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Mixed phase ammoniation for high-grade fertilizers,  
with a note on analytical methods

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1. Introduction.

1. One of the problems in manufacturing high-grade compound NPK fertilizers is the introduction of the ammoniacal nitrogen. Montecatini came up against the ammoniation process in 1955 when the Company began production-scale manufacture of a number of formulations of granulated complex fertilizers with a high nutrient content.

2. Production-scale manufacture was preceded by pilot plant manufacture at the Company's plant at Vercelli, some 50 miles west of Milan.

The purpose of the pilot plant was to study the behaviour of plant and instrumentation and the design adjustments required to produce the various grades.

In addition to the mixing vessels with agitators for the liquid-phase reactions, the pilot plant comprises one complete fertilizer cycle consisting of a granulator, drier, elevator, fines screens, oversize screens and mills for crushing the oversize. The fines and the crushed oversize are recycled to the granulator.

The experiments were begun by bubbling gaseous ammonia into the liquid phase, which could be phosphoric acid or slurries produced by reacting phosphate rocks with mineral acids (phosphoric, sulphuric or nitric).

This method immediately presented us with chemical and chemical engineering difficulties and these had unfortunate repercussions on both the costs and the properties of the product:

(a) low ammoniation yields, i.e. ammonia fixation, and insufficiently high levels of  $N_2$ , mainly due to the high temper-

atures reached by the slurries during this strongly exothermic reaction:

(b) difficulties in handling the ammoniated slurries owing to a tendency for them to crystallize and thicken, sometimes even to set solid, as the temperature fell.

These difficulties are, of course, even more pronounced when dealing with sulphuric/phosphate slurries which have a naturally high density (for example, when making 15-30-0 NP fertilizer).

3. Our first step was to split the ammoniation phase as follows: - cut liquid phase ammoniation to the point where ammonia losses were nil (this depends on the concentration of  $\text{NH}_3$  in the slurry); the partially ammoniated slurries then remain fluid enough to be handled during subsequent stages of the treatment;

- finish ammoniating in the solid phase, i.e., in the granulator where the ammonia reacts with the layer of liquid slurry on the surface of the granules.

Since our pilot plant was not designed in the correct proportions and our mechanical aids were rather inadequate, we met so many setbacks in the early stages that we did not think this method would succeed. However, after another series of experiments we managed to design and build a drum of fairly large diameter for the solid phase ammoniation, and after this our difficulties vanished. We were able to work with fairly thick beds of solid material in which  $\text{NH}_3$  losses were reduced to a minimum, the  $\text{NH}_3$  which still leaked out of the drum being recovered in a tower with phosphoric acid passing rapidly through it, then fed into the liquid phase ammoniation stage.

## 2. Ammoniation drum - design and working principle

1. Fig. 4 is a drawing of the improved granulation and ammoniation drum, as built by Montecatini for its modern plants manufacturing granulated complex fertilizers with a high nutrient content.

Without going into the details of design, we should like to mention the following features which are important from the functional point of view:

- a) the essential feature is the depth of the layer of material, which can be varied between a minimum of 50 and a maximum of 65 cm;
- b) the following are fed into the drum:-
- dry recycled fines and crushed oversize;
  - the partly ammoniated slurry which in the first section of the drum coats the granules with a thin film;
  - gaseous ammonia, through a feed tube placed close to the inner wall of the drum so that the ammonia is forced to pass through a thick bed of granular material and therefore has time enough to react with the surface film of liquid on the granules.;
- c) a scraper whose reciprocating movement is designed to clean the inner wall of the drum by removing the coating which inevitably forms upon it.

2. The drum shown in the drawing (Fig. 4) has a diameter of 2.57 m and a length of 3.00 m; it produces 18-47-0 di-ammonium phosphate and fixes ammonia at a rate of 500 kg  $\text{NH}_3/\text{h}$  with an absorption efficiency of 95-96%.

These figures will obviously vary with the product being manufactured, the moisture content and temperature of the granules, etc. The distribution of the total amount of ammonia between the liquid phase reaction vessels and the rotary drum (dry ammoniator) varies in ratios of between 3:1 and 2:1.

3. The ammoniator drum which we used originally was 1.62 m long with an internal diameter of 1.95 m, closed at the feed end and having a 78 cm diameter orifice at the discharge end; it had a 9% inclination and a speed of 10 rev/min. and was fitted with a mobile scraper to keep the interior surface clean. The solid product moving inside it thus has a constant fall of 60-65 cm. The ammonia was fed in through a perforated tube penetrating below the granules. The drum was aspirated and connected with the tower in which phosphoric acid was recycled. When manufacturing a 15-30-0 NP fertilizer in the plant described above with the split ammoniation technique,

we found that ammoniation efficiency was constant at about 97%, compared with the 93-94% efficiency obtainable when ammoniating in the liquid phase only.

Split ammoniation unquestionably improves the process from the economic point of view. We were in fact able to use more highly concentrated phosphoric acid (up to 35-40%  $P_2O_5$ ), reduce the quantity of recycled material, and increase the capacity of the installation.

In view of subsequent experiments made with various other products, we can also state that the use of final ammoniation in the solid phase enables us to raise the yield of ammonia fixed on the second hydrogen atom of the phosphoric acid to more than 95%, which makes it possible to upgrade the nutrient content of complex NP and NPK fertilizers with lower phosphoric acid consumption, while maintaining total ammonia yield at 96-97%.

### 3. Theoretical consideration of the reactions involved in ammoniation.

1. By means of laboratory experiments we subsequently confirmed and clarified the improved utilization of the acidity of the phosphoric acid resulting, as described above, from splitting the ammoniation between the liquid and solid phases. We tried in these experiments to reproduce normal operating conditions as far as possible. The experiments were carried out in a cylindrical reactor where  $NH_3$  gas from a cylinder was fed in at the bottom through a perforated tube. We placed in the reactor first phosphoric acid, sulphuric acid and phosphate rock in the correct proportions to produce a 15-30-0 compound. To be exact:

618.5 g Land Pebble phosphate with 33.95%  $P_2O_5$   
 1142.0 g 98%  $H_2SO_4$   
 4750.0 g phosphoric acid with 28%  $P_2O_5$ .

After the reaction resulting from the attack of the phosphate rock by the acids, which forms a slurry consisting of a mixture of phosphoric acid, sulphuric acid and chalk in suspension, we began the ammoniation. Gaseous ammonia was

Table A - Ammoniation of sulphuric/phosphoric slurry

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pH	V <sub>2</sub> O <sub>5</sub> % dry	H <sub>2</sub> SO <sub>4</sub> % dry	Distribution of P <sub>2</sub> O <sub>5</sub> (dry)					(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> % dry	CaSO <sub>4</sub> % dry	Moisture content Total %	Temperature %	Ammoniation time in minutes	Relative mean speed	
			H <sub>3</sub> PO <sub>4</sub> as P <sub>2</sub> O <sub>5</sub> %	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> as P <sub>2</sub> O <sub>5</sub> %	CaHPO <sub>4</sub> as P <sub>2</sub> O <sub>5</sub> %	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> as P <sub>2</sub> O <sub>5</sub> %	Total P <sub>2</sub> O <sub>5</sub> %						At	Totals
			4	5	6	7	8						14	2:13
1	0	11	39	-	-	-	39.1	-	18.8	45.6	50	-	-	-
1	3.2	0	37.6	0.3	-	-	37.7	14.8	18.1	38.1	105	14	0.23	0.23
1	8	-	10.7	24.6	-	-	35.4	13.9	17	34.2	120	40	0.18	0.20
1.7	9.5	-	4.1	29.2	1.3	-	34.7	16.8	14.1	32.4	114	50	0.15	0.19
2.3	10.2	-	1.8	30.3	2.3	-	34.5	18.7	12.1	31.6	110	58	0.09	0.16
4.0	10.7	-	0.4	30.5	3.2	-	34.2	20.4	10.4	30.5	105	65	0.07	0.16
5.1	11.4	-	-	27.5	4.6	1.0	33.3	23	7.7	29.7	97	75	0.07	0.15
5.5	13	-	-	18.9	8.4	5.8	33.2	30.3	0.2	26.3	92	100	0.06	0.13
5.9	14.8	-	-	9.1	8.5	14.7	32.4	30.5	-	25.1	88	140	0.04	0.11
7.3	16	-	-	2.4	8.4	20.7	31.7	30	-	21.6	84	200	0.02	0.08

