptionally large experiment got a product containin 39% P_2O_5.

Mr. DIDIER (North Africa): Prof. Talmi has been speaking of North African phosphates. Although I have not had much experience in this field, I do feel qualified to make one observation, namely, that the question of calcination is not very simple. In the Nort African phosphates of which I have had experience there took place a reduction of sulphate to sulphides, probably because of the orga substances and the calcination. There was an immediate release of much hydrogen sulphide on treatment with sulphuric acid. Has Prof. Talmi observed such phenomena, or are there any special precautions which should be taken during manufacture of decarbonat phosphates?

Prof. A. TALMI (Israel): In none of our experiments have we found H_2S. It is a substance which is easy to detect. I do not know why, in the case of the phosphate you mentioned, an evolution of H_2S, or a reduction of sulphate, took place, and I am wondering if this has not to do with the structure of your furnace and the existence of a reducing zone in it.

Mr. P. GAUDRY, (France): There is just one further question which I should like to ask.

There is no indication in the paper of how, after calcination of the rock, the calcium phosphate and the lime produced from the calcinated carbonate were separated. Is it, as I had thought, by a pneumatic method, or by some other?

Prof. A. TALMI (Israel): I think Mr. Gaudry is quite right, the paper does not mention the technique which is employed in the removal of the lime from the calcined rock. But I have already said that a good method for the removal of the lime from the calcined rock is based on the physical disintegration occurring when the lime is hydrated.

The CHAIRMAN: Now I am going to ask Mr. Bigot to introduce his paper.

PAPER 904: Influence of the origin and characteristics of the phosphate rock used in the manufacture of phosphoric acid by the wet process, by M. Bigot.

Mr. P. MORAILLON (France)(In loco M. Bigot): I have nothing to add. I should simply like to mention that M. Bigot embarked on this survey with the intention of comparing different natural phosphates from very varied sources with regard to their behaviour during the manufacture of phosphoric acid. Indeed, this work is essential for the operation of a phosphoric acid plant, before using any new type of phosphate or one with which the factory is not familiar.

The use of a new phosphate presents a number of problems, which I shall enumerate briefly:

1. The physical treatment to which the phosphate must be submitted. Is there need for calcination? What fineness of grinding is necessary?
2. The choice of type and size of plant.
3. Determination of optimum chemical conditions which must be used during the manufacture.
4. The question of consumption of raw materials and the yields which can be obtained.
5. Lastly, the question of ascertaining the degree of purity of the phosphoric acid obtained.

In order to answer all these questions, it was necessary to carry out a test to obtain practical results, this test to approximate as nearly as possible the conditions of industrial manufacture. This is what the author of this paper has done. He has shown the results obtained with different phosphates.

We should like to know what the Delegates' opinions of the results are, and should be glad if they would let us know what their own experience has been in this field.

The CHAIRMAN: Now I shall call on Mr. Beetz to open the discussion on this paper.

Mr. P. BEETZ (Belgium): Mr. President, Gentlemen, firstly, I should like to thank Mr. Bigot, - who, I think, is absent, - for the detailed statistical information he has supplied. This will enable many members of the ISMA to acquaint themselves with phosphates which they have not yet had occasion to use.

For most manufacturers of triple superphosphate or phosphoric acid, in the production of compound fertilisers, the choice of phos phates at their disposal is a small one.

Those who are near the North Sea can use Moroccan, Kola or Pebble phosphates; it would seem uneconomical for them to avail themselves of any others. For Great Britain, by an economic fluke Nauru phosphate also can be considered.

Certainly, for other members of the ISMA, it is interesting to know what results would be obtained with certain rocks if they were used in the manufacture of phosphoric acid destined for fertilisers South Africa is a country where phosphate is found. Other African possessions are also concerned with local phosphates. Phosphates are found in the U.S. in areas besides Florida. To develop a method by which one could arrive at the economic results obtainable with all these phosphates is obviously an interesting task.

Also, I think that the best way of introducing this paper is to pass on a few observations which we are able to make by virtue of our long experience in the manufacture of phosphoric acid.

Several years ago we developed for our own purposes, a method which enabled us to study using samples of some 50 to 100 kgs., as did M. Bigot, the behavious of phosphate rock when used for the manufacture of phosphoric acid.

We think, nevertheless, that these methods cannot be completely standardised. Each phosphate has had a long evolution. Some are volcanic rocks, others are more recent formations and the productio of phosphoric acid is very sensitive. It is difficult to compare different phosphates by methods which are to standardised. We prefer a method which has relevance to the industrial scale and whi permits assessment of the different variables which affect the economics of manufacture using various phosphates.

It seems necessary for me to point out that we decided that it was important to study the order in which the reagents are added to form the slurry. In fact, the results differ depending on the typ of phosphates and even of the sulphuric acid used.

We also think that it is necessary for the test to give crystal of the same size as in an industrial installation so that this experiment can test not only the reaction but also filtration. Reaction and filtration are inseparable because the solutions which come from the filtration provide the medium for the reaction. The amount of water in a phosphoric acid installation is most important and it is impossible, when assessing water usage, to separate the reaction from the filtration.

On the subject of filtration, we should like to be able to carr out filtration tests at the maximum vacuum capable of giving good performance. Certain cakes very easily support a vacuum of 600 mm and more. It is obvious that with such a vacuum the filtration is more rapid than with a vacuum of 200 mm. On the other hand, certa cakes would collapse, especially those which contain certain soluti which are slightly colloidal. In this case, the test also aims at fixing the best value of the pressure for use on the filter. This test is only important if one has available a filter which in industrial practice can operate at vacuums of 600 mm. or more. Of course, if a filter is used which can only operate with a vacuum of 200 to 300 mm., this test loses its value.

From the point of view of the crystal size, I think that not on the comparison between length and breadth should be taken into acco but also the thickness. To obtain good filtration the crystals mu be parrallelopiped and not platelike. Observation of the length/ breadth ratio alone hardly fixes the thickness of the crystals.

We see moreover the importance of this question, since in the paper which has been submitted we notice that Pebble VII gives 2,400 litres per square metre per hour, Morocco II 2,000 litres and Kola II 1,800 litres. While Kola is the purest phosphate and cannot have colloidal matter in solution, it is, nevertheless, Kola which gives the least good filtration.

Then, I should like to make some remarks on the fact that the tests, which must be carried out with a view to obtaining all information on using a given phosphate and a given sulphuric acid, must also take into account the fact that many users wish to have a phosphoric acid strength higher than 32% and generally one at about 50% for making concentrated superphosphate, so that the question of concentration is at least as important as the two other points. I am sure that most of those with phosphoric acid plants who concentrate acid will not contradict me on this subject.

I note, for example, in the paper by Mr. Schwehr (LE/913) on page 7 of the English text, that he works with a 2½% excess of H_2SO_4 solely in order to obtain maximum precipitation of calcium, for this calcium becomes a nuisance on the evaporation pipes. So, I think that for the reaction it is preferable to be able to have conditions best suited to the reaction without being influenced by concentration. Our procedure for concentration permits complete separation of the reaction process from the concentration process.

Finally, I think there is room for a certain amount of prudence and we should not become over-confident in these methods until they have been applied to trials with 50 to 100 kgs., and this for two reasons.

First of all, one of the important difficulties which the industry has always to face is sampling. What is a mere 50 kgs. as representative of a phosphate rock deposit? Should a sample of 5,000 tons be taken and reduced to 50 kgs.? On the other hand, should 50 kgs. be taken from the right of the bed, 50 kgs. from the middle and 50 kgs from the left hand side? It is obvious that the first method will give a sample which is never representative of what is given in actual practice. In the second method, there are more important variations. This is, in my opinion, the most suitable method, which should be used to deal with the problem of a new deposit. This latter shows that the sampling processes must be very flexible and not too rigid. In the same way the industrial process must be flexible so that it can be adapted to changes in the physical or chemical structure of the phosphate as mining advances along the seam.

This leads me to the second reason which causes me to exercise a certain prudence. It is the long experience which we have had with phosphoric acid.

In a small scale experiment, which can be done sufficiently often to make it easily reproduced, certain phenomena can escape unnoticed and not reveal themselves until the full scale is reached. Also, we estimate that to be quite accurate in yields and results when using a completely new bed of phosphate in a plant, it is necessary, in addition to these essential small scale experiments, to persuade the user to experiment with several thousand tons and to process them in a similar plant in order to obtain complete certainty of working.

One example, from amongst the most simple, is the way in which a test carried out on 50 or 100 kgs. can fix the amount of agitation which it is necessary to obtain when using vessels of about 5, 6, 7 or 10 metres diameter and 3 or 4 metres high. Will the same amount of agitation be necessary as was required in the small vessels? The results of agitation in a small vessel compared with agitation in a large one with solutions which are in the process of evolving gas, is a problem which is hard to solve on a small scale.

I have made several remarks on this paper and I hope that various members of ISMA will be able to get a more complete idea of what may be expected of small scale tests which are to be used as a guide for full scale operation.

Mr. P. MORAILLON (France): I thank Mr. Beetz for his very pertinent remarks which show that he has had much experience in the manufactur of phosphoric acid. I shall have to content myself with giving brief answers, otherwise the discussion will last too long.

With regard to the first question, we are entirely in agreement with Mr. Beetz. The manufacture of phosphoric acid is something very sensitive which often gives rise to unexpected behaviour. It is obvious that a test should be able to reproduce full scale conditions as exactly as possible. It was precisely with this in mind that we did our tests. Mr. Beetz emphasised that the test must be reproducible. Our test is not based on a single day's work. We constantly carried out comparisons between full scale behaviour and the results of our tests. For example, when we use a certain phosphate, we conduct simultaneously manufacture in the factory and test in our laboratories and we compare the results obtained. The same thing is done for filtration speeds. We take the slurry from the factory and test it in the laboratory in order to have always basic figures and to be able to compare results exactly, which gives us a basis for comparison with other phosphates.

In his second point, Mr. Beetz mentioned the question of the order in which reagents should be introduced to control the slurry. It is clear that in a continuous manufacturing process, the reagents are added simultaneously, but at different points. There is a particular method for each manufacturing process.

We have also studied the advantage of having, for example, preliminary mixtures of phosphate and phosphoric acid. But as wel as laboratory experiments, industrial experience showed us that it was always the simplest solution that was best.

The third point was concerned on the one hand with the size of crystals and on the other with the amount of water.

Our laboratory installation gives a crystal size which is quite comparable with that obtained on the full scale. Moreover the size can be more or less regulated by means of altering the degree of agitation in a laboratory test. If the agitation is too strong th crystals may be broken and be shorter than in the full scale unit. But by regulating the agitation the same dimensions can be obtained

With regard to the amount of water, it is obvious that the atta and the filtration are inseparable. If they are separated, it is simply to make explanation easier. With regard to the amount of water, we work under conditions similar to those in an industrial plant or under conditions using a theoretical amount of water.

Then Mr. Beetz remarked on the degree of vacuum for filtration. In fact, the experiments described in this papers were done, as Mr. Bigot indicated, under a 200 mm. vacuum, that is, under a vacuum lower than that in the plant, in order to increase the differences in filtration speeds between different phosphates.

This was the method used in the experiments described in this paper but since then, in other tests using the same rock, M. Bigot has also studied the influence of the vacuum on filtration speeds. It is obvious that the use of a high vacuum has proved particularly useful in the case of certain rocks.

As regards finding out if the filter can operate at a vacuum of 600 mm., I think that at present all industrial filters can work wi a vacuum of at least 500 mm. if not of 600 mm. Anyway, a vacuum c 500 mm. can be applied to different filters, whether they are horizontal rotary types or the type which use a rubber belt.

The next remark concerns the size of crystals. Mr. Beetz pointed out, with reason, that length and breadth are not the only factors determining the filtration speed, and that thickness plays an important part. I believe that Mr. Bigot has also emphasised t thickness; if it is not in this paper, then it is in another. We ourselves, attach great importance to thickness. If we have not put it in our tables, it is because we have no practical means of measuring it accurately. We evaluate the thickness only by microscopic examination. We try, however, to obtain crystals which are as thick as possible, without losing sight of the fact that crystal size is only one of the factors influencing the filtration speed, the presence of colloidal impurities being of much greater importance.

Mr. Beetz then remarked that certain manufacturers regulated the amount of free sulphuric acid in the phosphoric acid they obtain, in such a way as to avoid trouble in the subsequent concentration. Although this matter is rather outside our subject which is the comparison between various phosphates, I am in agreement with Mr. Beetz; the amount of sulphuric acid must not, in any circumstances, be regulated for this purpose, but solely for the manufacture of phosphoric acid. Of course, this can lead to acids which have a higher content of calcium than is desirable for the final concentration. Therefore a method of concentrating must be used which does not present too many preciptation and sealing difficulties.

Although, again, somewhat off the point, I should like to mention that there are two main processes for concentrating phosphoric acid; the process using concentration in a vacuum by means of exchangers heated by steam, and the various processes using hot gases; either counter-current circulation of the acid and the gases in a tower, or by allowing the very hot gases, produced by submerged combustion, to bubble up through the acid. There is a tendency towards preference for the concentration process with hot gases, which causes no trouble from incrustation.

There are certain concentration processes using exchangers which by means of very high recirculation, completely avoid the usual troubles, but I have had no experience of them.

Mr. Beetz then referred to the difficulties of sampling. Certainly many phosphate deposits are very variable and as the extraction proceeds, great differences can be seen. We arrived at the same conclusion as Mr. Beetz, namely that numerous tests must be carried out on a variety of samples. You can see that we have indicated several numbers for phosphates from the same origin, which correspond to different samples.

Since writing this paper, we have carried out tests on other samples which did not always give the same results. It must be remembered that the worst results should be taken into account when drawing up a full scale project.

With regard to the last three points, it seemed to Mr. Beetz that the test was a little too inflexible, but is not this precision indispensable for a methodical comparison between very different rocks? Moreover, as I have already mentioned, this paper was begun a long time ago. As the work progressed, we relaxed the experimental conditions, and we increased the number of variables, in order to enable us to adapt ourselves to extremely varied phosphates.

Also, it is obvious that if an industrial test could be carried out with several thousand tons, this would be the most preferable, once the process had been formulated in the laboratory. Unfortunately, this is rarely possible.

With regard to agitation, it is a purely physical question. It is very difficult to extrapolate from a laboratory stirrer. This becomes a full-scale problem which is different from the laboratory problem, and it must be tackled in a different way.

The CHAIRMAN: Thank you very much, Mr. Moraillon, for introducing Mr. Bigot's paper.

Mr. C. HEUDIER (Fr): I should just like to give you the latest results. Since this paper was written, we have studied six new rocks. Two Pebble rocks, about which I will not speak, because their results ar completely in line with those of the Pebble phosphates already studi Two Idaho, VII and VIII. The first six were examined to build a factory in Canada; the last two represent an actual sample of a phosphate which was finally used in this factory. As it happened th are a little different from the first six. In spite of this, the guarantees were met because, in any case, when guarantees are given they usually include a small margin of safety. The last two are th phosphates which you have already heard about or will hear about:

Recife, a rock from Brazil, which has only 58.75% P_2O_5. Its characteristics are a particularly high content of silica and alumini at the moment, it sets serious problems from the point of view of phosphoric acid manufacture. These difficulties have not yet been solved. There is a Recife 75, which is enriched, and contains less silica and alumibium, and we are going to study this when we have received a sample.

The second rock is Sukulu, from Uganda, a by-product of niobium extraction. This is a rich phosphate. It contains the equivalent of 90% tricalcium phosphate. It has a very low content of metallic oxide. By analogy with other very rich phosphates, difficulties ma be expected. In fact it gives a good phosphoric acid attack and has excellent filtration characteristics. This is all that I can say a the moment about the phosphates we have received recently.

The CHAIRMAN: We pass now to our next paper, which I believe is to introduced by Mr. Dee.

PAPER 912: "The Use of Different Types of Phosphate Rock in Single and Triple Superphosphate Production", by T.P. Dee, R.J. Nunn and K. Sharples.

Mr. T.P. DEE (United Kingdom): Mr. Chairman, Gentlemen, at Dr. New's request I did prepare a summary of this paper by way of introduction, which is printed at the back. I think perhaps it might be useful, order to refresh your memory, just to run through that.

The paper starts with an introductory section in which it is sho that the reactivities of phosphate rocks from different sources towar mineral acids can be correlated with two physical properties of the rocks. The reactivities are thus correlated with the carbon dioxide contents of the rocks and with the extent which their P_2O_5 contents dissolve in 2 per cent citric acid solution under carefully standardised conditions.

The importance of the iron and aluminium contents of the phospha rocks is also mentioned.

Laboratory investigations of the production of both single and triple superphosphate are described in some detail. In both cases relations are arrived at for Morocco rock - that is, from Kourigha - between the ratio of acid to rock used and the conversion to water-soluble P_2O_5 obtained. It is shown that fine grinding greatly facilitates speady reaction in single superphosphate production, but not in that of triple superphosphate.

The next section deals with certain practical consideration, namely receipt and storage or rock, grinding, control of acid and rock feeds, mixing of acid and rock, superphosphate dens. This section finishes with a note on economics and choice of rock.

Finally, information on the behaviour of various phosphate rocks, both in the laboratory and in the factory, is brought together. The rocks considered in this section are those from Morocco, from the Kourigha deposit, Gafsa, Safi, Nauru, Ocean Island, Florida, Senegal calcareous type and Kola. Finally some laboratory work is recorded on a sample of phosphate rock from the Palabora deposit in South Africa. Whereas most of the other rocks dealt with are undoubtedly of sedimentary origin, this one is an igneous rock. The evidence was that the rock was unsuitable for the production of superphosphate in the ordinary type of plant, but could be used to make phosphoric acid by reaction with sulphuric acid. It is thought that substantially the same is true of a number of other phosphate rock deposits on the eastern side of Africa, south of the Sahara Desert.

The CHAIRMAN: Thank you.

Now I shall ask Mr. Clark to open the discussion.

Mr. M.M. CLARK (South Africa): Before I start, Mr. Chairman, time is getting on, so if I tend to be a bit tedious remind me of it, please.

I think we have all read the paper by Messrs. Dee, Nunn and Sharples with interest. The trouble is that, having such a short time, it is a little difficult for us to deal with the terrifically wide field that it covers. That field, I think, can really be said to include II6 years since Lawes first made superphosphate, because the paper brings up most of the points that must have occurred to makers in the past.

I am sure that delegates will have a lot of questions of ask, so rather than take up time with my own I will just pick on a few points that interested me particularly and then leave the full discussion open to the meeting.

The first point that interested me was the tie-up between the fineness, or perhaps I should say the porosity, and the citric solubility of rock as affecting the rate of reaction when making superphosphate. The particular point which I personally should like to follow up is one mentioned on pages 4 and 5, the possibility of what the authors term a blocked void, particularly in Morocco and Florida rock. Thatsame possibility of an increase in the effective attackable area of phosphate, due not merely to increasing fineness but due to the uncovering of openings, has occured to me, and to my own Company, for many years, but it is extremely interesting to have confirmation of it from the authors.

In that connection, I would be very grateful if Mr. Dee could perhaps give one or two figures - not necessarily now - as regards the actual internal surface area in some of the later experiments he describes.

The question also of the determination of what one might call, for want of a better term, blocked acidity by extraction with a suitable solvent is no new idea, but I think very full credit should go, not only to the authors of the paper, but to Mr. R.F. Knight for chasing up the matter and finally evolving a suitable solvent, either dioxane or dioxane plus acetone.

In that connection I would be very glad to know whether Mr. Knight's work is likely to be published and also whether it is quite certain that in the extraction there has not been some extraction of phosphoric acid from the monocalcium phosphate formed.

Rather than take up more time with one or two further questions I had, Mr. Chairman, I would just like to refer to the very last poin in the paper, the question of the use of a Palabora rock, an igneous rock, from the Transvaal. That is, of course, of extreme interest to my own Company, as well, of course, as to Messrs. Fisons. The position is, as the authors mention in the paper, that there are to my knowledge at least six deposits down the eastern side of Africa, starting from the one mentioned, Sukulu, to Rawro which is near it. There is another one at the northern end of Northern Rhodesia and one in Nyasaland. There are two in Southern Rhodesia; there is the Transvaal one and we have rumours of another one in Tanganyika. These deposits, as had been indicated, are all of an igneous nature as the authors have said, they are likely to be of rather similar properties. But from analysis and trials on such samples as we have obtained, it would be very distinctly wrong to assume that the proper are identical. As Mr. Dee has mentioned, Sukulu rock is quite reactive and it has a very high phosphate content. At the other extremes we have the Palabora rock which needs quite a lot of up-grad and is very non-reactive.

Of course, all these igneous rocks are rather out of the field European users, with the exception possibily of Kola rock, but they are of, and will be of, increasing importance in the African contine which by and large is a very poorly fertilised one.

I would mention finally that with practically all these igneous rocks, it is absolutely essential to up-grade them. Taking the Palabora rock as an example, the material as mined only runs about 9 or IO per cent P_2O_5. To bring it up to the 33 or 34% necessary for ordinary fertiliser production, even assuming that the superphosphat process will work, involves a flotation process and also, before flotation, extremely fine grinding. That does help the manufacture

I will not take up the time of the meeting any more, Mr. Chairm but I would like to close with my congratulations to the authors on very interesting paper.

Mr. T.P. DEES (United Kingdom): Mr. Chairman, I thank Mr. Clark ver much for his introduction to the discussion. He has touched on som very interesting points. I think really he has only definitely ask me two questions.

I am afraid I cannot answer the first one. He asked for inter area measurements in regard to some of the later work mentioned in t paper. The only internal area measurements I have given are those determined by the Americans who, of course, have not worked on the African rock, so I am afraid I cannot give those.

He mentioned Mr. Knight's work on the extraction of the acids, and particularly of the acid from a superphosphate, and enquired whether we had checked up whether any acid was extracted from the monocalcium phosphate. This work was done quite a long time ago an I do not remember any work definitely to check that up. We were quite satisfied that the extraction of acid was complete without taking any from monocalcium phosphate. I think, as a matter of fac we had done some earlier experiments on those lines, even before Mr. Knight's time, and had satisfied ourselves in that respect. Certain when we added the acid determined in that way to the monocalcium phosphate determined by Mr. Knight's method, the two together added to the same as a water-soluble P_2O_5.

Continuing Mr. Chairman, I was interested in Mr. Clark's remark on Sukulu rock. If you care to turn to Table 3 you will see on the right-hand side the order of solubility in citric acid of the variou rocks which we dealt with, and you will see that Sukulu is pretty lo in the Table. It is certainly a little better apparently than Kola rock and considerably better than Palabora rock, but it comes a good deal below the North African and even the American rocks.

I would, in fact, like to ask Mr. Clark, when he says that Sukulu is reactive, whether he is referring to superphosphate production or phosphoric acid. The earlier speaker, I noticed, who said Sukulu is reactive, whether he is referring to superphosphate production or phosphoric acid. The earlier speaker, I noticed, who said Sukulu was quite reactive, was referring to phosphoric acid production, in which case I think we would agree. Now we have never done any experiments on Sukulu rock in superphosphate production and I would expect it to be rather inactive.

Mr. M.M. CLARK (South Africa): Mr. Chairman, I would merely say that such experiments as we have done were carried out on the laboratory scale, and also they may not have been as critical as regards rate of reaction as perhaps Mr. Dee's work was. We found the rock to be reasonably reactive on the laboratory scale in making single superphosphate, but I would not say that, if we compared it directly with Morocco on the plant scale, we would be quite so optimistic.

The CHAIRMAN: If there are no further questions, I will thank Mr. Dee, and we will pass on to the next paper.

The next paper is by Mr. Bigot. I see that Mr. Moraillon is coming forward again to present it.

PAPER No. 904: The possibility of making a 45% P_2O_5 phosphoric acid by the gypsum process, by M. Bigot.

Mr. P. MORAILLON (France): I have nothing to add to the text. I should just like to explaine the purpose of the work.

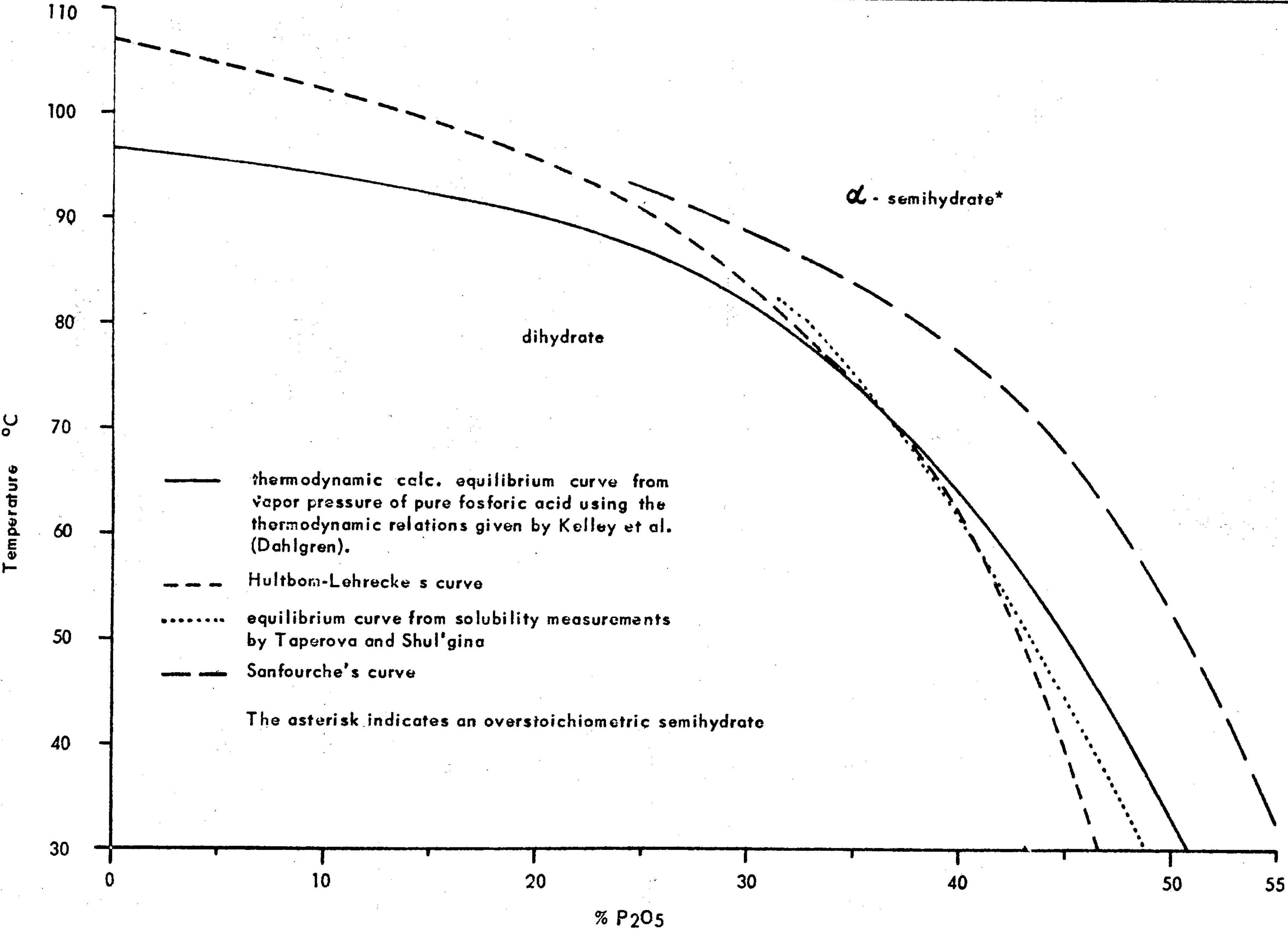
There are various manufacturing processes giving concentrated phosphoric acid direct by methods which precipitate either hemi-hydrate or anhydrite. These methods have one big inconvenience, that is to say the water balance question. For this reason we have tried to see if it was not possible to use the gypsum process for obtaining a more concentrated acid, and if we could exceed the limit which is generally recognised as 32-33% P_2O_5 for the strenght of acid obtained from the gypsum process. The work has shown that it is certainly possible to exceed these concentrations, and even to envisage full scale production.