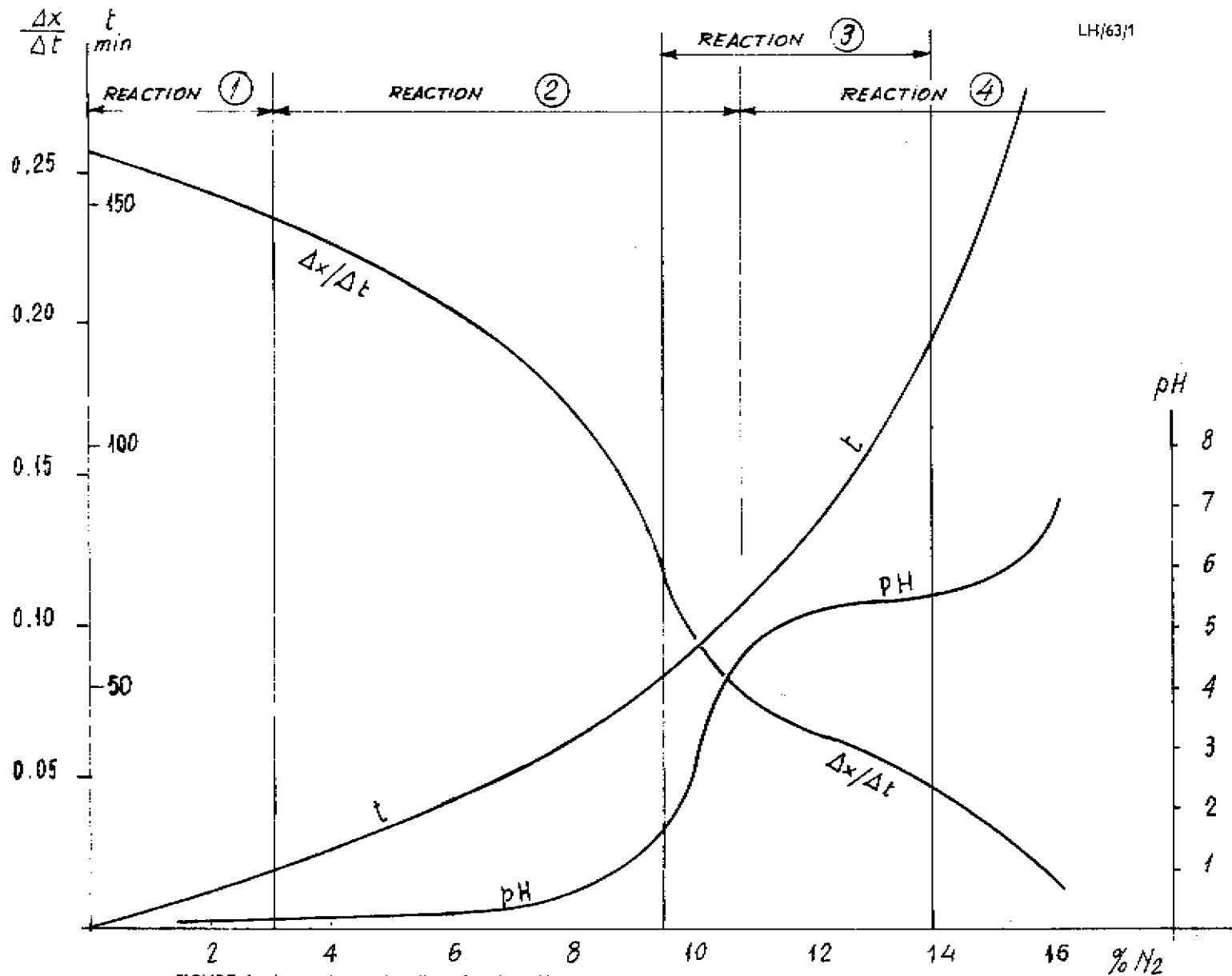


FIGURE 1—Ammonisation bouillies phospho-sulfuriques: pH; temps de réaction  $t$ ; vitesse d'absorption azote  $\Delta x/\Delta t$  en fonction de la concentration azote.

Ammoniation of phospho-sulphuric slurries: pH; reaction time  $t$ ; speed of nitrogen absorption  $\Delta x/\Delta t$  as function of nitrogen concentration.

Symboles :

HS =  $H_2SO_4$ CS =  $CaSO_4$  $N_2S = (NH_4)_2SO_4$  $H_3P = H_3PO_4$  (in %  $P_2O_5$ ) $NH_2P = (NH_4)H_2PO_4$  " $N_2HP = (NH_4)_2HPO_4$  "CHP =  $CaHPO_4$  "

%

Sur le sec

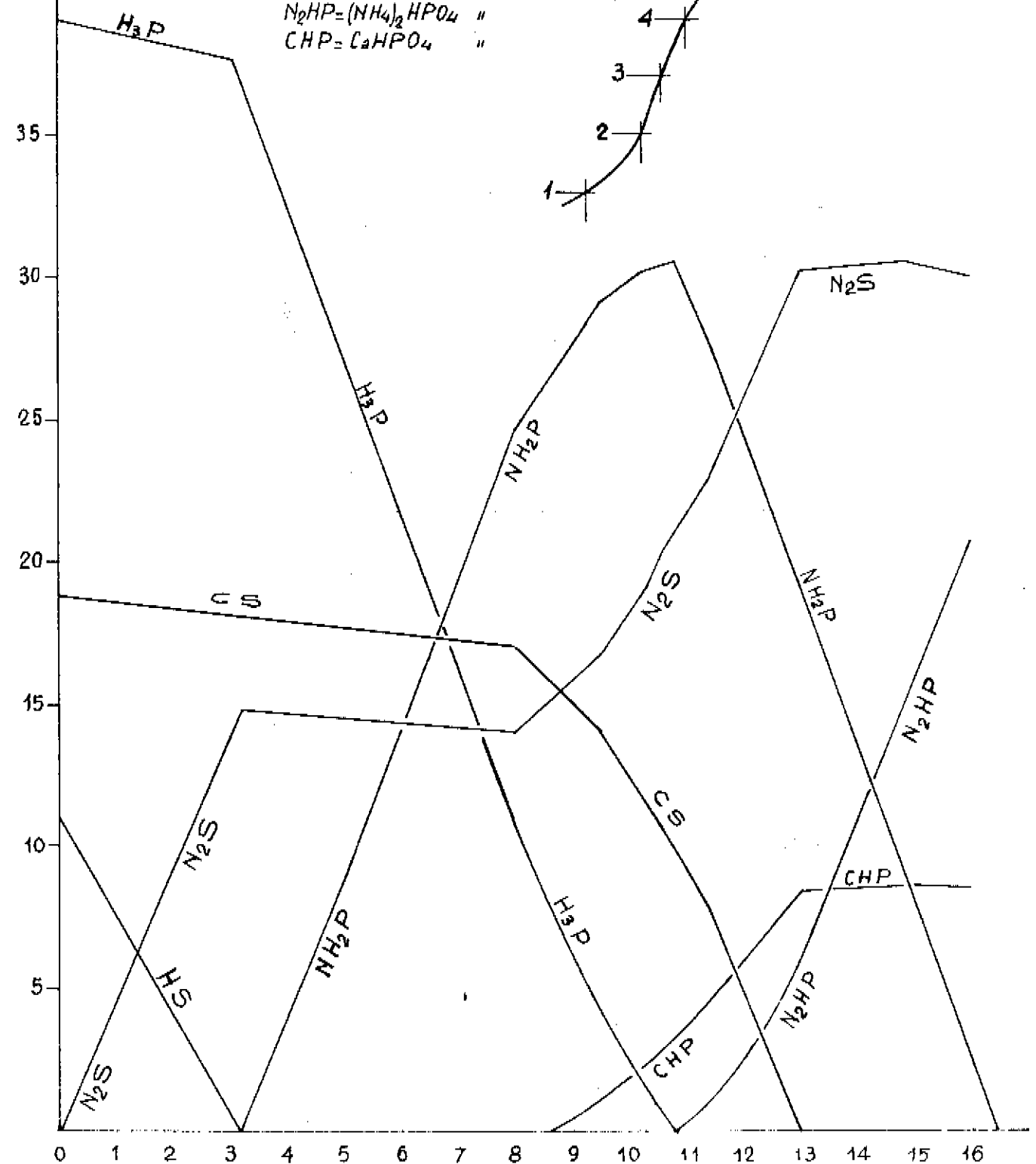


FIGURE 2—Ammonisation bouillies phospho-sulfuriques: composition (en %) en fonction de la concentration azote sur le produit sec.

Ammoniation of phospho-sulphuric slurries: composition (in %) as function of nitrogen concentration (dry product).