The CHAIRMAN: Now I will call on Mr. Hellestam to open the discussion on this paper.

Mr. S. HELLESTAM (Sweden): Mr. Chairman, Gentlemen, Mr. Bigot presents here a most interesting paper on a very difficult subject. Making phosphoric acid by wet processes still is the only economical way in most of our countries. But I think I can say that these processes are among the most difficult processes in the inorganic chemical industry. Every new process in this field which can be economical is, therefore, of great interest.

As Mr. Bigot points out in his paper, production of 45 per cent phosphoric acid without evaporation is in itself nothing new, but production of such an acid in a process where calcium sulphate dihydrate is formed is certainly new. Other processes, such as the Nordengren method and the newly published clinker method, produce the calcium sulphate as anhydrite. In Sweden we have recently built a plant using the Nordengren anhydrite method and this plant is at present being started up. Naturally, therefore, the possibility of producing an equally strong acid by a dihydrate method with its lower temperature is of very great interest for us.

According to Mr. Lehrecke's curve, it should not be possible to produce a 45 % acid above 40°C. The curve of Mr. Sanfourche, however,



AB Förenade
Superfosfat-
fabriker
Landskrona
Sweden

The transition
dihydrate - α - semihydrate*
of calcium sulfate
in fosforic acid solutions.

Figure 1

Dahlgren

Aug. 5, 1957

opens up quite different possibilities. As this seems to be the very point of the process, I should like to hear whether their work on this subject has been published or not, and how this work was performed and if it was made with technical acids and so on.

I have given you a diagram where several curves have been drawn giving the equilibrium between dihydrate and semi-hydrate. We see Lehrecke's curve and Sanfourche's curve. Besides these curves, one has been calculated by us thermodynamically using data and relations published by Kelly et al and vapour pressure data for phosphoric acid and another has been calculated by us from the solubility measurements of Taperova and Shul'gina. Kelly has published in the U.S. Bureau of Mines, Technical Paper 625, Washington 1941; and "Phosphoric Acid, its physical and chemical properties" is in Monsanto Technical Bulletin, number 1-26, November 1, 1946. Taperova and Shul'gina published their results in the "Journal of Applied Chemistry U.S.S.R. 13 (1940)", pages 643 to 652, and the same Journal, number 18 (1945), pages 521 to [illegible]3.

We can see from the curves that Lehrecke's, Taperova's and the thermodynamic curve correspond quite well in the zone of interest. The zone is from about 30 to about 45 per cent. Sanfourch's curve, however, differs essentially.

However, I am not suggesting that Sanfourche's curve is wrong because, according to the paper before us, dihydrate has indisputably been formed at much higher temperatures than possible according to the other curves. A possible explanation might be that the discrepancy is due to reaction inertia and that the dihydrate is, in fact, unstable in comparison to hemihydrate in the area between the curves, but that this area may be utilised in certain circumstances, for example, by seeding dihydrate nuclei. I should like to hear if you are of the same opinion, that this can be the answer to the problem.

The last part of the paper certainly seems to indicate that the 45 per cent dihydrate acid may have future technical possibilities. Still, the filtration speeds with acids above 40 per cent are rather low and so the filter area must be very large. The total efficiency seems to be about 88 per cent for 42.5 per cent acid. This 12% deficiency is the product of reaction efficiency and washing efficiency. I think it is impossible to have a big phosphoric acid plant running with such a low efficiency. But, as Mr. Bigot says, this is only the first step of a new process and it is with great interest that we look forward to future developments.

I am sure that the delegates present have many questions and points of view, which we should all like to hear.

Mr. P. MORAILLON (France): Thank you, Mr. Hellestam, for your observations.

The reply to your first question is that this work has been published for the first time at today's meetings.

With regard to the way in which this work was done, we were not concerned with determining the equilibrium, as in the case of the curves which have been given us, but we were working on the full scale conditions, in the same conditions as those which we used for the manufacture of a 32% P_2O_5 acid, simply modifying some details, either of the phosphate or of the chemical conditions prevailing. These modifications have been mentioned in the paper.

On the other hand, M. Sanfourche himself worked on pure products and studied the composition of the solid phases which existed in the different liquid phases, i.e. of phosphoric acid at different concentrations.

Thus it is interesting to see that our findings, obtained when using the actual conditions of phosphoric acid manufacture, corroborate those of Mr. Sanfourche.

Of course, there is still a mystery about the variations between the curves given by various authors and our own results. I think that there is an explanation in the works of Mr. Taperova and Mr. Schul'gina who have definitely indicated that in no case, is the dihydrate or the hemihydrate the stable phase, but that in all practical cases in the manufacture of phosphoric acid, it is the anhydrite which was the stable phase. According to these same authors, in all cases the hemi hydrate or the gypsum are in metastable states and they change, at the end of a very long time - it takes several years - into anhydrite.

We have been asked if our results were obtained by seeding th reaction slurry with gypsum. It is not due to this. We ourselv have actually done the opposite, that is, we have taken a slurry containing 40% P_2O_5 phosphoric acid and gypsum; we have raised th temperature in order to obtain hemihydrate and we only got this at 90°. Then we did the opposite, by cooling this slurry down to 70° and we again observed the formation of gypsum.

I do not know that I have explained this very well. We obtai re-hydration not by just holding the slurry, but by continuing man facture, that is, by continuing to add rock and sulphuric acid. A we again obtained, in the original slurry, the formation of gypsum in spite of the presence initially of hemi hydrate crystals. In other words, re hydration to the gypsum state was obtained by rene the slurry, but the hemi-hydrate crystals which were initially formed probably did not turn into gypsum, since these same crystal were kept at 20° for two months, and they did not become rehydrate

This proves that the formation of gypsum is not a question of seeding, but that it is the definitely metastable form which is obtained directly in the presence of a 40% P_2O_5 acid with a tempera between 70 and 80°.

With regard to the last question, it is certain that the yiel given in the paper we present are still too low for industrial man facture. But I can show that we have been able to improve manufa turing conditions and that we have obtained, in particular, higher rates of reaction, which are practically the same as those for the manufacture of 30% P_2O_5 acid. We have obtained a 98% conversion with crystals which are well formed and very thick.

On the subject of washing, I should emphasise that the result mentioned were obtained on a laboratory scale with one washing wit water. On an industrial scale, three or four methodical washings would probably be necessary, in order to make the maximum use of t small amount of water available and to obtain a correct rate of wa ing.

The CHAIRMAN: Thank you, Mr. Moraillon.

Mr. R. NORDENGREN (Sweden): As Mr. Bigot says, it has been a very long evolution and a very difficult one for the phosphoric acid processes, starting with 5% P_2O_5 concentration in about 1900 and t gradually going up to about 30% with a dihydrate process. After war, when good filters and filter cloth were available, the work which was commenced at Landskrona thirty years ago on the anhydrit process was again taken up. The demand for strong phosphoric acid has continually increased with the need for concentrated fertilise It is now very interesting for us to see that obviously there is a possibility of reaching higher concentration phosphoric acid, also with the use of the dihydrate process.

With regard to this question of the curve, I was not quite clear because I noticed that Mr. Sanfourche reached his value with clean acid and this is exactly as it is in the plant; these are two contradictory points.

In all cases we have tried the reliability of the Lehrecke cu For a number of years I think that more people than are here have known that the curve under ordinary conditions is very reliable. course, it is not a curve, it is a band, depending on how the manufacturing is done.

I have noted that in the experiments you have carried out you have classified the speed of filtration as kilograms of P_2O_5 per square metre per hour. I have translated these figures into litres per square metre per hour in order to make it possible to see the differences between our methods. If you take, for instance, 40% P_2O_5 - and I observe that these are your bad figures; it is not what you may be able to obtain - you have lowered the filtering speed from 815 down to 300. That means, in litres per square metre per hour, that you are lowering filtering speed to about 500 litres per square metre per hour. This is just to give the comparison with the normal method of expression.

This very low filtering speed is, of course, catastrophic and it is not possible to operate in that region. The normal speed is about 3000 litres per square metre per hour and in the anhydrite process it is about 4000.

You will no doubt be interested to hear a little of the Landskrona anhydrite plant in order to be able to compare notes. This plant has just about started up. It was delayed quite a bit owing to long-term delivery of materials. The plant is, like all other phosphoric acid plants, divided into two stages, the feeding department and the filtration department. The feeding department gives no difficulties at all because it can be completely automatic. The latter stage, however, is rather difficult to perform, and this would be exactly the same if the acid were made according to the dihydrate process, because the viscosity of the acid at this high concentration is so large that more than two filtrates will have to be taken. In reality we are using five filtrates: that is, four for washing and one for circulating acid. This circulation is made to diminish the viscosity of the slurry, and the recirculation of acid makes it very necessary to manage the filter properly, otherwise the losses will be high, because if five times the amount of P_2O_5 is circulated in the plant, a loss of I per cent on the filter will in reality be five times higher, and that will be the same for all processes dealing with high concentrations of phosphoric acid.

M. MORAILLON (France): It is true to say that the Sanfourche curves were determined when using pure acid, but our experiments were carried out, as I have said, on an industrial scale, where the phosphoric acid was present with all its impurities.

I think that the differences observed can be explained first of all by the manufacturing process and the greater or lesser homogeneity of the reaction slurry, the sulphuric acid concentration playing an important part, since this acid acts as a stronger dehydrating agent than phosphoric acid.

I thank Mr. Nordengren for the information he gave on his anhydrite process. We are entirely in agreement with him on the necessity of washing a large number of times in order to be able to obtain a good yield with a very small quantity of water. But it can be seen that in the anhydrite process, the quantity of water available is extremely small compared with the gypsum process. It might even be a negative quantity. At the moment it is necessary to introduce a concentration step somewhere in the process.

MR. C. HEUDIER (France): I should like to make one final point on the experiments and give some information to Mr. Nordengren on the subject of the filtration speed. It is not as slow as he says. At present the speeds which we have reached are equal to three-quarters of the usual speeds when using a 32% acid, which is not a prohibitive figure for industrial production.

With regard to the amount of sulphuric acid, the experiments were carried out using 30 grammes of H_2SO_4 per litre of phosphoric acid. In these conditions, the gypsum phase was stable up to a temperature just over 80°. When the amount of sulphuric acid rises to 45 gramm per litre, the hemi-hydrate phase is the stable one at 75°. It is, therefore, important to keep a perfect homogeneity in the reaction sl

Studies of the influence of sulphuric acid strength on the crys form is not yet finished, but is still continuing.

MR. T.P. DEE (United Kingdom): Mr. Chairman, the position of this curve which we are considering does seem to be in some doubt (Mr. Nordengren has referred to it as a band). I should also remark tha hemihydrated calcium sulphate seems to have a rather doubtful composition. I believe the molecules of water can vary between 0.4 ar 0.6.

When we looked into this question in I946, we took into accoun all the published information and drew this curve representing the r table equilibrium between gypsum and hemihydrate. The curve we produced was a little higher than any of those shown here. It sta on the vertical axis at about the same temperature, but came down t the horizontal axis only at 67°C.

Now on the strength of that we were encouraged in the laborato to try to produce acid of 45 per cent P_2O_5 at 55°C, and in the laboratory that was quite successful. We did not carry the work further at the time. For one thing trouble was expected on the la scale with washing the filter cake with a reduced quantity of water And there is also the difficulty that Mr. Bigot has mentioned of th higher viscosity causing lower filtration rates.

MR. P. MORAILLON (France): I think that taking our results into consideration our reaction curve would, in fact, come a little abov the highest curve, that of Sanfourche. We are still not perfectly sure of the points, especially when, as has been indicated, it is r more a band than a well-defined curve.

THE CHAIRMAN: Gentlemen, this is a very interesting paper and I a sure the discussion could go on for a long time, but I think I have to thank Mr. Moraillon now for presenting the paper and we must go to the next one.

The last paper this afternoon is by Mr. Tessier. Would he co forward now and introduce it to us please?

I am told that it is going to be Mr. Moraillon again.

MR. P. MORAILLON (France): The author of this paper has endeavoure clarify the question of fluorine in the manufacture of superphospha Many papers have already been written on this subject. The questi with which Mr. Tessier is concerned is whether the calcium fluoride found in superphosphate comes from a reprecipitation of calcium flu or whether it is calcium fluoride initially present.

The experiments have lead to a hypothesis that all the fluorin in the apatite is at first liberated in the form of hydrofluoric ac which in turn gives rise to a certain number of secondary reactions Conversely, the fluorine in the free calcium fluoride is practicall never attacked in normal conditions of superphosphate manufacture, even in phosphoric acid production.

THE CHAIRMAN: Now I shall ask Mr. Dee to open the discussion on th paper.

MR. T.P. DEE (United Kingdom): Mr. Chairman, Gentlemen, Mr. Tessier has brought before this conference an important subject. The fluorine content of phosphate rock is of increasing interest. It is said that the deposits of calcium fluoride are being rapidly depleted and phosphate rock may well become the principal source of fluorine. It would then be of importance to the industry to drive off and recover as much fluorine as possible during the production of phosphate fertilisers.

Mr. Tessier is to be complimented on the clear arguments by which he has arrived at his conclusions from his experimental evidence. As to the latter, however, I have some criticisms to make.

I was concerned at first by the lack of reference to earlier work. However, he does refer to Mr. Delomenie's paper of I955, and this author referred to the paper by Dr. Whynes and myself given to the Cambridge conference in I953, which itself gave a number of literature references, so perhaps it can be argued that the chain is complete.

Mr. Tessier's main practical conclusion is that the addition of silica - preferably a kieselguhr - during superphosphate production effects a large increase in the proportion of fluorine liberated. He bases this conclusion on the results of his experiments numbers 2, 6, 9 and I0, as set out on page 3 of the English translation. The weakness is that there are only four experiments to cover changes in four variables and that, in comparing any pair of results, one finds that more than one variable has been changed. An important variable about which he gives no information is the temperature attained, which may have differed in the four experiments. One does not need to be a statistician to realise that such evidence is inconclusive. I suggest, in fact, that one cannot from these results be sure whether the high proportion of fluorine evolved in experiment 9 was due mainly to the high concentration of acid, the high proportion of acid, the addition of phosphate in three batches or the addition of silica.