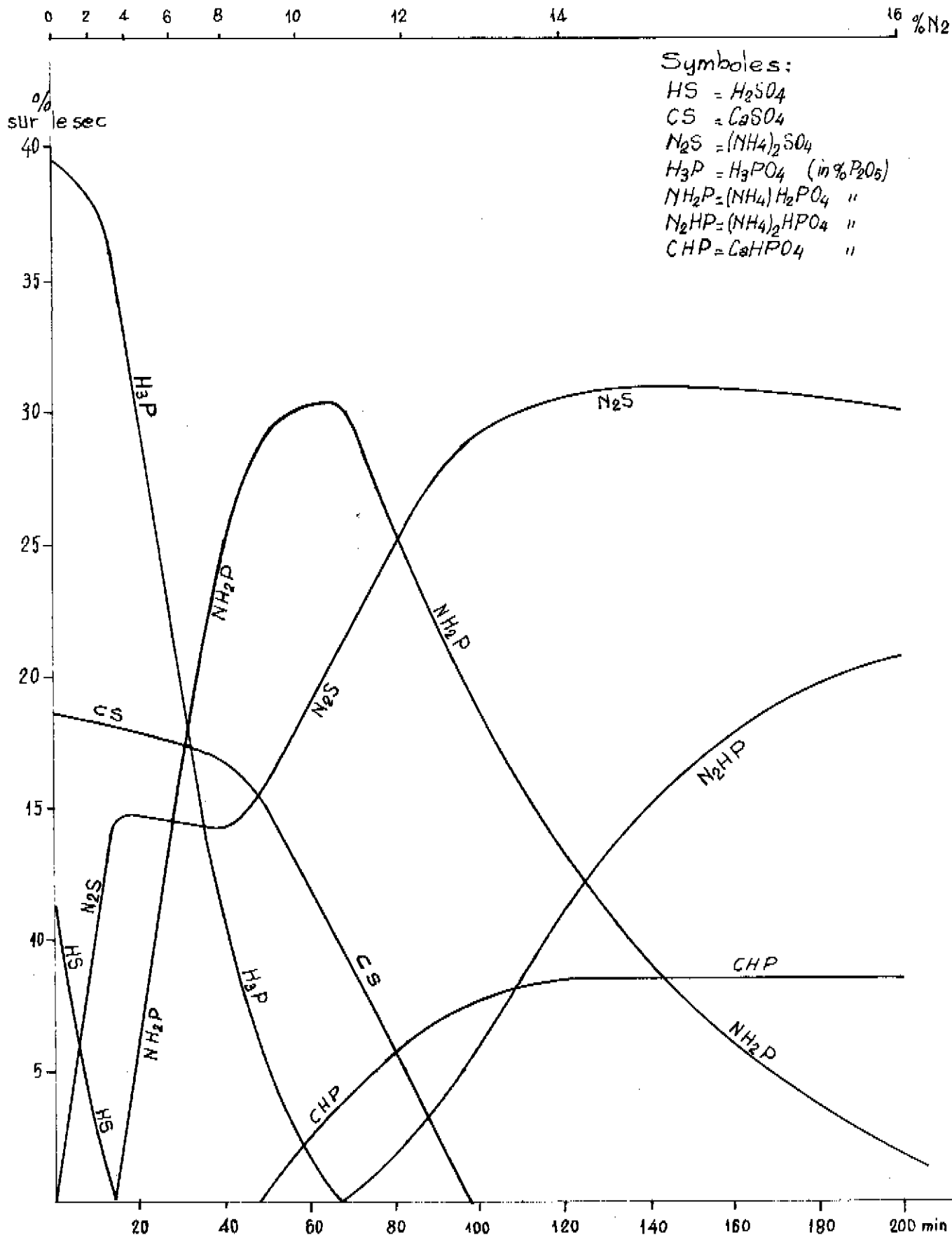
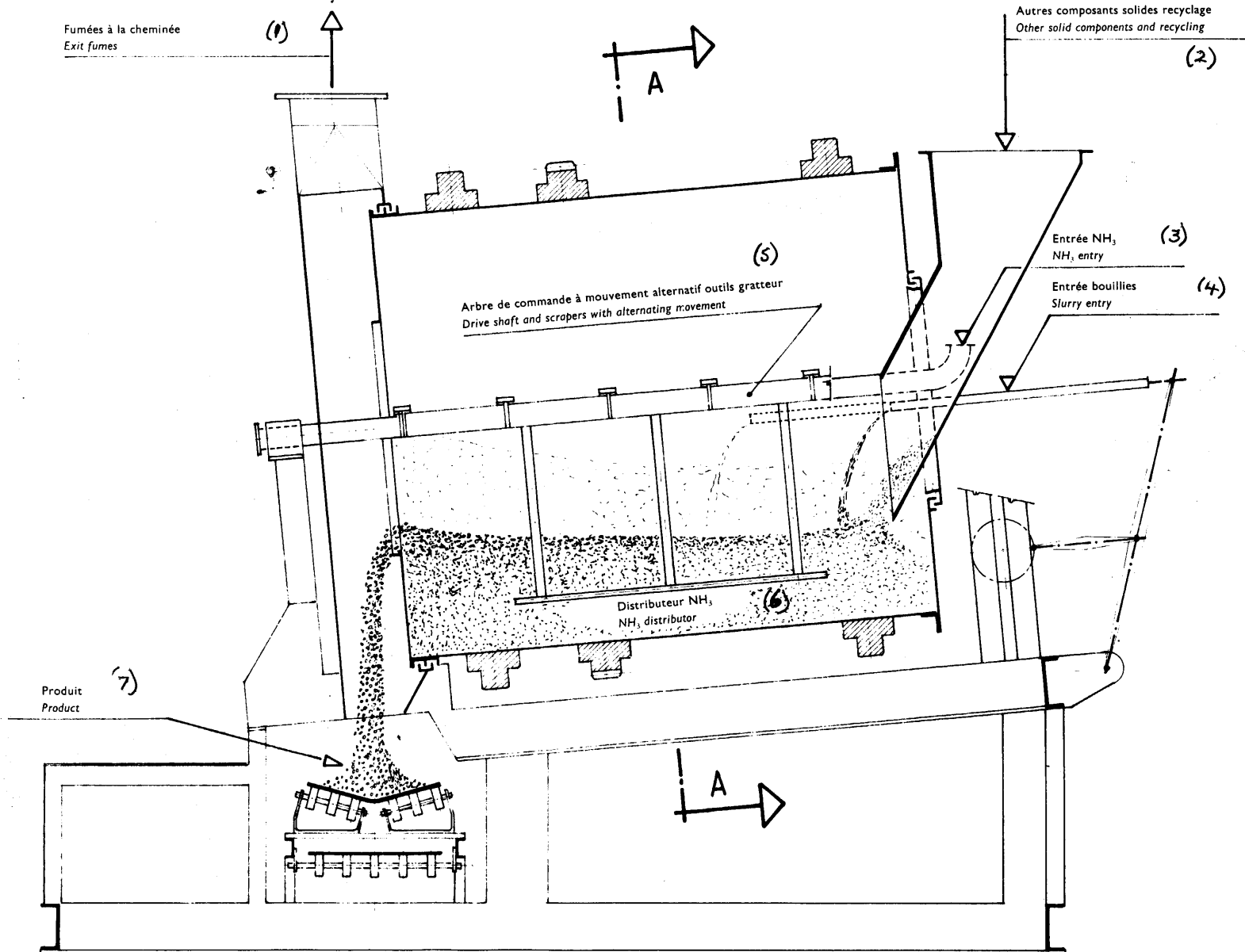


FIGURE 3—Ammonisation bouillies phospho-sulfuriques: composition (en %) en fonction du temps de réaction.

Ammoniation of phospho-sulphuric slurries: composition (in %) as function of reaction period.

FIGURE 4a—Tambour granulateur d'ammonisation. Ammoniation granulation drum.



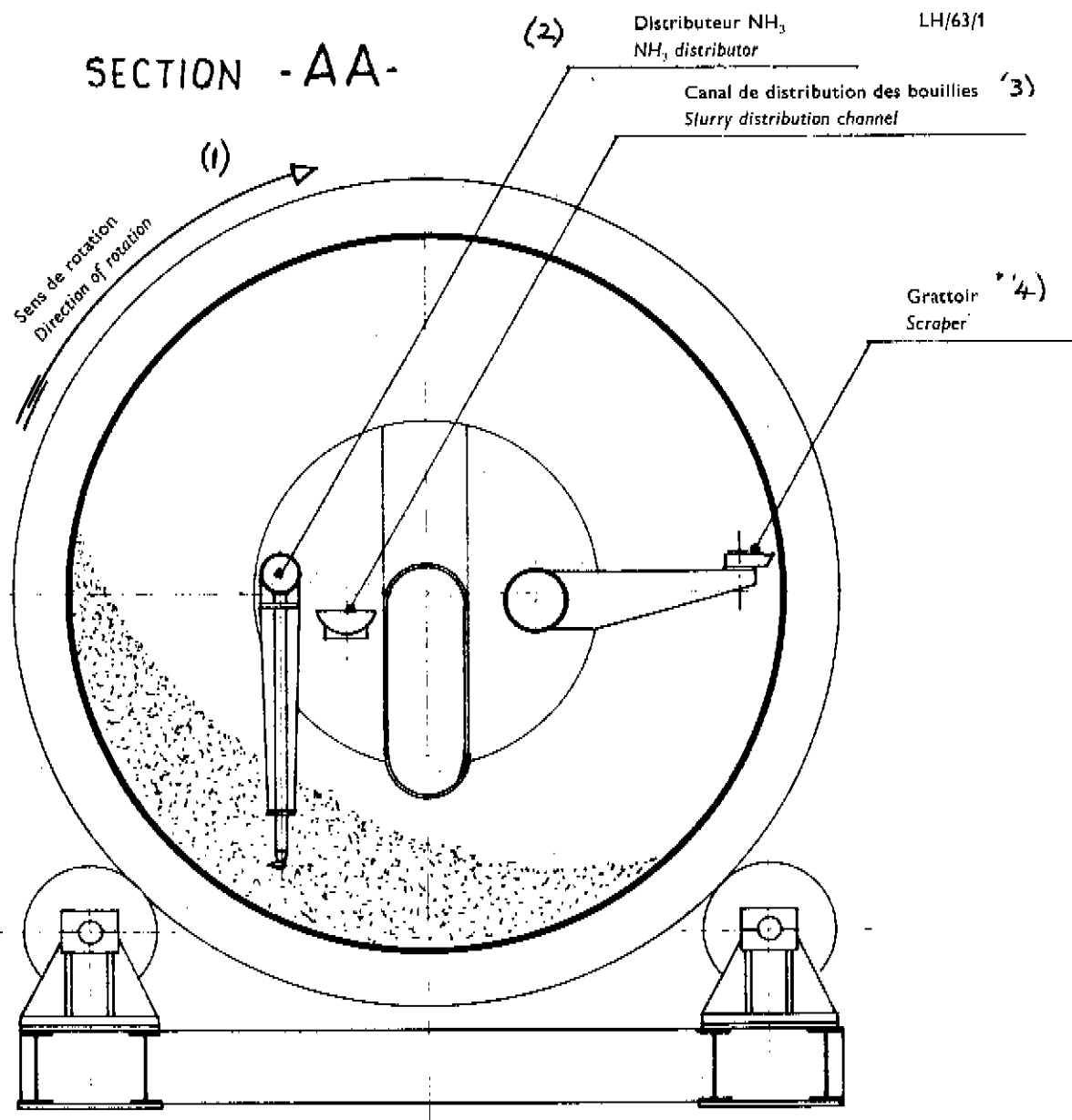
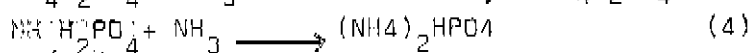
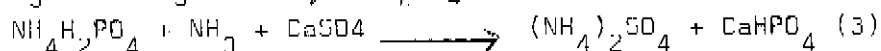
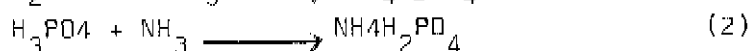
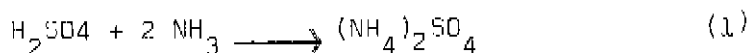


FIGURE 4b—Section du tambour granulateur d'ammonisation  
Cross-section of the drum

fed in at a constant rate through the perforated tube.

2. At intervals, after measuring the pH of the mixture and its temperature, we took samples of the slurry so as to obtain a scale showing the products of ammoniation. We determined the various components, anions and cations, of the slurry samples. Table A and Figs. 1, 2 and 3 show the results obtained.

To make it easier to understand our subsequent argument, we give below the main reactions which occur during the absorption of ammonia by sulphuric/phosphoric slurries. There are 4:



The secondary and subsequent reactions have no interest for us within the limits of the present study.

Table A and Figures 2 and 3 show the salts of phosphoric acid in terms of their  $\text{P}_2\text{O}_5$  content. The curves show the variation in  $\text{P}_2\text{O}_5$  between the various forms as a function of nitrogen concentration (Fig. 2) and ammoniation time (Fig.3).

Fig. 1 plots the course of pH, again as a function of the percentage of  $\text{N}_2$  in the dry material, while the lines represent the speed of nitrogen fixation and the time required for the reaction.

3. A study of the figures shows one fact right away: the reactions set out above occur qualitatively in the order given, but not quantitatively. Reactions (1) and (2) are very rapid, but the neutralization of  $\text{H}_2\text{SO}_4$  to  $(\text{NH}_4)_2\text{SO}_4$  clearly precedes that of  $\text{H}_3\text{PO}_4$  to  $\text{NH}_4\text{H}_2\text{PO}_4$ , so that it is not until all the sulphuric acid has been neutralized that monoammonium phosphate begins to form.

It is also clear that reaction (2) is almost complete before the slurry reaches a pH of 1, while free phosphoric acid disappears entirely at a pH of 4.5

Transformation of the phosphoric acid into monoammonium phosphate (2) is still taking place when reaction (3) begins, i.e. the reaction between  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{NH}_3$  and  $\text{CaSO}_4$ , giving

ammonium sulphate  $(\text{NH}_4)_2 \text{SO}_4$  and dicalcium phosphate  $\text{CaHPO}_4$ . In fact the dicalcium phosphate (less soluble than the  $\text{CaSO}_4$ , which explains the course of the reactions) begins to appear at a pH of 1 which progressively increases with the increase in the concentration of the monoammonium phosphate, up to the point when reaction (4) begins, after the total disappearance of free phosphoric acid.

Reaction (3) is complete at pH 5.5.

The pH curve (fig. 1) reflects the course of these successive reactions by the changes in its various portions:

- completion of reactions (1) and (2) with the simultaneous disappearance of the hydrogen ions released at the first dissociation of the phosphoric acid -  $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$  coincides with the rapid changes in pH in the section between 9 and 11%  $\text{N}_2$ ;
- reaction (3), which is a double substitution, coincides with the section showing the least pH variation, which occurs when the  $\text{N}_2$  concentration rises between 11 and 14%;
- finally, reaction (4) which leads to the progressive disappearance of the second hydrogen ion of the phosphoric acid is shown by the new direction of the pH line.

Reaction (4) starts at pH 4.5.

The rate at which the monoammonium phosphate is converted to diammonium phosphate rises to its maximum after the complete disappearance of the calcium sulphate at the end of reaction (3), the pH being about 5.5; see the bend in the  $\text{N}_2\text{HP}$  line in Fig. 3.

Increasing the  $\text{N}_2$  concentration causes the speed of the reaction to slow down appreciably (tangent to the lines in Fig.3) until it reaches equilibrium:



Referring therefore to the course of the pH curve, we may say that the less steep section represent rapid reactions and the steeper sections occur when the reactions are slowing down.

4. As a result of the procedure explained above, we were able to measure ammoniation time and to find the mean relative speed of the reactions involved.

In view of the fact that these are multi-molecular

reactions, it is not a simple matter to calculate the speed of variation of the molecule concentrations in the reacting masses for sufficiently short periods of time.

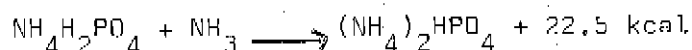
We therefore decided to determine the mean speed per unit time with reference to the amount of nitrogen  $A_x$  fixed during the period of time  $A_t$ .

The rate  $V$  can be expressed as  $\frac{A_x}{A_t}$ . In this way, only one magnitude is required for all reactions.

Table A, cols. 13, 14 and 15, gives in addition to the ammoniation times the mean relative speed for the various periods of time, expressed in terms of the amount of  $N_2$  fixed by the acid slurry in one minute. This same speed is represented by the line  $A_x/A_t$  in Fig. 1.

The values found after the pH reaches 5.5 refer exclusively to reaction (4) because the complete elimination of the calcium sulphate prevents any further formation of dicalcium phosphate. It will be noted that the speed of reaction falls rapidly as the saturation point of the second hydrogen atom of the  $H_3PO_4$  is approached.

5. Bearing in mind that reaction (4) is reversible and exothermic:



then, by the law of mass action,

$$\frac{NH_4H_2PO_4 + NH_3}{(NH_4)_2HPO_4} = K$$

and it will be seen that at a given temperature a state of equilibrium will be reached, depending upon the concentration of the substances involved in the reaction. In fact, the rate of formation of diammonium phosphate is fairly rapid at the beginning of the reaction, due to the high concentration of monoammonium phosphate; but, when the diammonium phosphate concentration begins to rise, the rate of decomposition of this salt offsets the rate of formation, until a state of equilibrium is attained. Thus, to encourage the reaction and induce an improved formation of diammonium phosphate, and also to increase the efficiency of  $N_2$  fixation,

thus raising the nitrogen content of the finished product, we must:

- i) increase the concentration of the reacting substances.;
- ii) increase the amount of ammonia.;
- iii) lower the temperature of the mass. As we have said, the reaction is exothermic and from a temperature of about 85-90°C the diammonium phosphate has an appreciable vapour pressure.

6. When ammoniation is carried out entirely in the liquid phase, as in the experiment described, these three conditions cannot be attained without encountering technical difficulties. If the concentrations are increased, this means there is less water in the system, which facilitates the crystallization of the salts in solution and inhibits the complete absorption of the gaseous ammonia.

An increase in the amount of ammonia fed into the saturator means a loss of ammonia, since the escaping  $\text{NH}_3$  will be considerably diluted by water vapour and there will be no advantage in recovering it. It is therefore extremely difficult when working with the liquid phase to combine a high ammoniation yield with good  $\text{NH}_3$  efficiency because the one occurs at the expense of the other.

In practice, it is not even feasible to lower the temperature, because of the risk of the mass crystallizing or setting solid. This not only reduces  $\text{NH}_3$  fixation, as explained above, but makes it difficult to handle the product between the granulator and the drier.

Ammoniation in the solid phase, however, i.e. on the solidified product, enables us to achieve our aim, since neutralization is pushed to the second hydrogen atom of the phosphoric acid without creating any of the difficulties described above. In fact, using this process, the slurry - pre-ammoniated in the liquid phase and still perfectly fluid and easily handled - is distributed round the rotary drum which has the triple task of ammoniating, granulating and dewatering the solid mass on its way through.