Both Delomenie and Whynes found no increase in fluorine evolution to be brought about by the addition of silica.

Mr. Tessier's main contribution to theory appears to me to be his argument that there is a delicate balance between the reactions by which the hydrofluoric acid initially formed goes either to calcium fluoride or silicon tetrafluoride. Under some circumstances, I suggest, the addition of silica has a favourable effect on this balance whereas under other conditions it has no effect.

MR. P. MORAILLON (France): I will begin by apologising to Mr. Dee for not having referred to the work of Mr. Whynes, but as Mr. Dee himself said this paper was mentioned by Mr. Delomenie, we did not want to write a complete list of previous authors, which would obviously be very long, for many authors have published papers on this subject.

Mr. Dees remarked that the effect of the addition of Kieselguhr was not clearly shown in the experiments, bearing in mind that several factors were varied at one time. This is quite true. It is certain that a more extensive laboratory study would have been preferable, but it did not come within our scope. In fact, the idea was to find out a means of increasing the amount of fluorine evolved. We proved that it was possible, by proper choice of a number of factors, to increase this amount by very considerable proportions. We are now sure of the effect of the addition of Kieselguhr, but as a result this study was not continued as it was of no further practical use for us. The experiments were done in a Works laboratory, which is solely concerned with problems of immediate practical interest.

THE CHAIRMAN: Gentlemen, this closes our business for today. We meet in Santiago in two days' time, but before we leave I am sure that you would want me to thank all the people who have prepared papers for this afternoon's meeting and all the people wh have taken part in the discussions.

(The Meeting adjourned)

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LE/58/37C
Ist October, I958.

TECHNICAL MEETINGS

Spain, 24th - 27th September I957

Session 111 - In the Chair, Mr. F. Iglesias Saenz

THE CHAIRMAN: Ladies and Gentlemen, we continue the technical meeting we began two days ago.

Before opening the discussions, I should like to say that we feel very sorry on account of the delay in travelling from Madrid to Santiago yesterday.

We now start the meeting with the first paper, which is number 909. Mr. Angus please.

PAPER 909: Fertiliser packaging and weighing, with particular reference to weighing, by J. Angus

Mr. J. ANGUS (United Kingdom): In view of the time at our disposal I do not think it would be appropriate for me to indulge in lengthy opening remarks to the paper. All I want to say is that I am conscious that there are many ways of effecting control of weighing and this is only one of them. There are many types of equipment which may be used. We have described one. I feel very envious of the next speaker, because he has developed not just a way of controlling equipment which he has purchased, but he has developed a weighing machine itself.

I do not think I should add any more to my paper. I would be pleased to answer any questions.

THE CHAIRMAM: Now I ask Mr. Van Es to open the discussion.

Mr. A.V. VAN ES (Holland): Mr. Chairman, Gentlemen, as an apprentice in the fertiliser industry I feel extremely grateful for the few very precious minutes I have been given to open the discussion. Quite obviously my questions must be regarded as put by one who is eager to learn and should not contain any undue criticism.

So far I have learned that the materials we have to handle in the fertiliser industry have their own ideas about where they want to end the trips we have stipulated for them, this being mostly in places where we do not want them at all. They want smooth roads and some of them even insist on air-conditioned rooms. Bearing all this in mind - and also that they want the very best of travelling suits and if they are not given these they will deteriorate and arrive at the customer dressed in rags instead of bags - I would like to ask the following questions:

Mr. Angus, could you agree that a valve bag is the wrong ready-made travelling suit for fertilisers?

Secondly, could you agree that the reason for pre-weighing is mainly due to the fact that the valve bag packers are still of inferior working quality as regards the weighing?

Thirdly, should we not in the fertiliser industry try to get rid of the valve bags?

Fourthly, am I right in assuming that you would accept weighing in the bags themselves, because you check on your weighing machines by way of the filled bags so I think you deem the deviations in weight of the empty bags of negligible?

Then we come to the fifth question. These are general questions you will appreciate. As both the customer and his legal protector want the proper weight in the bags and nowhere else, should not the fertiliser industry then insist on a weighing machine design where the weighing is effected in the bag and there is no pre-weighing in another hopper.

Then my sixth question is, would you think that the extra costs for sewing bags on an appropriate machine could be justified by bette delivery to the customers? If you deliver them in valve bags, as soo as the fertilisers peep out of the valves they start to deteriorate the bag next to them, and if you close the bags in another way I do not think they will look so smart when they arrive at the customer.

These are my general questions. There are a few more questions directly connected with Mr. Angus' paper.

I must say I have found great consolation in reading his paper, because I read the story of the many nursing troubles he has had with the four patients, the four weighing machines, each of which is responsable for an hourly value of £3 worth of fertiliser. To this never-ending task I think we must say that Mr. Angus and his staff ha set themselves with great courage and perseverence and, judging from the figures we find in the paper, apparently with great success.

This brings me to my next question: I would like to know very much, Mr. Angus, if you have any screening or polishing generally of your products between the piles and the weighing machine. If so, is that finishing equipment - I mean the screens - near to or far away from your weighing room?

Now I come to my last question: in how far is the improvement o your products of the last five years responsible for the better resul you get with your weighing equipment?

Lastly, I would like to make a small contribution to the questio which have arisen in Mr. Angus' paper as to coating. We have had in my Company a beneficial result with soft and loosely-attached rubber lining on a steel reinforcement. We get a better result when it is loosely attached than when it is vulcanised on. Most attention shou be given to smoothing the weight so that when we are rounding the valleys between the sides of the hoppers and attaching rubber there w have the best results.

Hot spraying of polythene on heated metal surfaces requires a special design of the steel containers in order to prevent their formation by this pre-heating. Then again we have found that the hot sprayed polythene layer has a rougher surface than the rubber and, therefore, is less successful than soft rubber.

There are rumours that by applying mixtures of plastics it would be possible to overcome this difficulty of a rougher surface. We have no experience of our own and I would much prefer to find out whether the rumours are true.

Mr. Chairman, Gentlemen, this brings me to the moment when I have to thank you for your patience, which has brought you to the end of what I have to say in order to assist in opening the discussion on Mr. Angus' paper.

Mr. J. ANGUS (United Kingdom): The first three questions dealt with the valve bag: could I agree that the valve bag is the wrong type of package for fertilisers? I think I could agree, if the bag is made of hessian. I believe a valve-type bag in hessian is very difficult to use for high speed packing. But all the weighing and packing to which I have referred in my paper has been in paper, and I am sorry I cannot agree that the valve bag is not suitable.

The bag we used in the weighing equipment I have described was an open-mouth bag sewn at either end. Our reason for choosing it, as is the case for all of us when we are making decisions, was economics. At the time when we installed this equipment a valve bag cost I¼d. more per bag than an open-mouth bag, and the cost of having a man with a sewing machine to close bags at a rate of 30 tons an hour was much less than the extra cost of the valve. That is not so now, when valve bags are made with pasted ends, and in the new equipment we are installing we are proposing to use a valve type of package.

With regard to weighing in the bag itself, Mr. Van Es asked whether we should consider this to take account of the variance in weight of the bag. I would be very happy to do so if I knew of equipment which could pack at high rates and weigh in the bag itself. I should be most interested in using it. But the variance in the weight of a bag, which perhaps has a total weight of I¼ pounds, is a matter of perhaps 5 per cent of I¼ pounds. It is a very small amount and we are not achieving that precision on the weighing machine. So I think the technical problem of weighing in the bag itself at a very high speed is likely to be more costly to solve than any advantage you get from improved precision.

Nothing I have said should be taken as indicating that I would not like to weigh in the bag itself. I just do not know how to do it.

There was a question as to whether we screen before weighing. This is an important question. It is obvious Mr. Van Es has had the same troubles as we have had. It is necessary because we store our fertilisers in bulk and until three years ago, until we had a research department, we used to have setting in the stores. Now, of course, we do not have these troubles and perhaps we could dispense with screens. But for anybody who produces a fertiliser which is liable to set slightly in bulk storage before it is reclaimed and bagged, it is important to have a screen before the weighing machine. We have a very simple screen with nip rolls to break down any agglomerations of granules. This is immediately above the hopper.

Then Mr. Van Es touched upon the problem of spillage from the valve bag. That is a disadvantage of the valve bag and I think that the root of the solution is to put your fertiliser into the bag just before it goes to the customer, not months before it goes to the customer, to have large bulk stores and to pack when the customer wants his product. I think it is much cheaper to store in bulk than it is to store in bags, and to pack and dispatch your product in a bag a matter of hours before it reaches the customer.

That touches on the question of appearance. There is the questi of moisture pick-up in a valve bag because the valve is open, or is liable to be a little open. We did studies using hydroscopic materials in sewn bags and compared them with valve bags. There was no significant difference; there was a slight difference but it was not significant. I think the choice between valve and sewn bags is solely one of economics. It depends upon the cost of the different bags at your factory gate, and the rate at which you pack. If you are packing at very low rates I do not think it is important; if you a packing at very high rates I think, now that pasted end valve bages ar available, it pays to use them.

I feel sure that my examiners will remember some of the questions I have forgotten. I just cannot find them here.

Mr. Van Es was good enough to touch on the problems of chutes feeding the weighing machines. Like him, I think that loose rubber is very, very helpful. Where plastics are concerned, I think that materials like holloplast or formica - they are expensive - are good if they are wiped, if they are used in such a way that they can be wiped with a paraffin rag, that they can be given just a little lubricant to help smooth movement of material past them.

Lastly, there is the question of the customer and his legal protection. You know, I do not think this is so important as at first sight it may seem to some of you. At least, I do not feel it is important in countries where there is no monopoly. If there is one business, and one business only, serving a country, then I think it is very important that the legal protection of the customer should be stringent. But in countries where there are a number of competing organisations, then there is a natural method of protection. In Britain we have Weights and Measures Regulations, and I have a copy with me if anybody wants to read all the way through them. Weights and Measures Regulations are based on the fact that there is bound to be statistical variance. Some of you, I think, feel that it is too great, but if it were made closer then the cost of the fertiliser to the customer would go up, because we would just have to put a little more fertiliser into each bag to make sure that we did not transgress the Regulation, and the customer would pay. So I do not think it is very important.

There was the question as to whether the improvement in our product over the last few years was responsible for improvement in weighing. I do not think so. I think the product we were making ten years ago, after we have installed the screens before the weighin machines, after we had put them in, was just as susceptible to precision in weighing as our present product.

<u>Mr. O. HALBERG</u> (Denmark): Mr. Chairman, Gentlemen, in point (5) in the conclusion, Mr. Angus establishes the fact that:

> "There is a minimum level of product in the storage hopper below which erratic weighing occurs and it is necessary to ensure that during normal working the product is kept above this level."

In our bagging plant, which the delegates to the technical meetings in Denmark in 1955 had the opportunity to visit, we have gon a step further in order to obtain a regular supply to the automatic weigher, as we have inserted a table feeder between the storage hoppe and the weigher. For obtaining quick filling of the weigher, a smal hopper is fitted between the table feeder and the weigher. This hopper can take a pre-load of about 70 per cent to 80 per cent of the total weight. This pre-load drops into the weight hopper immediately at the beginning of the weighing operation so that there is time enough for the weigher to quiet down after the impact of the pre-load and before the fine weighing operation. We have had very good experience of this arrangement.

Mr. J. ANGUS (United Kingdom): I think that is a substantial improvement on what we have and I would like to have it also. The only case where it may not be worth going to the expense of the added complication is where you do not have to change the product often. If you have to change the product often it is important not to have to maintain a level in a hopper above the scales. If you do not have to change, if you are packing the one product from month to month, then I think what you have done is to provide an additional complication, but as we have to change our products I feel it would be an advantage.

Dr. K.C. SCHEEL (Germany): I am completely in agreement with all Mr. Angus has said. We are also, of course, using valve bags in Germany. But the position is slightly different in Germany inasmuch as the customer asks or prescribes what type of bag he wants. In the case of Germany, is is the peasant who wants to have jute bags and, therefore, they have to satisfy the customer and supply them with jute bags. That entails a lot of sewing. They have to change the type of bags according to what the customer actually requires. They are able to attain an output of 20 to 25 tons with one single apparatus.

I was very interested to hear about the work done by Mr. Angus, whereby it was possible to prevent the caking of the fertilisers when stored. This problem has been discussed on various occasions in these circles and in Germany we have tried all the well-known methods, including drying and then cooling after drying. But we had some difficulties in the treatment, if the fertiliser is mixed with ammoniated mixtures.

In connection with fertilisers containing ammoniated mixtures, powdered material was added, but that gives an additional difficulty, namely that you get a tremendous amount of dust in the storage quarters I would like to know whether some of the delegates have solved the problem of dust.

Mr. J. ANGUS (United Kingdom): We do not produce a dusty fertiliser and so we have not been obliged to solve the problem. I am sorry I do not know any way of overcoming troubles if you have a very dusty fertiliser. Our method for preventing setting of fertilisers does not require coating and so we do not make a dusty product and we do not have the difficulties that you do find with it. We may have in the future and I do not know what the solution will be.

Dr. K.C. SCHEEL (Germany): There may be a slight misunderstanding. We granulate the fertilisers, but it is only through adding powdered material after granulation to avoid caking, that the problem of dust arises.

Mr. J. ANGUS (United Kingdom): Yes, I understand that, but our method of preventing the materials setting does not require coating and so we have not yet had the solve your problem, and I do not know how to do it.

Mr. L. DIDIER (North Africa): My question is also concerned with the effect of "anti-caking" about which we have just spoken.

Mr. Angus drew attention to the caking in the bags. I would like to ask a question about the subject of caking in sacks.

You told us Mr. Angus, that it was preferable to bag the fertilise immediately before delivery. But in certain cases, one is obliged to do this beforehand and sometimes a considerable time before. Could yo tell us from your experience how high the bags should be, the degree of pressure permissable, and how long in advance it is permissable to bag the fertiliser - on the one hand, for fertiliser with a sulphate of ammonia base as in England; and on the other for fertilisers with an ammonium nitrate base? Is there a danger, as I fear, in bagging the fertiliser too long in advance, and in storing the sacks under considerable pressure?

Mr. J. ANGUS (United Kingdom): We can store fertilisers 40 bags high for a year or two without them setting.

Mr. L. DIDIER (North Africa): That is perfect. It probably applies only to fertiliser with a sulphate of ammonia base.

Mr. J. ANGUS (United Kingdom): Yes.

Mr. L. DIDIER (North Africa): You have no experience with fertiliser with an ammonium nitrate base?

Mr. J. ANGUS (United Kingdom): No.

The CHAIRMAN: That closes this discussion. Thank you very much, Mr. Angus.

We continue with the next paper, number 900, "Automatic weighing of fertilisers", by Mr. Moyrand.

Mr. J. LEROLLE (France) (In place of Mr. Moyrand): The President, Gentlemen, in face of the difficulties which are encountered in keepin mechanical apparatus in good repair, and also in maintaining the precision of weighing machines, Mr. Moyrand has endeavoured to bring to our notice a machine which uses compressed air to the greatest extent possible. I should like to explain several points about this machine which were perhaps not very explicit in the paper: the method of compensation for the effect of the fertiliserfalling into the bag, the possibility of additional facilities for filling valve bags, and also of sending the product by conveyor for loading on to the wagons.

The control experiments, the results of which are given concisely in this study, relate to a fairly moist 16% powdered superphosphate, a to a fairly dry powdered 10-10-15 compound fertiliser, and finally to 10-10-17 granulated complex fertiliser.

In the course of these experiments, we used a chronometre to chec accurately the time of the weighings, and the completion and movements made by the operator.

Mr. O. HALBERG (Denmark): Mr. Chairman, Gentlemen, the automatic weigher described in this paper is an interesting solution of the difficult task to weigh and to pack fertilisers satisfactorily. The is, on the one hand, to make the weighing so that the customer is supp with the weight of fertilisers for which he is charged, and, on the ot hand, so that the surplus weight is reduced as far as possible; and finally the packaging plant shall have a great capacity so that the co of bagging are kept low.

I should like to ask Mr. Lerolle if he could give some supplementary information on weighing accuracy of the weigher.

In Denmark a law exists on Measures and Weights, the purpose of which is to ensure that measuring and weighing instruments used in purchasing and selling are made correctly. There do not exist any legal provisions stating outright how great a deviation from the nominal weight is allowed in the sale of goods - for instance, of fertilisers in bags - but in practice one can reckon on being on the right side if the weight of the filled bags is within the limits, which are equivalent to twice the weighing tolerances. According to this law, any weighing instruments used for the sale of goods shall be of a pattern approved by the Department of Weights and Measures and have to be verified and stamped by a Weights and Measures Inspector.

In the case of automatic weighing machinery for fertilisers, the tolerance of verification required for single weighing is: for I00 kg. bags, plus or minus 200 grams, and for 50 kg. bags, plus or minus I50 grams. For the average of ten arbitrary weighings, it is: for bags of I00 kg., plus or minus 200 grams, and for 50 kg. bags, plus or minus I00 grams; that is, for both I00 and 50 kg. bags it is plus or minus 0.2 per cent.

According to information given by Mr. Angus in the paper which has been presented previously today, similar regulations are in force in the United Kingdom.

All the tolerances in the Danish law are to be understood so, that the bags should all be within the limits. It is not quite clear to me whether the weigher in question would meet the Danish legal requirements; that is, the verification tolerance for single weighings should be: for I00 kg. bags within 0.2 per cent, and for 50 kg. bags, within 0.3 per cent. The verification tolerance for ten average weighings is plus or minus 0.2 per cent for both I00 kg. bags and 50 kg. bags, so it must be understood that no weighings may fall below these limits.

Now I should like to ask a few questions concerning the weighing machine. Firstly, how does the supply of fertiliser to the hopper occur? Is there in existence any automatic regulation of the height of the material in the hopper?

As has already been mentioned in Mr. Angus' paper, from our experience it is of decisive importance to the weighing precision of an automatic weigher that the supply of material to the weigher is absolutely regular. Irregularity in the feeding of the weigher causes reduction of the weighing precision.

Lastly, has this weigher been put into production and is it on the market? If so, who is the supplier?

Mr. J. LEROLLE (France): With regard to the operation of the machine, I think it is more essential to know the times of the different actions, weighing, pre-weighing, and any other information of this nature, rather than the detailed description of all the compressed air-circuits in the installation.

Concerning the time, there is in general a pre-weighing time of 5 to 7 seconds - 4,5,6 seconds. The time of the completion of the weighing, that is to say the second stage of the weighing, is around 6 to 8 seconds. This is always longer than the time of the first weighing.

With regard to the control by the French service of weights and measures, I am able to say that the machine has been registered by the General Inspector of weighing instruments. He has made some extremely advanced studies from the point of view of precision. Mr. Moyrand has put forward several suggestions in this paper concerning a graph showing the degree of error, in particular the Gauss curve. This machine therefore corresponds to the legal weighing normes.

As for the hopper feed which feeds into the machine itself, this paper was not directly concerned with that problem. But it is a fac that the feed in the hopper must be supplied regularly. We often instill in the hopper a devise to ensure an even flow of the product into the bag.

To reply to the last question, this bagging plant is constructed by a French manufacturer and is now on the market. We are able to furnish any information to anyone interested about the operation of the machine and answer any questions about its production and sale.

Mr. P. CAMBAU (France): I would like to ask a question about the use of the machine which has just been described. If the result which has been stated is in fact correct, and if it is a case of bagging either powdered or granulated material at the same time, that, in my opinion, seems to be a very important advance in our industry with reg to bagging and weighing. But if I have understood correctly, it applies only to bagging in open mouthed sacks. Consequently, the subsequent operations must follow at a correspondingly speedy rate; that is to say 400 bags per hour or 6 to 7 bags per minute in the cas of bags weighing 50 kg. We are therefore faced with the problem of sewing or closing these bags.

Mr. J. LEROLLE (France): We have two bagging machines delivering the bags to one sewing machine. One operative is engaged in the bagging operation itself, and another works the sewing machine.

Mr. P. CAMBAU (France): I did not know that there was in existence a sewing machine which was capable of producing 20 tons per hour, tha is to say 6 to 7 bags a minute. If this is the case, the problem seems to be solved. The whole difficulty appears to me to be the question of sewing the bags at the rate of 20 tons per hour.

Mr. J. LEROLLE (France): I think the details given to Mr. Cambau answer this question. There is in existence a machine normally capable of sewing 400 bags per hour.

Mr. MACDONALD (United Kingdom): On page 2 of the paper reference is made to a device which prevents bags from being released when the weighing error is in excess of some predetermined figure. This is a very valuable contribution and I should like to know to what limits t automatic device works. The difficulty of check weighing at the spe of the main bagging machine is that there is usually insufficient tim In general the accuracy of weighing is roughly inversely proportional to the time. If the author has overcome this problem and can give high accuracy of check weighing at the speed of bagging, it is a very big contribution.

Mr. J. LEROLLE (France): In the note on Page 2 to which Mr. MacDonald refers, the sentence seems to be a little obscure. In realit it is a question of a security system to prevent bags being released in case of a gross error. It can happen, although only very rarely, that the bag is weighed inaccurately or that there is an escape of compressed air, etc. In this case, the bag cannot be released. Bu this is not a system of control.

Mr. A. T. BROOK (United Kingdom): Mr. Moyrand has devised a machine which, I think, is very good for continuous high-speed weighing, but the paper does not refer to different grades. I would like to ask one or two questions about the changes of grade and the accuracy which may result.

If the mean error is plus or minus 35 times, how many bags in the hundred tested would be outside those limits?

Secondly, what means are provided on the machine for allowing for quick changes in bulk density? Most fertiliser machines have to deal with fertilisers which are constantly changing in their nature. What means have you provided for a quick readjustment of the machine to allow for a change in bulk density of the material.

Lastly, I did not hear the opener of the discussion very clearly and I wonder if I could ask an indirect question to him as to whether the limits of plus or minus I50 grams bags and plus or minus I00 grams for I00 kg. bags referred to the inherent accuracy of the machine or the limits they were allowed in the weight of the filled bag for dispatch.

Mr. J. LEROLLE (France): With reference to the percentage of bags within the indicated limits, I would like to point out that these experiments are statistical experiments which have been carried out on series of I00, 50, I50 and 300 bags. As I previously said these experiments refer to tests made for the Service of Weights and Measures. The results they gave were the graphs which we have drawn, and I can show these to Mr. Brook if he so wishes. These are the Gauss curves, indicating the percentages at the points of inflection etc. What really counts for the manufacturer is the amount of fertiliser sold to the client. For example, we have shown that, using 50 kg. bags there is a 99% probability that the actual weight lies between 999.620 kg. and I,000.540 kg. per metric ton. We have also observed other errors, and have other figures which I am able to show you. In particular, we have taken the mean errors corresponding to the part of the Gauss graph contained between the two points of inflection: we have found mean errors of 25 grams, or as the case may be 30 grams, which correspond to a percentage of the integral of these bags varying between 69, 60, 7I, 78%.

As for the other question, we have not foreseen any special difficulty arising from changes in density, it being understood the measure of the fertiliser is by weight and is not volumetric. It would probably be advisable to readjust the weighing system, when changing the type of fertiliser.

The CHAIRMAN: Thank you very much, Mr. Lerolle.

We follow with the next paper which is number 906, "Routine Laboratory Control of Paper Bags."

Mr. S. HELLESTAM (Sweden): Mr. Chairman, Gentlemen, first I should like to make a correction: on page I, line 5 of the second paragraph, you read, "complaints increased markedly owing to bursting when packed." Please read instead of that, "... to bursting of bags when stored and handled."

In this paper we have only given a short description of the methods we use to control the delivery of the paper bags we use. Of course, there are plenty of methods which can be used, and I am not sure whether we have found the right or the best one. We have no opportunity to try all of them.

Perhaps the only new and interesting thing in the paper is the method we use to test the strength of the paper, the impulse method. Th method was worked out by the Paper Institute of the Royal Technica University in Stockholm. The method shows why the results were v similar to the results from a drop test. With all that, drop testing of bags would be the best method to control the strength o the bags, but, of course, it is impossible to use the drop testing a routine control.

Perhaps I can give you some figures which show the similar re Filled bags were tested in a drop tester and the drop number was c pared with different methods of measuring the strength of the pape The impulse method had a correlation coefficient of 0.83; the Mul test 0.73; breaking stress 0.32; and the breaking strain only 0. Of course, if the correlation coefficient is I.00, the results are similar; so you see that the impulse method is very good.

The CHAIRMAN: Now I ask Mr. Sherwin to open the discussion.

Mr. K.A. SHERWIN (United Kingdom): Mr. Chairman and Gentlemen, in prefacing the discussion with a few remarks, I do not wish to dwell detail upon the paper itself, but rather to refer to a different approach which we have given to this same problem.

In the first place I think we ought to pay the tribute to our manufacturers of paper at home that they have given us, since I946 that is, after the war - the very greatest co-operation. I think can claim that we have progressed side by side and shared in a lot the developments that they have made from time to time.

In other words, we feel that we know something of the difficul that face the paper manufacturer and we do not feel that we are our selves in the position to lay down specifications for the paper whi would be reasonable for them to adhere to. We are approaching thi problem from the point of view of the user and naturally we judge t sack rather by its performance as a complete unit than by the mater itself of which it is made.

I might now refer to the vapour permeability test which, I thi is one of the main features of the paper by the author. We do not ourselves see any great virtue in using water vapour permeability because we are not at all sure that this is the thing that we reall want to measure when judging a piece of union paper, that is the sa wich paper using bitumen. We have convinced ourselves - not on scientific grounds perhaps - that the measurement of the degree wit which air can pass through the paper under pressure is a sufficient indication of the quality of the paper itself. In fact, the faults occurring in this protective ply were originally quite obvious and c sisted in the main of areas where insufficient bitumen had been appl These were quite easily discovered by this method of testing.

The method of testing was very completely described by a paper placed before this Association in September I953 by Mr. Brook and entitled "Packaging of Phosphate Fertilisers."

If I may now just briefly refer to our ideas on testing, it wou consist of taking, say, 20 bags at random from a consignment of new bags and examining one or more of those to see whether there were any obvious failures before putting the bags into actual use. We have, in fact, satisfied ourselves that, in general, faults - that is, a failure of a sack to contain the contents adequately - usually resul from some fault which is not directly attributable to the paper itse

May I just instance the type of thing which we look for? The size of the sack is of great importance, because fertilisers have different bulk densities. Branding, printing errors and the like. Pre-creasing: our bags have a top for folding when they are being sent. Pasting: we find sometimes that the paste has run and there is sticking between adjacent plies; we look for that and try to keep it to a minimum. There are numerous faults in sticking which I feel it is unnessary to go through in detail. Also the nesting, as we call it, of the plies: that is, when we examine the edges the plies must be seen to lie very closely in their folds. (The bags have a gusset and when the paper is pressed flat all the folds should nest together, should lie together). Also the seams should be staggered, not all occurring in line together.

I think I have said quite enough in the opening of the discussion. I suggest that it is the method of approach to the problem which should be the main consideration.

Mr. S. HELLESTAM (Sweden): I would only add to that, concerning the strength of the paper, that the drop test not only measured the strength of the paper, but also the design of the bag. The design of the bag is our design and we wanted a method to control the paper manufacturers. Therefore, we chose the impulse method that only measured the strength of the paper.

The CHAIRMAN: Are there any other questions?

Mr. A.T. BROOK (United Kingdom): May I make one point? I think one very valuable test of a filled bag is the drop test, for a point which has not been mentioned: when sacks are being made and used very quickly, at the start of the busy season, very often the paste itself is not set. A filled bag test shows up very quickly whether the seams are properly stuck and we have found that that is probably one of the biggest individual sources of failure. I could give Mr. Hellestam details of our test separately. It is so quick that it is suitable for a routine test.

Mr. S. HELLESTAM (Sweden): May I ask Mr. Brook, do you think it is possible to use the drop test for routine control of all paper bags in big quantities?