The granules formed are coated with a thin layer of

slurry which is fixed on the surface of the granule and solidifies as a result of the neutralization of the second hydrogen atom by the  $\text{NH}_3$  gas, forming diammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$ , which crystallizes.

Reaction (4) is therefore encouraged, since the ammoniator drum provides the three necessary conditions listed above. To sum up:

- i) The pre-ammoniated slurry, with a water content which may vary between 25 and 40%, has a moisture content of only 4-5% after mixing with the recycled solid material; this is an excellent result which cannot be achieved with other systems.
- ii) The semi-ammoniated slurry forms a thin film on the surface of the granules, thus offering a considerably greater area to be exposed to the gaseous  $\text{NH}_3$ .
- iii) A larger amount of  $\text{NH}_3$  gas can be introduced. The second hydrogen atom of the  $\text{H}_3\text{PO}_4$  can be used more effectively and a better  $\text{NH}_3$  recovery can be effected because it is not upset by the presence of an excessive percentage of water vapour.
- iv) The semi-ammoniated slurry leaves the saturator at a temperature of about  $1000^\circ\text{C}$ . This is too high for further  $\text{NH}_3$  absorption. After mixing with the cold recycled material in the ammoniator, its temperature drops to  $60-65^\circ$  which is much more favourable for fixing the rest of the ammonia.

#### 4. Conclusions

As a result of our laboratory experiments which have been fully confirmed by our industrial experience, we can say that split ammoniation, partly in the liquid and partly in the solid phase, quite clearly represents a definite advance in the production of NP or NPK complex fertilizers, whatever the method used to acidulate the phosphate rock. This advance applies equally to the chemical engineering side, since it improves operating conditions, and to the economic aspect, since it cuts production costs.

Two-phase ammoniation enables us to create better conditions for utilizing the hydrogen ions of the phosphoric acid. By encouraging the formation of a salt on the second hydrogen



atom it is possible to achieve a yield of 95%, while when ammoniating in the liquid phase only, it is difficult to raise this figure above about 75%.

This means that it is possible to reduce the amount of  $P_2O_5$  from  $H_3PO_4$  in high-grade fertilizers produced by ammoniating sulphuric/phosphoric reaction slurries. In the case of diammonium phosphate, i.e. when ammoniating  $H_3PO_4$  alone, it is possible to obtain increased concentrations. Indeed, in the Vercelli pilot plant we produced a 20-50-0 grade.

The split ammoniation technique also makes it possible to improve ammoniation efficiency to over 97%, whereas, when operating in the liquid phase only, serious difficulties are encountered in reaching even 95%.

With split ammoniation, the plant can be simplified by reducing the size of the reactors for the liquid phase, because part of the ammoniation - the solid phase - is done inside the granulating drum. There is, moreover, no need for concentrators and ancillary equipment such as this type of plant normally requires, so that investment and maintenance costs are lower.

All the phases in the process we have described are continuous; only a limited number of units is required to operate them, and these can be fully automated.

In one of our plants manufacturing granulated high-grade fertilizers which was initially designed for liquid phase granulation only, production capacity has increased by 25% and costs have decreased by 40% since it was converted to operating split phase ammoniation.

##### 5. Notes on analytical methods

For complete objectivity, we should finally like to examine such drawbacks as are likely to arise from the use of split ammoniation. These drawbacks concern the vexed and much discussed question of analysis for the determination of water and citrate-soluble  $P_2O_5$  when complex fertilizers are to be imported into certain foreign countries.

A full discussion would be extremely lengthy and would take us away from the subject of this paper. However,

we feel it is appropriate to state the problem clearly, even if briefly.

Everyone is aware that all countries where fertilizers are manufactured have established official methods for determining their content of the three main plant nutrients - nitrogen, phosphorus and potassium.

The analytical methods used in the various countries for nitrogen and potassium are equivalent and produce results which are comparable for practical purposes and do not give rise to argument; but the question is much more complicated when it comes to determining the "useful" or "available" or "soluble"  $P_2O_5$ .

In other words, N and K are determined as an overall percentage and, although the methods used differ, the values obtained are absolute and hence reproducible and comparable; but when we come to  $P_2O_5$  the problem is doubly difficult because the percentage which interest us is not the total but the  $P_2O_5$  which can be utilized by plants. Consequently, this fraction must first be extracted from the fertilizer, then determined in the extract, and while it is relatively easy for the various countries to reach agreement on how to determine the  $P_2O_5$ , there is complete disagreement on the method of "extraction".

Three types of medium are used for extraction:

- i) acid medium, or Wagner's 2% citric acid solution, now used only for basic slag;
- ii) neutral medium, a more or less concentrated solution of ammonium citrate, brought to a pH of exactly 7 (Italy, Netherlands, U.S.A., Canada);
- iii) alkaline medium, an ammonium citrate solution containing a variable amount of free ammonia, and thus having a variable pH (Germany: Petermann citrate at about pH 8.0; France: Joulie citrate at about pH 10.5).

In addition to the variations introduced by the differences in strength and pH of the ammonium citrate solution, there are those arising from the differences in methods of use: ratio

of citrate to sample taken, extraction temperature, time of contact, etc., to mention only the main ones.

Obviously these diverse methods will give very different results and hence the interminable discussions which go on at international meetings called to decide upon a standard method of analysis - something for which all countries feel a genuine need, particularly at a time when commercial links and international exchanges are being extended. Nevertheless, no agreement has yet been reached, either in the O.E.C.D. or in the I.S.M.A. Common Market Committee's recently set up Special Commission for  $P_2O_5$  which held its first meeting at the offices of the Superphosphate Industrie G.m.b.H. in Hamburg in September, 1962. This meeting was followed by an intensive exchange of notes, proposals and counter-proposals between the delegates of the Common Market countries who attended the meeting.

It can, however, be said that, while Germany, the Netherlands, Belgium and Italy are clearly tending towards the adoption of the neutral citrate, France alone continues to hold out insistently for the alkaline citrate.

Why do the two citrates lead to different results, and why are certain countries willing to adopt the neutral citrate, while others are reluctant to discard the alkaline citrate? We shall try to explain this briefly, although it is difficult to summarize all the arguments raised by this problem.

Phosphoric acid - or, to be more precise,  $P_2O_5$  - can be present in complex fertilizers in a number of forms (here at least, every one agrees the percentage should be stated): completely water soluble (monocalcium phosphate, ammonium phosphate); completely soluble in water and neutral citrate, or moderately alkaline or Patormann citrate (precipitated dicalcium phosphate); partly soluble in very alkaline or Joulie citrate (reverted dicalcium phosphate, i.e. a different form from precipitated dicalcium phosphate, precipitated tricalcium phosphate, etc.).

According to the manufacturing process and - this is where the question ties up with the subject of this paper - particularly according to the degree of ammoniation and the pH

reached when ammoniation is complete, complex fertilizers contain phosphate in a number of different forms, as mentioned above. The further ammoniation is taken, the more we obtain forms of calcium phosphate which are less soluble in alkaline citrates.

Thus, while fertilizers which contain only water-soluble  $P_2O_5$  in the form of monocalcium phosphate and ammonium phosphate give the same  $P_2O_5$  result when determined in the different extraction media, the differences become more obvious as we move towards fertilizers containing  $P_2O_5$  in the form of precipitated dicalcium phosphate, reverted dicalcium phosphate and precipitated tricalcium phosphate which, we repeat, is a function of the degree of ammoniation.

However, since these analytical results are relative and not absolute, i.e., they depend on the extraction medium selected, there would appear to be no difficulty in agreeing on one or the other citrate. But this is where the picture is considerably complicated by the intrusion of economic and agronomic factors, which completely exclude any hope of international agreement.

The countries in favour of a neutral citrate argue - why should we give up a medium which enables us to analyse a higher percentage of the  $P_2O_5$  which has undoubtedly been put into the product? We are not trying to cheat the farmer by selling him  $P_2O_5$  which the plants can only partly utilize, nor do we wish to make him a free gift just because the analytical method we use does not determine all but only part of the  $P_2O_5$ . In point of fact, the neutral citrate is not only closer to the actual conditions under which plants absorb phosphorus but it also enables us to determine all the available  $P_2O_5$ . There is as yet no incontrovertible proof that the extra  $P_2O_5$  determined by the neutral citrate, as against that determined by the alkaline citrates, is not just as useful from the agronomic point of view, since precipitated dicalcium phosphate (insoluble in water and soluble in citrate only) is an excellent fertilizer, and U.S. exports

have shown that tricalcium phosphate or natural apatite when finely ground is gradually assimilated by plants, over a period of time.

At most one can talk of a greater speed of assimilation, but no one can pretend that an excessive speed of assimilation is an agricultural advantage in a fertilizer. Indeed, the present trend is towards less soluble, slow-acting fertilizers which leave a "reserve" of plant nutrients in the soil. The supporters of alkaline citrate (France and the countries under French influence) reply that the alkaline citrate provides an adequate method for distinguishing the various forms of  $P_2O_5$  and determining just the part which is important from the agronomic point of view.