Mr. A.T. BROOK (United Kingdom): One has to have a sample programme and check a number. We check first an obvious fault in paste by inspection of empty bags, and then a number of each consignment are filled and drop tested. That will indicate if the whole consignment has a faulty pasting.

Mr. J. ANGUS (United Kingdom): I would like to ask the author whether he has used this method of testing paper - for his whole paper deals with paper and not with bags - to test the paper after the bag has been used. Has he tested paper at the crease? Has he tested paper where it has been pasted? Has he tested the paper where it has been in proximity to sewing?

Mr. S. HELLESTAM (Sweden): In answering that question, I can give you as an example a test we made with bags stored only one week with fresh P K, potassium super. This test showed an effect of hydrochloric gases. The fresh paper or new bags had impulse numbers of 10 to 12. After only one week of storing the inner ply had a value of only 3; it was useless; the second 8, the third 9, and then 10, 10,10.

Mr. A.I. COLEMAN (United Kingdom): Mr. Chairman, it is of great interest to listen and to read through the paper which has been given about the tests which are applied for the routine control of the quality of the paper sacks. It is perhaps not directly relevant to the subject of the paper, but it would appear that these tests and ma of the weaknesses of the packages which are used today derive from th fact that we are using paper. The weaknesses of paper itself as a structural material, the weaknesses of the methods of construction th have to be used, such as pasting, such as the use of many plies of paper, such as the use of bitumen, such as the need to sew or to use valve packing, all derive from the fact that we are using paper.

I would like to associate myself with the comment of Mr. Sherwi who said that in the post-war years the paper manufacturers have hel the industry enormously to overcome the limitations of paper, but it due to their co-operative spirit that the number of complaints we re from customers today is so low. Also it is perhaps a good thing th with all these difficulties, the cost of the paper sack at least in country is only about 5 per cent of the cost of the fertiliser sold. I believe in many other industries packaging costs are considerably i excess of 5 per cent.

A number of experiments have been made in recent years in which plastic materials have been employed either by themselves or in conjunction with paper. The main problem which appears to emerge is t high cost of the package when made in this way. So, in conclusion, I would like to ask the author whether he would agree that there is today a very great incentive for the paper manufacturers to give further consideration to other materials of package construction.

Mr. S. HELLESTAM (Sweden): I agree with Mr. Coleman that paper is n a good method for packing, but I think it is impossible today to use plastic. We have tried to use polythene for the inner ply but it i too expensive. I still think that paper will be used for many year

The CHAIRMAN: Thank you very much for your interesting paper and we the meeting of this morning.

(The Meeting adjourned.)

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TECHNICAL MEETINGS

Spain, 24th - 27th September 1957.

Session IV - In the Chair, Mr. J. Dior (France)

THE CHAIRMAN: Gentlemen, we are about to start the last meeting of our Technical Congress in 1957.

Before calling upon Mr. Heppenstall to present his interesting paper, I would like to inform you that the time allocated to us today is very limited, when considering the importance of the papers we are about to discuss. Also I would ask you all to be as concise as possible so that the maximum possible can be said in the minimum of time.

PAPER 911: THE CONVERSION STAGE IN THE MANUFACTURE OF SULPHURIC ACID BY THE CONTACT PROCESS,

by G.C. Lowrison and F. Heppenstall, (United Kingdom)

THE CHAIRMAN: I call upon Mr. Heppenstall to speak.

Mr. F. HEPPENSTALL (United Kingdom): Mr. Chairman, Gentlemen, in view of what you said, Mr. Chairman, I do not think it is necessary for me to add to the summary of the paper, except that I would like to say that we chose "The conversion stage in the manufacture of sulphuric acid by the contact process" as our subject as we believe that this part of the process lends itself to the possibilities of modification in details and possibly in basic design.

Dr. H. ACHENBACH (Germany): Mr. Chairman, Ladies and Gentlemen, I wish to congratulate the authors for their interesting and exact paper. In it the historical development of the contact process for the production of sulphur trioxide and/or sulphuric acid is shown as well as many details of the mechanism of the reaction of the oxidation of SO_2 to SO_3.

For the chemist of the plant who has to manage the contact process plant for the production of sulphuric acid, it is advantageous to read and to think over such a resumé on the basic theories and other practical results of the contact process. I think the chemist will find some incitement in this paper.

The production of crude and refined sulphur increases more and more. This raw material for the production of sulphuric acid, therefore, becomes cheaper and cheaper. Therefore, the producers of sulphuric acid are more interested in using sulphur than pyrites.

At the same time, the procedure of burning is consequently simplified and correspondingly the furnaces for sulphur have lower investment costs. But gases of higher concentration of SO_2 originate from the use of elemental sulphur. As the authors say, these gases have other conditions for the conversion in reaction with a catalyst than the gases of pyrites origin.

This paper, with its tables and diagrams going into every detail, is very useful and explicative in respect of the corresponding changes and other procedures with the high grade - that is, concentrated - SO_2 gases.

It is also interesting for the chemist to have a comparison of the maximum temperatures being reached in the roasting of pyrites and in the burning of sulphur, as well as a comparison of gas temperatures at the different SO_2 concentrations resulting from pyrites or sulphur.

I would only remark that the formula shown at the bottom of page 2, concerning the roasting of pyrites, FeS_2, has to be correcte so that, not four, but only two molecules FeS_2 are in reaction with the 5½ molecules oxygen to Fe_2O_3 and 4 molecules SO_2.

With regard to the temperature of the SO_2 gases produced in the roasting of pyrites, one must mention that these gases come to the converter very much cooler because they have been purified, mostly liberated from arsenic and also by the drying process. To the contrary, the SO_2 gases from burning sulphur need not be purified and liberated from arsenic and can, therefore, feed the converter with higher temperatures.

Generally, the high temperature of the gases from the burning o sulphur is used for the production of steam. Consequently the temperatures of these gases become lower. Nowadays this production of steam is possible and usually the flash roasting and turbulent be furnaces. In the latter times at the hearth roasters too; I name the firm Humboldt, and others.

In my opinion, it is not necessary to make further remarks on this comprehensive paper of the authors, because this paper, as has been mentioned before, is not open to any other questions or comment Thank you very much.

THE CHAIRMAN: Perhaps someone would like to ask a question?

Mr. J. LEROLLE (France): May I ask the author whether he has studie the influence of impurities arising from the combustion of dark sulphur on the catalyst?

Mr. F. HEPPENSTALL (United Kingdom): Yes, we do burn a certain amount of dark sulphur and we have considered the possibility of removing the bitumen using Fullers earth, but the quantity of Fuller earth required is very considerable and it would mean installing a very large filtration plant. Although we filter our sulphur at the present time, that does not removed the bitumen, or only a very smal proportion of it, and we find, when we are burning the bitumen and sulphur, we do get what we call a steamy exit.

Mr. J. LEROLLE (France): Has the influence of tar on the catalyst been investigated?

Mr. F. HEPPENSTALL (United Kingdom): We have not, up to the present time, found that it has any effect on the catalyst.

Mr. L. ALVES (Portugal): Mr. Chairman, I would like to make one remark on the subject of the formula on page 12 of the English text. There we have the final formula, $r = K_1$ and so on. As you know, in the original work of Hougan and Watson this preparation was of the solid gas inter-phase and not of the main stream of gas. So I want to ask the author this: if we made corrections to the coefficients, if this formula can be adopted to be valid or to be held to the main stream of gas --

Mr. F. HEPPENSTALL (United Kingdom): We took this formula from the paper by Calderbank and we accepted the formula as being correct.

Mr. L. ALVES (Portugal): Anyhow, I think it is a very interesting subject to see under what conditions it can be adopted, because it i a little different from the original work of Hougan and Watson.

Mr. F. HEPPENSTALL (United Kingdom); Yes. I would like to take tha question with me and refer it back to you in due course.

Mr. T. CESCA (Italy): We have also carried out the same experiment with the catalysts and we have ascertained that the conversions exceeded the equilibrium values.

Mr. F. HEPPENSTALL (United Kingdom): Well, you cannot exceed the equilibrium curve, of course. Perhaps I have not understood the question.

Mr. T. CESCA (Italy): We have found some points in the experiments which exceed the curve of the equilibrium. The equilibrium is influenced by the catalyser in some way or other, we think.

Mr. F. HEPPENSTALL (United Kingdom): I have not come across that work.

Mr. T. CESCA (Italy): In your experiments have you ascertained something similar?

Mr. F. HEPPENSTALL (United Kingdom): This work is not experimental work, but calculations from recognised formulae.

Mr. T. CESCA (Italy): I am under the impression that you would have made some experiments on these lines.

Mr. F. HEPPENSTALL (United Kingdom): We have not done any actual practical experimental work.

THE CHAIRMAN: If no one wishes to say anything further, it only remains for me to thank Mr. Heppenstall for submitting a very interesting paper of far-reaching scientific importance. I am sure I am interpreting correctly your feelings in expressing my thanks to him.

PAPER 907. A NEW SULPHUR DIOXIDE CONVERTER, by Rolf-Bertil Eklund and Sigvard Hellestam, (Sweden).

THE CHAIRMAN: I call upon Mr. Hellestam to say a few words.

Mr. S. HELLESTAM (Sweden): Mr. Chairman, Gentlemen, I should like to draw your attention to Figure 3. There you have the influence of SO_3 on the reaction rate. You can see that the rate of reaction decreses, with increased partial pressure of sulphur trioxide, much more noticeably than as a result of the reverse reaction alone.

Mr. Calderbank never investigated the influence of SO_3, and I think this is the first time this has been mentioned here.

Mr. Eklund, who made the kinetic and laboratory study of the catalyst, was investigating the particle size of the catalyst. You have the three curves in Figure 4 and it is interesting to see that it is only the outer millimetres of the catalyst cylinders which are working. Therefore, if you decrease the particle size of the catalyst you will have much more effective catalyst per rate. The catalyst cylinder is not working in the reaction.

THE CHAIRMAN: I believe Mr. Jadot would like to make some comments.

Mr. E. JADOT (Belgium): Mr. Chairman, Gentlemen. The study of a special case is always made in certain well-known colleges and during post-graduate instruction. It can also be profitable for our meetings and Messrs. Eklund and Hellestam have submitted a very interesting case for our consideration.

The problem which the authors had to solve is one that frequently confronts technicians, namely, to carry out a profound modification of an existing installation.

In an effort to solve this problem they have examined three points in particular:

1. To conceive a new converter for sulphur dioxide;
2. To carry out firstly a thermodynamic investigation of the catalytic oxidation of sulphur dioxide;
3. To recover a part of the energy usually wasted in the production of sulphuric acid by the contact process.

I should like to make some comments on these three points.

Point No. 1. As certain details of the problem are not available we are unable to convey an appreciation of the converter. We wil simply state that it is by no means cumbersome that it requires a minimum weight of steel and that it allows an easy isolation. Or the other hand, some essential parts are not readily accessible.

Point No. 2. The physical study of the oxidation of sulphur dioxi made by the authors should have for its object to place the cataly in the most advantageous position and to use the minimum quantity of catalyst, thus reducing as far as possible both the initial cap tal outlay and maintenace costs. (Losses in charge should be reduced as far as possible).

The authors inform us that the converter had been conceived f a production of 100 tons a day with a possible increase of 20%. The quantity of the catalyst used should amount to 20 tons, i.e. 300 litres of catalyst (Density 0.7) per ton of acid produced per day. Although there are catalysts on the market which give the same performance - 98% conversion - for quantities of less than 240 litres.

Should we conclude therefrom that too large a safety margin h been used in the calculation? We are inclined to believe that th is so since during the experiments the converter demonstrated that it was capable of taking a charge of 200%. It is possible that t catalyst used, had a low reaction co-efficient.

If the first hypothesis is correct, we are somewhat doubtful about the possibility of making use of the surcharge as the increas in loss of load would become excessive.

Many other questions could be asked in regard to this point. We should like to mention only the following: Since when has this converter been in service? Which were the major incidents of exploitation since that date? What increase in loss of load has there been since it has been put into service?

Finally, the last point, No. 3: recovery of energy. As shown by the figures submitted this recovery is far from being negligibl - 0.25 tons of steam per ton of acid produced - seeing that the recovered energy from the combustion of pyrites results apparently in a production of about 1 ton of steam per tone of acid.

The authors, therefore, obtained an additional recovery of 25

Some questions:

(a) Is the boiler a forced circulation boiler?
(b) What criteria have been taken into account when fixing the working rate of the boiler?
(c) How is it possible to produce at will saturated or superheated steam?
(d) What are the incidents as far as the functioning of the boiler is concerned since it has been put into service?

It remains for me to wish a long life for this new converter to the satisfaction of Messrs. Eklund and Hellestam who have conceived it and for the profit of their Company.

THE CHAIRMAN: I call upon Mr. Hellestam to reply.

Mr. S. HELLESTAM (Sweden): With regard to the amount of the catalyst, it is right that the amount of gas per litre is rather large, but there are some reasons for this.

The first is that the total efficiency of 98 per cent depends on the gas composition and the gas composition depends on whether sulphur or pyrites is used, and on whether the cinders from the pyrites furnaces are Fe_2O_3 or Fe_3O_4.

The second reason is that we wanted low pressure drop in the converter and, therefore, we used catalyst cylinders with a large diameter. If we had to use 5 millimetres instead of 7 to 8 millimetres the quantity would be much less.

The third reason is that when we constructed this converter someone thought that it would be very difficult to get an even distribution of a gas over the rectangular area. Therefore, I decided to put in some more catalyst over the theoretical amount. Now we have made measurements we can see that the gas distribution is very smooth, very even. Therefore, for the next converter we have not used more than the theoretical amount.

With reference to the working time of the converter, it has now worked for 14 months and we have had no trouble. We started it up in one week and it has run very smoothly. The pressure drop has not yet increased.

Concerning the boiler, we use a forced circulation boiler of the La Mont type in the furnaces, the turbulent furnaces. We get about one ton of steam per ton of sulphuric acid, or 1.6 to 1.7 tons of pyrites. Part of this steam is used to cool the gases in the converter, and, by this means, is super-heated in the converter. After the converter, the steam can be used super-heated or we have a water spray in the steam to obtain whatever degree of super-heating we want.

May I correct myself? The steam production is 1.2 tons per ton of sulphuric acid, or 1.7 per ton pyrites.

We have had no trouble with the boiler.

THE CHAIRMAN: Any questions?

MR. T. CESCA (Italy): In the document the installation of an electric furnace in the interior of the circuit is mentioned, which permits the introduction of SO_2 directly from the blower or directly across the blower or across a heat exchanger. The introduction can be effected from the last heat exchanger. When the temperature has risen to 450°, it is necessary to add a heat exchanger. This means that it is possible to carry out catalysis with less electric power.

Mr. S. HELLESTAM (Sweden): The only purpose of the air preheater is as a starting device. On starting the converter fourteen months ago we blew dry air through the heat exchanger into the bottom of the converter with steam on. When the temperature of the air had risen to that of the steam, the steam was shut off and the electric furnace with a capacity of about 300 kilowatts introduced. When the air temperature reached about 400°, we shut off the electric pr heater and introduced SO_2. The converter then started.

MR. T. CESCA (Italy): In the first instance you use the steam in order to heat the boiler.

Mr. S. HELLESTAM (Sweden): Yes, it is to heat the air.

Mr. T.P. DEE (United Kingdom): Mr. Chairman, I wish to refer to Figure 5, that is one of the numerous curves. I take it that the figures against these curves are degrees of conversion. In other words, the rate of reaction as calculated here varies continuously with the degrees of conversion. I would like to ask if the author have tried to calculate a rate coefficient, since this method must be rather inconvenient - more calculations. In other words, have you tried to arrive at a rate coefficient which is dependent on the rate of conversion?

Mr. S. HELLESTAM (Sweden): I am not sure of that. I think you will have to consult the leterature mentioned here: the work of Mr. Eklund, "The rate of oxidation of sulphur dioxide with a commer cial vanadium catalyst."

Mr. J. LEROLLE (France): Have special steps been taken to ensure the distribution of gas at the top of the converter?

Mr. S. HELLESTAM (Sweden): Yes, there is a distributor to spread the gas over the whole surface.

Mr. J. LEROLLE (France): Have special precautions been taken to ensure the distribution of SO_2 in the tubes?

Mr. S. HELLESTAM (Sweden): No.

Mr. J. LEROLLE (France): Have special precautions been taken agai corrosion especially at the bottom of the converter where the tempe ture is rather low?

Mr. S. HELLESTAM (Sweden): Perhpas we have to change the button changers in five years or something like that. It is on the stee at the button. It is easy to change these changers: you draw the out and put a new one in.

Mr. J. LEROLLE (France): I would further like to ask whether the loss of pressure of 570 millimetres is determined from the entranc of the cold SO_2 to the exit of SO_3 or from the upper portion of the converter to the exit of the SO_3.

Mr. S. HELLESTAM (Sweden): The pressure drop is the whole pressur drop across the converter, so it is the sum of the pressure drops in the catalyst layers and the exchangers.

Mr. A.I. COLEMAN (United Kingdom): Mr. Chairman, I would like to say that I found the reading of this paper a refreshing experience For many years the design of sulphuric acid plants has been traditional and empirical. Boards of directors have notoriously been m ready to accept the standard designs of tradition from contracting companies than they have been to give liberty to the inventive faculties of their technical staffs.

On this occasion it appears that necessity was the mother of invention and I think the company concerned is much to be congratulated on having encouraged this successful departure from traditio practice.

Mr. K.A. SHERWIN (United Kingdom): I should like to comment on Figure 2. The rate of reaction is considerable even when the partial pressure of SO_2 is zero, and this does not quite agree with the text in which the author says that the diagram indicates a direct relationship between the root of SO_2 pressure and the rate.

Mr. S. HELLESTAM (Sweden): I do not understand the question.

Mr. R. NORDENGREN (Sweden): It is a misprint in the Figure. The zero should be on the left side and not where it is now.

Mr. K.A. SHERWIN (United Kingdom): That is right.

THE CHAIRMAN: I think the discussion is exhausted and I would like to thank Mr. Hellestam for the work he has done, for the precise details submitted, and, above all, for the way in which he replied to all the detailed questions pur to him and which often have been really intricate. We shall now continue with the following paper:-

PAPER 910: SULPHURIC ACID MANUFACTURE: SOME FACTORS AFFECTING CHOICE OF PLANT, by A.W. Thompson (United Kingdom).

THE CHAIRMAN: I call upon Mr. Thompson to say a few words.

Mr. A.W. THOMSON (United Kingdom): Mr. Chairman, Gentlemen, I have nothing to add to my paper at this time.

THE CHAIRMAN: We will now ask Mr. Lerolle for his views.

Mr. J. LEROLLE (France): We have recently made a comparative study of the cost of contact units. In such a study it is important to state precisely the factors included in the figures given. This study has dealt with units ranging from 15 to 300 tons a day, based on pyrites and on sulphur.

As far as pyrites are concerned we have taken for the small units multiple hearth roasters without heat recovery; for the large units a roaster with a fluidised bed with heat recovery.

Regarding sulphur, we have taken into consideration a simplified plant for the small units and a more complex plant with improved heat recovery for the large units. In every case, site piling before erection and engineering costs have been taken into account.

In conclusion we have found that units based on pyrites are about 50% dearer than units based on sulphur.

If we take a 100-ton-a-day unit as an index of investment, the relative cost for a 15-ton-a-day unit would be 165, and for a 300-ton-a-day unit, 77.

On the other hand, the amortisation fund and maintenance costs which are on the whole proportionate to the investment, represent an importan percentage of the cost price of sulphuric acid and the difference in the cost price of acid of a 15-ton-unit and a 300-ton-unit is considerable: it could be estimated a 2 frs. per kilogramme or even more.

Unfortunately we have no recent comparative figures for plants with Kachkaroff towers.

As to the choice of raw materials, we found that the use of H_2S is on the increase. We ourselves have two acid plants utilising this raw material and a third is under construction. We are well satisfied. Obviously, the acid unit should not be too far away from the refinery producing H_2S and could be connected with it by pipe-line.

Sulphur, obviously is an attractive raw material the use of which is increasing, but pyrites still holds favour. We are constructing, at present, a 300-ton-a-day unit for pyrites, another plant in the Far East, and this after having constructed and put into service pyrites units in other countries. The newer processes of roasting and of scrubbing gases, the progress made in design of hea recovery boilers and means of maintenance, have greatly reduced capital costs. It a plant is installed in the vicinity of a pyrit mine, and if, in addition, the cinders are marketable, a unit based on pyrites can readily compete with a sulphur unit.

THE CHAIRMAN: I call on Mr. Thompson to reply.

Mr. A.W. THOMPSON (United Kingdom): Mr. Lerolle has said that his indications for pyrites burning contact plant are only 50% greater than the price for sulphur, as compared with the practically 100% which I have indicated. It is possible there may be some differen in the type of plant. We have taken the traditional type of gas purification, that is dry Cotterels, followed by washing towers and wet Cotterels before going to the conversion stage. That, togethe with differences in local costs, which, as I have indicated in my paper, can make a big difference to the relative charge, is probabl the reason for the difference.

THE CHAIRMAN: I call upon Mr. Didier.

Mr. DIDIER (North Africa): I should like to ask the author a short question. He stated that pyrites was competitive and even advantage in tower plants if the price of pyrites dropped 65% below the price sulphur. I do not think that there will be many people who will profit by such a reduction - apart from owners of pyrites mines and by those who can buy pyrites extracted at the mine from another mineral. This is a very particular case.

I believe, that in general, for those who have to buy pyrites i the normal way from mines which are far from the plant Mr. Thompson' classification is not very appropriate. If the contact process bas on sulphur is ahead, the classification thereafter should be as foll tower process with sulphur, tower process based on pyrites, and final owing to complications and investment costs the contact process base on pyrites. That is how I visualize the classification of the general case of pyrites users.

Mr. A.W. THOMPSON (United Kingdom): I do not think that the tower pl based on sulphur can be preferable to the tower plant based on pyrit unless the price of the pyrites is very, very much higher than the price of sulphur. If sulphur is competitive with pyrites as a raw material, surely the sulphur contact plant which is cheaper than the sulphur tower plant is the preferable plant to use.

Mr. L. ALVES (Portugal): I have one remark to make as far as the comparison between the furnace for roasting pyrites is concerned. Mr. Thomson makes a comparison on the basis of capital costs and hea recovery, but there is a point, especially for Portuguese and Spanish pyrites, which is also very important: it is the question of copper recovery. Copper in Portuguese and Spanish pyrites is a very important economic source and copper recovery is a fraction of certain constitutents of pyrites. These constituents are saved in differen manners, according to the rate and temperature of reaction of roasti So when we are roasting the pyrites in the fluidised bed process all the arsenic remains in the pyrites and then the quantity of copper i very different.

Now the question I put to Mr. Thomson is this: is this problem without interest in England or do you think the problem is practiall solved?

Mr. A.W. THOMPSON (United Kingdom): I agree that the fluidised bed furnace leaves most of the arsenic in the cinder. In Great Britain however, the recovery of copper from the cinders is not of great importance. Most of the cinders are used in iron manufacture and t copper is, in fact, an embarrasment. The pyrites we prefer to burn contains very little copper and consequently the problem has not bee approached from that angle.

THE CHAIRMAN: I think the discussion of this question can be considered as closed. Certain factors influencing the choice of the type of sulphuric acid plant have been studied but, obviously, such a study can only give an indication. In every country there are different economic circumstances which may influence the final choice.

I thank Mr. Thomson very much for having examined this question and for drawing attention to certain difficulties. We now propose to take the next paper.

PAPER 934: REMARKS ON THE RUNNING OF A SULPHURIC ACID PLANT WITH B.A.S.F. FURNACE AND INTENSIVE SYSTEM OF ORDINARY STEEL TOWERS, by A.G. Fidalgo.

Mr. A.G. FIDALGO (Spain): Mr. President, as I cannot express myself adequately in French, I would ask you to authorise me to speak in Spanish. Mr. Salsa Serra will be good enough to translate for me into French. I have, however, nothing to add to my paper.

THE CHAIRMAN: We will, therefore, ask Mr. Macdonald to submit his questions.

Mr. J.P.A. MACDONALD (United Kingdom): Mr. Chairman, Gentlemen, I have much pleasure in opening the discussion on this paper, a task which is made easier by the most interesting visit to the Pontevedra factory yesterday afternoon. This was of particular interest to me because in my Company we have a plant which is the first example of a combination of flash roasting with a tower system, in our case of the Peterson type. Mr. Fidalgo is to be thanked for giving so much information and particularly dealing with the difficulties experienced. Clearly this plant has been very successful except for one point: namely, the cooling system in the furnace. The key problem is how to construct such a plant economically where there is no practical use for steam.

I will, therefore, concentrate my remarks on this aspect, for the problem is a very important one. So difficult is the solution that in one recent case, I know, multihearth furnaces are being installed rather than face the complications of steam generation where steam is not required.

I note that consideration is being given to conversion of the plant to raise steam at 30 atmospheres for cooling, and I would mention that the present trend in the United Kingdom is towards even higher pressures; with 45 atmospheres cast iron covering of the boiler tubes can be eliminated and all cooling done by plain mild steel pipes.

I would like to ask if consideration has been given to the following possible ways of improving the present plant. If the tubes cooled by steam at 0.5 atmospheres gave sufficiently good performance in the boiler, could the bed be modified to permit the use of similar cast iron covered tubes instead of the present mild steel plate?

Secondly, could the present bed be operated using another cooling medium such as heavy oil leaving the boiler to work on 0.5 atmospheres steam?

Thirdly, if steam at 30 atmospheres is the only way, can the boiler system be made very simply? Could a forced circulation boiler be associated with a high pressure condenser in closed circuit and expensive features, such as steam drum boiler mountings, etc., be largely eliminated?

Lastly, could the cooling be effected by admission of water to the bed either below or above the grate? The amount so required is less than that necessary for reaction in the tower system and so is acceptable for the next stage in the process.

I will close by once more thanking Mr. Fidalgo for his most interesting paper and expressing the hope that he will successfully overcome all these problems.

Mr. IGLESIAS SAENZ (Spain): It is not possible to use casting to the turbulent chamber, because the frequent breakdowns and starts of the furnace produce sudden changes of temperature, with the risk of breaking the casting.

Mr. J.P.A. MACDONALD (United Kingdom): Can I try another explanation? In the present boiler the tubes are mild steel covered in cast iron and they have worked reasonably well. The difficulty is in the reactor, where mild steel plate is used for heat exchanging. Could the design of the bed be altered so that the cooling is done with the same type of heat exchanger as is used in the boiler, namely a mild steel tube covered in cast iron?

Mr. IGLESIAS SAENZ (Spain): Besides the use of steel tubes lined with cast iron in a turbulent chamber it would be rather complicated owing to its particular nature. This does not happen in the boiler where the coils are composed of straight tubes which can also be substituted more easily. Other systems employed for the turbulent chamber tubes covered with a special welding have not yet been tested at Pontevedra.

As for the use of other means of refrigeration, such as for instance heavy oil, we do not have any experience so that we cannot say whether satisfactory results can be reached or not.

Mr. J.P.A. MACDONALD (United Kingdom): The installation of a boiler working at 30 atmospheres is expensive, and my question was whether any simplified heat exchanger could be devised which excluded the expensive features of a normal high pressure boiler. These expensive features are items like the steam drum, boiler mounting, etc., and I asked if a heat exchanger, with forced circulation, having a heating side and a cooling side, could eliminate some of these expensive items.

Mr. IGLESIAS SAENZ (Spain): Although it is planned to replace the actual system by high pressure steam, this change will not take place until we have got some further experience from tests we are now realising and which have given some favourable results at the pipe coils of the boiler.

The substitution by pressure steam will take place in a single circuit through steam condensation. This system is partly inspired by the working of the Schmidt-Hartmann boiler.

As to the fourth question, some tests with water admission to the turbulent chamber have been realised, but they have caused difficulties at the Cotterel so that at present we only use air.

When we started working with it, we only used little air and a 15.5% SO_2 concentration. At present the SO_2 concentration amounts to 12-13%, but the tests made with water admission have been unfavourable both for the working of the Cotterel and on account of corrosions.