In support of this contention, they claim to have shown by means of appropriate agronomic experiments that in fact the alkaline citrate alone indicates the agronomic value of complex fertilizers. An Italian NP fertilizer which, with the Joulie citrate, registered only 7.5-8%  $P_2O_5$ , is alleged to supply to the soil and in due course to the plant an amount of phosphorus corresponding to this percentage and not the 16% indicated by the neutral citrate.

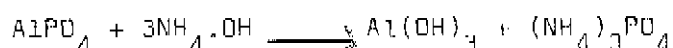
The supporters of the neutral citrate reply:-

a) it is doubtful whether the last word on this question can be supplied by laboratory experiments or restricted field trials. However carefully such trials are carried out, they simply cannot reproduce actual soil conditions with the many variants due to the chemical and physical properties of the soil itself as well as climatic conditions. Moreover, the trials would have to extend over many years and even then the results would not be definitive.

It is a fact that the Italian fertilizers whose  $P_2O_5$  content was determined by the neutral citrate have always satisfied the requirements of agriculture, and no-one has ever suggested that their use has been less agronomically successful when compared with other fertilizers whose  $P_2O_5$  content is determined by the Joulie citrate.

b) the alkaline citrate method does not work in the presence of magnesium because ammonia forms insoluble ammonium magnesium phosphates in an alkaline medium. It is, however, well known that products containing magnesium make excellent fertilizers.

c) aluminium phosphate (Phosphal and Superphosphal) and fertilizers which contain it cannot be analysed by either neutral or weakly alkaline citrate, but only by strongly alkaline citrate. Why? Doubtless because in this case it is not a matter of a physical change where the phosphates are dissolved in the citrate, but of an actual chemical reaction:



The ammonium hydroxide precipitates the aluminium in the form of the hydroxide and all the phosphate is held in solution as soluble ammonium phosphate.

How can anyone insist on the one hand that the neutral citrate dissolves too much  $\text{P}_2\text{O}_5$ , including some which is not available, while on the other hand upholding the agronomic value of the aluminium phosphates which are insoluble in water and only partly soluble in neutral or moderately alkaline citrate?

At this point, it was logical to put forward the only compromise which could make possible an agreement and any necessary modification of analytical methods.

Italy put the proposal to the I.S.M.A. Common Market Committee in the following terms:-

Adopt all three extraction media:

- (i) 2% citric acid
- (ii) neutral citrate (acc. to the standard method of the American A.O.A.C.)
- (iii) Doulie alkaline citrate

but use (i) for basic slag, (iii) for aluminium phosphate and (ii) for all complex fertilizers.

This proposal is being studied by the I.S.M.A. Common Market Committee and we hope in the interest of all that it will attract the support it deserves.

Whatever the outcome, we can at least conclude that so long as the Italian proposal remains unadopted, all fertil-

izers which contain some reverted form of  $P_2O_5$  which is not completely soluble in alkaline citrate (i.e. fertilizers manufactured by double-phase ammoniation with all the industrial advantages we have described) will encounter difficulties when it is desired to export them to countries which still insist on the determination of the  $P_2O_5$  content by extraction with Joulie alkaline citrate with a pH of 10.5.

DISCUSSION

Mr. F. BARZOCCHINI (Italy) : The introduction of ammoniacal nitrogen into highly concentrated NP or NPK compound fertilizers was tackled by the Montecatini Company in 1955, using the methods described in the paper, i.e. with double phase ammoniation - liquid and solid phases - of the slurries obtained by reacting phosphate rock with mineral acid (phosphoric, sulphuric or nitric) with or without filtration of the gypsum. Operating in this way we obtained :

- (a) An increase in the ammoniation yield up to about 97 % as a result of the lower temperature of the ammoniated slurries.
- (b) Better use of the H ions of the phosphoric acid. In fact, we obtain salification yields of the second hydrogen atom of about 95%, whilst we have difficulty in achieving even 75 % when operating solely in the liquid phase. In the case of diammonium phosphate, i.e. in the ammoniation of  $H_2PO_4$  alone, this enables us to achieve higher grades. In the pilot plant at Vercelli we were able to achieve a 20-50-0 formulation.
- (c) A reduction of about 30% of the volume of the reactor required for the liquid phase and a simplification of the necessary installations. The solid phase ammoniation takes place in the granulator, and it is no longer necessary to concentrate the slurry. The additional apparatus for this purpose can thus be eliminated, resulting in a decrease in the cost of installation and maintenance.
- (d) Double phase ammoniation permits the use of more highly concentrated phosphoric acid, up to 35 or 40 %  $P_2O_5$ , and, consequently, the reduction of the amount of recycled material and an increase of about 25% in plant capacity. This result has been made possible by the development of the ammoniator granulator drum described in section 2 of the paper and illustrated in fig.4.

The much discussed question of methods of analysis for the determination of water and citrate soluble  $P_2O_5$  is of equal importance. Intensive, double phase ammoniation leads to the formation of types



of calcium phosphate which are less soluble in alkaline citrate. The Italian methods of analysis, as well as those of the Netherlands, the U.S.A. and Canada, use solutions of ammonium citrate with a pH of exactly 7. Certain countries continue to operate with an alkaline citrate medium, and this practice should be reviewed, because when a phosphate with a high iron or aluminium content is used, it is possible that the amount of  $P_2O_5$  determined may be reduced by the presence of insoluble substances in the alkaline reagent.

MR. J.P. WAPENAAR (South Africa) : We all know, of course, that there is now a steady general trend towards the production of higher analysis fertilisers. Thus, a paper on this subject makes an important contribution to progress within the industry at the present time. The authors describe in detail the work carried out, firstly to confirm the chemistry involved and, secondly, to develop and prove the ammoniator-granulator. In conclusion some comments are made on methods of analysis of  $P_2O_5$ . The authors are to be congratulated on the very thorough way in which the data have been presented. Although there is not much that has been left unsaid, there are a few questions I should like to ask.

Firstly, although the granulator has been described in some detail, not much has been said about the liquid ammoniating unit. Could the authors perhaps give us some further details, including the retention time, with regard to this unit ?

Secondly, it would be of interest to know the rate of recycle to product take-off in the granulator.

Lastly, I should welcome an indication of the product size range and the granule strength which was obtained.

I do not propose to put any questions on the section of the paper dealing with analytical techniques, as the authors have stated that this problem is currently under consideration by the ISMA EEC Committee; but there may be delegates at the conference who may wish to comment on these procedures and who are better qualified to do so than I am.

MR. BARZOCCHINI : The granulation achieved with this system is perfect. The granules are completely round and of an almost uniform size. Obviously, there is a rather strict screening. The amount of material recycled is about 8 times that of production: for a production of 10 tons per hour about 80 tons of material is recycled. Ammoniation in the liquid

phase is carried to about pH 5.5. This corresponds to 75% of the ammonia in the liquid phase and 25% in the solid phase. The screens used after granulation have mesh sizes of 4 x 20 mm for the oversize and 2 x 20 mm for the fines, but about 80% of production is between 2 and 3 mm.

MR. F. NOUYRIGAT (France) : As rapporteur for the French Commissions which have studied the problems of fertiliser analysis, and as the representative of Ets. Kuhlmann, I should like to make certain comments on the methods of analysis and the observations of the authors of this paper.

Before dealing with the fundamental problem - that of  $P_2O_5$  - I should like to draw attention to one small detail, namely that as far as the analysis of potassium is concerned, it is not total potassium which is generally analysed but water soluble potassium. Certain potassic products contain water insoluble potassium, such as leucite, which has only a low fertilising value.

With regard to the determination of  $P_2O_5$  in its various forms, Mr. Barzocchini and Mr. Monaldi have indicated the broad outlines of this question. However, it should be pointed out that Belgium has not adopted neutral citrate.

In order to examine the technical problem in closer detail, it should be firstly noted that, among the various forms of  $P_2O_5$  found in fertilisers, distinction should be made between water-soluble mono-calcium phosphate, hydrated di-calcium phosphate and anhydrous di-calcium phosphate; then come substances more basic than the di-calcium form, particularly the hydroxy-apatites, either natural or artificial and more or less crystallised; and finally we have the natural chloro- and fluo-apatites. The limit of water solubility cuts this sequence between mono- and di-calcium phosphate. Neutral citrate solubility cuts it right in the middle of the basic phosphates of the hydroxy- and hydroxyl-apatite type. Alkaline citrate solubility, depending on whether we use the concentrated French Joulie citrate or the less concentrated Petermann citrate, cuts the list after the anhydrous di-calcium phosphate (in the case of Joulie citrate) or in the middle of the anhydrous di-calcium phosphate (in the case of the Petermann citrate).