Mr. T. CESCA (Italy): Mr. Fidalgo said in his paper that it is possible to roast granules in a turbulent bed if they are larger than 6 mm. I am of the same opinion, provided that the pyrites is of a decrepitant nature, as, for example, Rio Tinto. On the other hand, if the pyrites is not decripitant, then granules of 6 mm. are too big, and a smaller granule must be used.

Mr. F. IGLESIAS SAENZ (Spain): The difficulty of burning bigger sized iron pyrites which can decrepitate is only one of the mechanica working of the dosifier. Owing to the irregular form of the pyrites grains which are bigger than 12 mm., the passage through the distributor has been clogged, a fact which can be avoided with a greater charge where the size has no influence.

For iron pyrites, which decrepitate badly, the size of 6-8 mm. has been totally satisfactory.

The advantage of using a bigger sized pyrites granule is that most of the ashes escape from the furnace and that the dust passing to the boiler and the Cotterel is largely reduced.

Mr. T. CESCA (Italy): I was surprised by the low temperatures of the cinders from the fluidised bed. That is a temperature ranging between 640° and 700° Celsius. At the same time I observed that the desulphuration was very satisfactory seeing that only 1.1% to 1.3% of sulphur had been found in the cinders.

I asked myself how can this phenomenon be explained. In the course of yesterday's visit, I observed that the roasting surface of the furnace is 2.9 square metres, i.e. that the furnace had been planned for a much larger capa city than yesterday's charge. The low sulphur content is therefore explained by the low charge present.

This leads to another conclusion. If, in future, installations were to receive a much larger quantity of pyrites, temperatures would automatically rise and a satisfactory desulphuration would be ensured by the much higher temperatures.

Finally, this furnace is very flexible as far as functioning is concerned with a low or high charge of pyrites.

Mr. F. IGLESIAS SAENZ (Spain): Mr. Fidalgo would like to explain that although the furnace has been provided for 50 tons of pyrites, the cooling of the turbulent chamber is designed for 40-45 tons.

The furnace has been running satisfactorily with charges between 33 and 45 tons. Tests realised even with a charge of 28 tons have shown the possibility of practically employing it, although perhaps the furnace will have to be attended to more carefully.

THE CHAIRMAN: Gentlemen, we may consider this discussion closed. We owe a debt of gratitude to Mr. Fidalgo who by his explanations has enhanced the very interesting visit made to Pontevedra yesterday. In fact, we do know how to thank him for his thought-provoking paper which completes in such an admirable manner the friendly reception by the Sociedad Productos Quimicos Ibericos.

We shall now procede to our last paper.

PAPER 935 : VAPOUR PRESSURE IN H_2SO_4 - $HNOSO_4$ - H_2O, by J.J. Azofra.

Mr. J.J. AZOFRA (Spain) : The paper we are now presenting is given without any great claims, solely as a starting point for a number of experiments, because there is such a lack of correlation between the data and the divergencies apparent in the wide literature which has recently been published on this subject.

In this paper we have merely tried to see whether the data obtained from experiments, i.e. the total vapour pressure measured, obeys the law which can be deduced from that of Clausius Clapeyron and can provide a method of discovering the order of the values to be determined without other means of determination.

We have not mentioned the work of Pozine and Fleriskaia, Benkowski, Kiriev, Koudrivtzev and other Russian authors, amongst whom Varlamov should be especially mentioned. This would entail discussion and analysis of their results which we could not claim to do without the necessary evidence from our own work. This will not be forthcoming until we have finished the present experiments being carried out in our laboratories. These are aimed at solving the diverse aspects of the problem and are basically :-

1. Accuracy in the analysis of sulphur nitrates.
2. Accuracy and control in the gaseous phase.
3. Dissociation and nature of the liquid phase.
4. Study of the hydrolysis reaction and solvation of nitrosylsulphuric acid.

The work of F. Seel and Meier together with that of Deschamps opens up a recent field with regard to this last item.

We have refrained from making any comment on the values given, solely because they differ from those already in existence and, as Pozine says, the differences may amount in certain cases to eight times the known value.

For this reason we have not given in our conclusions the limited figures obtained from our data, and we have prepared different acids by diluting the most concentrated with a solution of sulphuric acid.

CHAIRMAN : At this meeting we are allowing ourselves only five minutes for the introduction of a paper, and as this time has already been exceeded, we may perhaps call upon the next speaker, Mr. Storrow.

DR. J.A. STORROW (United Kingdom) : It is difficult to do justice in a verbal discussion to a paper of this type, which presents important experimental data, as inferences drawn from the experimental results depend on a mathematical analysis of the thermodynamic functions involved. So far as his data are concerned the author has already answered my first question as to the comparison of his experimental results with those of other workers such as the fourteen Russian authors referred to in "Absorptionprogresse in der Chemischen Technik" by W.R. Ramm (p. 356 et seq., Verlag Technik, Berlin 1953). * Readers of Mr. Azofra's paper may be interested in comparing therewith the Russian data apparently obeying Henry's Law :

$$p = E.x$$

between p the partial pressure of N_2O_3 in the gaseous phase, and x the weight fraction of N_2O_3 in the liquid phase. The constants E are available for various concentrations of H_2SO_4 in solution at various temperatures. The present author's paper in Fig. 2, 3, 4, 5 shows a similar linear relationship between total vapour pressure of the solution and $HNOSO_4$ concentration. A full comparison of all these data would be instructive as it appears that they only agree with Mr. Azofra's data at some acid concentrations.

Expression of the present data by a logarithmic plot of total pressure may be questionable as the system may not be in reversible equilibrium and also the summation of various partial pressures may follow a more complex exponential relationship with temperature. Though the analysis of total pressure functions may be technologically valuable, care is necessary in analysing these functions for specific energy quantities, e.g. for Loc dp/dT the energy associated with the change of phase in the Clausins-Clapeyron equation. If the Kirchoff relation L = Lo + aT is accepted, the Eucken equation referred to by Mr. Azofra should be

$$\mathrm{Ln}\ p = \frac{-Lo}{RT} + \frac{a}{R}\ \mathrm{Ln}T + C$$

with a and C as constants. Mr. Azofra has taken $\frac{a}{R} = 1$, but the analysis of his data does not justify this. I suggest that a preferable form is provided by an Othmer plot

$$\mathrm{Log.}\ p = \frac{L}{L_W}\ \log p_W + C$$

where p_W and L_W are the vapour pressure and energy of vaporisation respectively for a reference substance. Using this plot for total pressure, with some reservation, the author's Fig. 10, 11, 12, 13 become straight lines, which indicate clearly which deviating data are probably in error and allow the deduction of the negative value a/R. These plots appear advisable and may assist in delineating the author's nitration and denitration zones, although they no longer show the gradient changes regarded as significant in Mr. Azofra's analysis.

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* A bibliography of these Russian authors is held by ISMA London offic

THE CHAIRMAN : I suggest that, owing to the limitations of time, Mr. Azofra and Dr. Storrow could perhaps discuss these analyses more fully following the meeting. (This was done, Mr. Azofra being shown the analyses of the data made at Fisons' Levington Research Station, England. Mr. Azofra's written reply is as follows.)

Mr. J.J. AZOFRA (Spain) : I am very grateful to Dr. Storrow for his collaboration, which I accept with pleasure, as well as his offer to discuss the matter privately.

As I said in my introduction, I am familiar with the work of the Russian authors and of Varlamov's criticism of it, but perhaps that which Dr. Storrow puts forward is more unfamiliar.

With regard to the values found to be effective for acid solutions of 70 - 75% we have found that there are anomalies, as you have mentioned, and I cannot tell you anything further about these. It seems to be a question of :-

A change in the composition of the system ?
The formation of new compounds ?
Are there, as Varlamov says, phenomena of solvation ?

Such is the problem. We did not take partial pressures but the sum total of the experimental data for we did not know the water vapour pressure, not knowing the effect of the solute in the solution, nor the degree of its dissociation. But, again, do we know what proportion of the N_2O_3 was dissociated, and whether the components of dissociation are altered or transformed in the presence of the residue ? Here again are new field of study which must be explored in order to arrive at the values for which we are looking.

I repeat, our figures are experimental, obtained by the static method, with the errors peculiar to this method and to analytical control.

We used Berl and Saenguer's formula, because this is one of the rare cases in which it can be applied to total pressure obtained by the static method. Our aim at present in the face of a similar problem is to see whether, for the concentrations studied, a comparison can be established with the results of the authors cited above. We have not, however, gone any further than this. On the other hand, the efforts of the Russian author, Varlamov, quoted so many times, to find a mathematical expression comparable to that of Kirchoff were unfruitful, because, probably, as you have already said, the phenomenon is a complex one and not, I think, merely a physical one. The only reason we have made known these results is because though we know how to achieve them experimentally we cannot explain the numerous questions which they raise.

CONCLUSION

THE CHAIRMAN : Before closing the meeting, or rather, before handing the chairmanship over to Mr. H. Stevenius-Nielsen, I would like to thank you for your close attention and thank in particular the authors of the papers who lead us on to the high plane of mathematical science, demanding very close concentration.

Mr. H. STEVENIUS-NIELSEN : Mr. President, Gentlemen, the presence here of the President of I.S.M.A. is not only a great honour for our technical conference and for all of us, but it also stresses the importance of this section of the work of I.S.M.A.

In the name of the delegates, I would like to thank you, Mr. President, most cordially. I am sure that everybody will agree with me that the technical meetings in Spain have been a success from every point of view and, as Chairman of the Technical Committee, I should like to express once more my sincere thanks to all who have contributed to this result.

The President, Mr. Grandgeorge, has kindly consented to close the meetings, and I ask him to say a few words.

Mr. GRANDGEORGE : Mr. Chairman, Gentlemen, I have followed your wo with great interest and pleasure and my only regret is that I have not been able actually to take part in these Madrid meetings, for which I must apologise.

First of all, I should like to thank our Spanish friends, and, in particular, Mr. Capelo Portabella, Mr. Iglesias Saenz and Mr. Domingo, as well as the S.A. Auxiliar de la Industria Quimica, Productos Quimicos Ibericos S.A., and Sociedad Anonima Cros, for the welcome extended to us, for the organisation of this meeting, for their receptions in Madrid and Galicia, and for the trouble they have taken in rendering this journey as enjoyable as possible, not only for the delegates but also for the ladies who by their char have contributed so much to the success of this conference. I am sure that every one of us will take back unforgettable memories of this journey combining artistic beauty with picturesque landscapes, which found expression last night in the presentation of Galician folklore.

When Mr. Capelo suggested his country as a venue for our Technical Conference in 1957, we knew how much the attraction of Spain would encourage the technical experts of I.S.M.A. to make the "pilgrimage to Compostela."

Eighty-five delegates representing sixteen nations attended the meetings. Many of them have come from far away, and I should like to thank everybody for the interest taken in technical problems which is confirmed by their presence.

The merit for having created these contacts belongs to our former president, Mr. Robert Standaert. Right from the beginning, he was able to create an atmosphere of technical comradeship which remains the most important factor in mutual confidence which is the mainspring of any intellectual exchange. But I think praise must also be given to our friend, Mr. Stevenius-Nielsen, whose technical authority played such an important rôle in fostering the atmosphere which we observe to-day: a friendly atmosphere, excluding all desire for, or intention of commercial competition, and only allowin the spirit of co-operation to expand with the object of attaining th most economic solution of the problems which the different companies have entrusted to their technical experts.

This atmosphere is clearly reflected by the number and importan of the subjects discussed, representing scientific studies of the highest order connected with the daily work of our firms, such as production, storage and packing.

One of the characteristics of these exchanges has been of particular significance to me who attends the technical meetings for the first time : it is the examination or rather close interrogatio of the authors of the papers. Is not this the best proof of the quality of these papers and of the interest they arouse among the delegates ?

On various occasions I have had the opportunity of attending international meetings and I believe that the success of the technical meetings of I.S.M.A. is based to a large extent upon the working method which you adopted at the suggestion of Dr. Raistrick of Scottish Agricultural Industries Ltd., at Edinburgh. The nomination of a speaker for each question seems to me a happy idea and marks an interesting step forward in the organisation of our meetings.

Would you permit me, Mr. Chairman, to make a few suggestions for the future ? It seems to me - and I believe I am speaking on behalf of some of you - that it might be of interest to transform the nominated speaker into a "manipulator" who would make a choice from the questions which come to the minds of the delegates when the subject is introduced, thereby bringing about a more general discussion of the problems which exercise your minds.

Secondly, it seems to me that the papers dealing with pure research, which certainly are of the greatest interest to all I.S.M.A. members, could usefully be supplemented by actual facts of industrial experience which every one of you can observe in the course of your lives and which could be brought to the knowledge of all concerned to great advantage. The exchange of observations made by such experienced technologists as yourselves during your daily industrial routine may profitably bring about an improvement in our industry.

Finally, I would like to make an observation in regard to the programme of future meetings. Would it be possible, Mr. Chairman, to provide, apart from the official meetings and visits to works, an occasion for contact between the participants in order to exchange personal views ?

In order to make ~~on~~ re-establish these contacts after an interval of two years, it is necessary to provide an occasion, and very often it is at the moment of parting that these exchanges of personal views begin, and these, to my mind, are of particular interest to us all. Do you not think that from the first day an afternoon should be set aside for informal discussion and private conversations, reinforced with a glass of whisky, with a view to developing these personal contacts to which I myself attach great importance, in order to create an atmosphere favourable to the exchange of technical points of view?

I should not like to close this session without thanking our very charming secretaries, who have performed such an arduous task, which was rendered particularly difficult by the technical nature of the discussions.

I would also like to mention how indebted we are to Mr. Carpentier and Mr. Morgan for their contribution to our work. Not only have they revealed themselves as able translators, but they have also shown in their translations a spirit of discernment which I appreciate.

On behalf of you all, I have sent congratulations and best wishes to our Vice-President, Mr. Scheibler, on attaining his seventieth birthday.

Gentlemen, it only remains for me to wish you all a pleasant end to your sojourn, favoured by sunshine which has accompanied us on our journies, and a safe return to your respective countries, thanking once again our Spanish friends for the organisation of this congress which will go down in the history of I.S.M.A.