Bearing this in mind, we must obviously consider what form of

$P_2O_5$  should most appropriately be determined, and whether one should choose a reagent which does not operate beyond the mono-calcium form, beyond the anhydrous di-calcium form, or else beyond the hydroxy and hydroxyl-apatite. It is well known that ammoniation, when operated too intensively, produces what we may call a reversion of the  $P_2O_5$ , with, firstly, the formation of water-insoluble compounds, and then citrate-insoluble compounds. These compounds have been the subject of study for a considerable time, and we have not yet been able to determine their exact form. Recent publications, particularly in the U.S.A. seem to indicate that we are concerned with hydroxy- or hydroxyl-apatite. These same American studies - the most recent publication was in 1961 - considered the agronomic effectiveness of ammoniated superphosphates in relation to the extent of their ammoniation and of their hydroxy-apatitic  $P_2O_5$  content. Although neutral citrate is long-established as the official citrate in the U.S.A., several of these authors (especially authors belonging to the T.W.A., in 1961) observed that the alkaline citrate used in certain European countries gives an indication which is much closer to the fertilising value of the superphosphate than is provided by neutral citrate.

I should like to comment on the affirmation that neutral citrate gives a better reproduction of the conditions of phosphorus absorption by the plant. The fact that the pH is 7 does not bring us any closer to natural conditions. Far from it. Any assimilation on the part of the plant is brought about by reactions with substances secreted by the roots, and here there can be no question of neutrality. Compounds are formed and reactions occur with more or less weak acids.

With regard to the rapidity of the action of the various forms of  $P_2O_5$ , it is quite evident that even natural phosphate rocks have a certain value in particular cases, especially on very acid soils; but this in no way reduces the additional value of more soluble forms, for whilst the natural phosphates can be used in certain cases on acid soils to produce a good yield, they cannot be used on other soils, whilst the more soluble forms can be used to good effect on both acid and non-acid soils.

A similar qualitative comparison can be made between mono and

di-calcium phosphates on the one hand and the more basic phosphates (reverted phosphates) on the other.

I should also like to say a few words in relation to the nature of the action of the citrates. The authors seem to indicate that this involves a physical solubilisation. There has never been any question of a physical solubilisation with regard to the method of solubilisation by means of citrates: it is merely a question of the formation of calcium compounds through the medium of the citrate, the calcium being taken into compound form to such an extent that the amount of free calcium in the solution is insufficient to precipitate the insoluble calcium phosphates, at least the di-calcium phosphate. The same thing occurs with regard to Phospal: in this case, aluminium compounds are formed by the citrate. This is an exactly parallel phenomenon: to convince oneself of this one only has to consider the value of the various constants of dis-association of the various compounds - on the one hand the citric compounds and on the other the product of the solubilisation, whether it be calcium phosphate or aluminium phosphate or even iron phosphate. We find a solubility in the case of Phospal which is absolutely similar to the solubility of calcium phosphate. The precipitation of aluminium at the pH of Joulie citrate seems scarcely possible, since aluminium is more soluble in this pH than in the pH of the neutral citrates. To prove this one has only to make an experiment by putting a small amount of precipitated aluminium phosphate in the corresponding quantity of Joulie citrate, and it will be seen that it dissolves completely.

Regarding the compromise suggestion put forward by the authors, it can be shown immediately that as far as citric acid is concerned everyone has long been in agreement as to its application for basic slag. Similarly, however, everyone is equally persuaded that citric acid is too active a reagent to be recommended for many other fertilisers. As for admitting neutral citrate as a valid citrate for all other fertilisers,

this will systematically lead to counting reverted  $P_2O_5$ , as soluble  $P_2O_5$ , i.e.  $P_2O_5$  more basic than the di-calcium form. Manufacturers, particularly in France, have been faced with this problem of reversion for a long time, and have been led to make a very close study of their products, precisely in order to limit reversion as much as possible. This is naturally justified by a considerable number of agronomic experiments. No Manufacturer would take pains to avoid the sale of his products at more advantageous terms if he was not aware that there were disadvantages. And again, as I mentioned before, this has been confirmed by recent American studies, particularly those carried out by the T.V.A.

I should also point out that the use of neutral citrate leaves the door wide open for all kinds of fraud, since it solubilises up to 50% of the  $P_2O_5$  in soft phosphate rock of the Gafsa type, without any other previous treatment. In view of this observation, I think that there is at least a degree of risk which should not be incurred.

Finally, I should like to say one last word about the point which has been justly emphasised by the authors, concerning the interference of magnesium during solubilisation by alkaline citrates. At the beginning, this naturally represented a major defect for alkaline citrates, since it led to a limitation of the application of these citrates in the case of fertilisers rich in magnesium. Work which we carried out, at AFNOR in particular, led us to prescribe a maximum magnesium content beyond which these methods were not applicable. Up to now, therefore, this was a drawback for the use of alkaline citrates, and we were the first to recognise it. However, we have subsequently been able to overcome this difficulty by using an idea which Mr. Dahlgren gave us at Opatija two years ago: we eliminate the interference from the magnesium by using oxine to form an insoluble compound. O-hydroxy-quinoline gives an insoluble compound with Mg and this eliminates the surplus magnesium in the solution. One can then operate in conditions of normal solubilisation, equivalent at least to neutral citrates from the point of view of acceptable limits for the MgO content. I should mention that this use of oxine has no effect on the properties of the

alkaline citrate with regard to the various calcium phosphates, for at this pH the oxine does not precipitate the calcium. One can prove this by a small experiment: we can treat Gafsa phosphate with Joulie citrate in the presence of oxine, and we shall find that we do not solubilise any more phosphate than in the absence of oxine, whilst with neutral citrate we solubilise nearly 50%.

Dr. F. BARZOCCHINI : The official Italian method for the determination of  $P_2O_5$  prescribes the extraction of the  $P_2O_5$  in two stages (aqueous extraction - citric extraction), and thus the residue from the aqueous extraction, when brought into contact with the citrate, is neutral in all cases, even when we are dealing with alkaline fertilisers. This is a not inconsiderable advantage. We may note, in this regard, that the alkaline Patormann and Joulie citrates were conceived with a view to neutralising the free acidity in straight fertilisers (superphosphate and triple superphosphate) in order to prevent the acidity from solubilising a part of the unreacted mineral phosphates during the extraction, and hence a certain amount of insoluble  $P_2O_5$ , which has no agronomic or commercial value.

The two-stage solubilisation not only provides a further interesting detail relating to the value of the fertiliser, i.e. the water soluble  $P_2O_5$  content, but also permits the use of neutral citrate, which is much closer to the natural pH of soils and plant juices. This is not the case with alkaline citrates which operate in totally unrealistic pH conditions. The French have often objected to neutral citrate on the grounds that it also solubilises a part of natural soft phosphate rock and hydroxy-apatites (either natural or precipitated) which would have no agronomic value.

We certainly cannot dispute that neutral citrates do have this solubilising property, but we should like to make two remarks on this subject :

- (a) straight and complex fertilisers obtained either by reacting phosphate rock with mineral acids, or by means of wet process phosphoric acid, can no longer contain any

natural hydroxy-apatites or soft phosphate rock which, precisely because of their high re-activity, are the first to disappear during the reaction, in contra-distinction to hard and crystalline apatitic phosphates which remain to varying degrees partially unreacted. The most some of our fertilisers can contain is reverted phosphate (precipitated tri-calcium and hydroxy-apatite), which are partially soluble in neutral citrate.

(b) It has been demonstrated, particularly in America, that natural phosphate rock, especially if finely ground, has a definite agronomic value, i.e. the plant does succeed in using part of its phosphorus content.

Hence we do not see why it is a disadvantage for neutral citrates to be able to determine analytically the proportion of  $P_2O_5$  in phosphate rock which is assimilable by plants and has an agronomic value. Moreover, if the plant can use a part of the natural tri-calcium, soft-apatitic and hydroxy-apatitic phosphates, why should it not use the same products when they are precipitated? And why should we refrain from determining them? Similarly, from the French point of view, why should we prevent the Phospal producers from using Joulié citrate because it gives them much higher values than neutral citrates, when it has been demonstrated that all the  $P_2O_5$  determined by the Joulié citrate is assimilable by the plant?

Italy has on several occasions frankly expressed the view that it will be extremely difficult to agree on the adoption of a single method of  $P_2O_5$  extraction.

Methods of  $P_2O_5$  extraction are not quantitatively exact: on the contrary, they are relative and empirical. (This problem does not, in fact, arise for nitrogen and potassium, for which the unification of methods of analysis is already practically achieved, since all countries have already agreed to adopt the most modern methods). Each country has officially adopted the method of  $P_2O_5$  determination which, whilst respecting agronomic requirements, is the best suited to grade its own fertilisers produced by its own processes which are themselves governed by economic and commercial

factors.

If alkaline citrates are applied to Italian fertilisers (and not only to Italian fertilisers), the values for water-~~and~~ citrate-soluble  $P_2O_5$  which they provide are consistently and distinctly inferior. How can we be asked to change all our methods simply to permit the analysis of our products by means of alkaline citrates, when, far from providing any compensatory factors, such a step would be economically harmful?

From the French side, we hear that alkaline citrate is better suited to express the real agronomic results of phosphatic fertilisers and that it is thus in better conformity with the rules of commercial discipline.

In this regard, we can assure you that our fertilisers continue to give excellent results in our soils and are, moreover, widely exported to foreign countries which have never complained of agronomic results inferior to what might be expected from the declaration of plant nutrient content based on analysis by means of the Italian or American neutral citrate.

We fully understand that this line of reasoning is equally valid for the other countries, particularly France, which can only analyse those of its fertilisers based on calcium aluminium phosphate by means of the strongly alkaline Joulie citrate. And if the various "Phospal" fertilisers cannot reasonably be analysed by means of the neutral citrates because this would give excessively low analytical results and would not correspond to the agronomic value of the products, we do not see why our complex fertilisers should not continue to be analysed by means of the neutral citrate, instead of the alkaline citrates which give lower analyses and do not correspond to agronomic results.

The sole authority which should be allowed to express a definite judgment is the plant, which is ignorant of analytical diatribes and commercial interests, etc.,.! But since this is not possible, we can only rely on the results of experimental trials in the field. Unfortunately, agronomic trials in the field not only require a considerable amount of time and effort,



as well as heavy expenditure, but can give debatable, uncertain results, which are difficult to interpret because the factors and variables affecting them are too numerous, unknown or unmanageable. Is it worth our while that we should now engage on such an uncertain path as this? And for how long should we delay the unification of our methods?

Italy has on several occasions proposed the only means of reconciling the opposite points of view : a renunciation of an impossible unification and the maintenance of the two citrates, alkaline and neutral. The alkaline citrate should be reserved for fertilisers based on aluminium phosphate, and the neutral citrate should be used for all other fertilisers. We should now like to put forward this compromise once more: even if it does not completely satisfy chemists and scientists, it nevertheless allows industrialists to find a satisfactory basis of agreement.

We venture to hope that this effort on our part, in view of the economic benefits involved, will attract more attention than has been the case so far, especially as it would obviate for all of us an enormous amount of work and exchanges of results which might only lead us deeper into the forests of confusion and would only serve to make more rigid the positions of the various parties.

M. P. HUREL (France) : As the convener of the Common Market group concerned with technical questions, and analytical matters in particular, I should like to draw attention to the fact that the paper by Mr. Barzocchini and Mr. Monaldi was prepared before the recent discussions which took place in Paris.

I think the authors agreed that we should consider our recent discussions as valid and should pursue the programme arranged at Paris in an effort to solve these analytical problems. At the end of their paper, the authors propose a compromise which is certainly of interest; but I think that, before deciding on this compromise, we should continue to study the problems discussed at our Paris meeting and then draw the necessary conclusions.

We therefore hope that the authors will agree with us to respect this principle, in view of the fact that this paper before us today preceded these discussions.

MR. Y. BERQUIN (France) : My Company, Potasse & Engrais Chimiques (P.E.C.), like Montecatini, has been concerned for some time with the problems of liquid phase ammoniation in more and more highly concentrated media. We arrived at the same conclusion as the authors of the paper, i.e. that the thicker the slurry becomes, the more unfavourable become the ammoniation conditions, the absorption yield and the rate of fixation. Thus, an efficiency curve can be established, and at a certain point on this curve it is better to pass over to solid phase ammoniation. In 1958, we took out some patents on this problem, and we are still working on the matter. The problem seems to us to be linked to the use of more and more highly concentrated acid. I am thinking in particular of nitric acid, since we traditionally react our phosphate rock with nitric acid, with the possible admixture of other mineral acids. The advantage to be derived from the use of this increasingly concentrated acid, from the point of view of economies in the drier, is very quickly limited by the practical impossibility of liquid phase ammoniation. Therefore we also approached the problem with the idea of operating in two stages, a first stage in the liquid phase, since ammoniation is then very easy, as long as the slurry is relatively fluid, and a second stage in the solid phase. Here we have adopted methods which have not yet been industrially applied, and which differ slightly from those indicated by Mr. Barzocchini; but thanks to our method, our rate of recycling has been very considerably decreased. With different formulas and different acids our recycle ratio is always in the neighbourhood of one or two units - between 1 and 3 - 1 for example. But naturally this involves the use of fairly concentrated acids, and thus the moisture content of the material is low, which accounts for the low rate of recycling.

The amount of ammonia which we introduce into the solid phase is often distinctly greater than that indicated by Mr. Barzocchini, but this is a natural consequence of what I have said above. I believe I have given a partial reply to the

objection which might be made by Mr. Wapenaar with regard to recycling.

As far as the remarks of Mr. Nouyrigat are concerned, I must say that the P.F.C. Company, after a great deal of analytical study has arrived approximately at the same conclusion as Mr. Nouyrigat, and we consider it a matter of honesty towards the farmer to use the French type of citrate or, at most, the Petromann citrate. But the neutral citrate seems to us to be really too favourable and does not provide the consumer with an adequate guarantee.

With regard to superphosphate ammoniation, I should just like to point out that our analytical work on this subject has led us to observe that the fairly intensive ammoniation of superphosphate seemed to render it insoluble in the citrate solution when the determination was completed by the usual magnesium citrate method, whilst other methods gave a higher indication of available  $P_2O_5$ . We realise, in fact, that despite the relatively low temperature in which we operated, the formation of condensed phosphates, of the pyro-phosphate type, for example, occurred. These phosphates are soluble in the citrate reagent, but are not precipitated by magnesium. In order to return to the ortho-phosphoric acid stage, the liaison must be destroyed, and then the precipitation proceeds normally.

Mr. BARZOCCHINI : The rate of recycling is in strict relation to the rate of granulation. Obviously, a better rate of granulation would enable us to reduce the rate of re-cycling below that mentioned in my paper. However, the results quoted by Mr. Berquin are undoubtedly remarkable.

With regard to his remarks concerning methods of analysis, I see that we Italians, and even Americans, are not honest people, because we sell products which do not correspond analytically to the requirements of commercial practice.

Mr. NOUYRIGAT : With regard to Mr. Berquin's remarks, I should like to confirm that there can, indeed, be condensed  $P_2O_5$  in certain cases, and this complicates the problem still further, particularly if pyro-phosphate is involved. I should incidentally point out that whilst it has been proved that metaphosphates, particularly calcium metaphosphate, can be perfectly assimilated by

the plants, the problem has not yet been entirely solved with regard to pyro-phosphate. All the conclusions that we have drawn in France, concerning the solubilisation of the various citrates, have been arrived at with this possible effect of condensation in mind; for, naturally we can use methods other than the magnesium citrate method to determine  $P_2O_5$ , and in any case, the magnesium citrate method can be modified to determine total  $P_2O_5$ , including condensed  $P_2O_5$ .

MR. WELDER (U.S.A.) : I am sure that Mr. Barzocchini is familiar with the work done at the T.V.A., and I would be most interested if he would tell us in what respect his practice of pre-ammoniation and the design and operation of the rotary drum ammoniator differ from the T.V.A. system.

The idea of pre-neutralisation has become generally accepted in the U.S.A. in all granulation systems. Even in the case of the Dorr-Oliver system, we now ammoniate in the blunger, or the rotary granulator if we use one. The advantages of pre-neutralisation are basically simple. As mentioned in my paper to the ISMA Technical Conference in Stockholm in 1959, if you look at the phase diagrams of the systems I describe, and particularly the ammonium phosphate system, you will see that at an ammoniation rate of 1.4 to 1.45 N to  $P_2O_5$  we are at a point of maximum solubility. One can thus operate with a much thicker slurry and then complete the ammoniation in the blunger or rotary granulator. This is the basic reason why it is possible to operate with higher rates, because there is a lower dryer load and lower circulating loads.

With regard to the question of citrate solubility, I do not think we have any intention of changing the present method of determining availability as used in the U.S.A., but there is a growing tendency to recognise the importance of water solubility, to the extent that there is considerable argument as to how much of the  $P_2O_5$  should be water soluble. Perhaps this is a more logical approach than to argue whether the  $P_2O_5$  should be totally water soluble or soluble by some

other arbitrary method.

Mr. BARZOCCHINI : In reply to Mr. Weber, I should simply like to give a brief account of the way in which we arrived at the process described in my paper.

In 1950/51 we carried out trials with the "conditioner" described in a paper presented by Mr. J. T. Proctor, of H. Richardson & Co., York, England, to the Fertiliser Society (Proceedings No.7. September 1949).

From these trials we developed a rotating reaction chamber for the production of superphosphate. This type of reaction chamber is still functioning in several of our factories. After this development, we tried to obtain granular superphosphates (and other fertilisers) direct from these chambers. We were not able to achieve positive results, but it was at this point that we thought of injecting gaseous ammonia into the circulating mass to complete the ammoniation of the slurry. In other words, we arrived at solid phase ammoniation as a means of complementing liquid phase ammoniation for highly concentrated  $P_2O_5$  fertilisers; whilst the T.V.A. (if I have correctly understood) adopted the pre-ammoniation of phosphoric or sulphuric acid in order to reduce the amount of liquid entering the drum during the production of relatively low grade fertilisers, and of thus decreasing the amount of recycled material. Unfortunately, I am not acquainted with the T.V.A. ammoniator drum, but I think the practical results of the two processes are undoubtedly parallel.

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