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In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

STUDY OF THE CONSTITUTION OF TERNARY FERTILISERS
OBTAINED BY THE REACTION OF AN AMMONIUM SULPHATE
SOLUTION WITH NATURAL CALCIUM PHOSPHATE IN THE
PRESENCE OF A POTASSIUM SALT

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This paper is a summary of the results of my research carried
out over the past ten years and directed towards the determination
of the composition of some of our ternary fertilisers which are
produced by reacting phosphate rock, mixed with a potassium salt,
with a hot salt solution consisting of a solution of ammonium
sulphate in sulphuric acid or in a mixture of sulphuric and
phosphoric acids.

Simple chemical analysis can do no more than detect ions.
Selective extraction by means of suitable solvents makes it
possible to determine the nature of certain salts present, but
this procedure, although carried out with all due precautions,
gave no absolute assurance of the pre-existence, before the
solvent treatment, of the salts thus determined in the fertilisers.
Moreover, the scope of the method was fairly limited. However,
the partial results thus obtained were confirmed by x-ray diffraction
diagrams. We made extensive use of this technique, firstly using
the Debye Scherrer method, with photographic recording, and then,
subsequently, using a diffractometer technique with graphical
recording of the scanning of the spectrum by Geiger counter.

We studied the equilibria of all the groups of salts likely
to be found in our fertilisers, using both chemical analysis and
spectral analysis by x-ray diffraction.

It was thus possible to detect constituents of these complex
mixtures and determine compounds which chemical methods alone
would never have revealed.

It was possible to identify all the rays of certain salts
or combinations of them, although some of these rays were found
to be systematically displaced to the left or right, causing us
to suspect the presence of solid solutions, which we then reconstituted
and studied. This aspect will be discussed later.

The salt solutions.

The salt solutions consisted generally of a solution of ammonium sulphate in sulphuric acid. The amount of ammonium sulphate and the concentration of the free sulphuric acid obviously varies according to the fertiliser to be manufactured.

We investigated the following ternary system: NH4OH, H2SO4, H2O. We drew ternary diagrams of the mixture, with respect to its molecular and ionic composition: SO3 (NH4)$_2$ O, H2O. Thus it seemed much more convenient to draw these diagrams with the following constituents: NH3, H2SO4, H2O, expressed as per cent by weight of the mixture, since our factories usually expressed the composition of their salt solutions in terms of these three components.

These equilibria have been studied by others long before us, and we re-embarked on this work solely to identify the solid phases and their domains of existence.

The following known compounds were isolated in this way:
Am2SO4
Am2SO4, HAmSO4
HAmSO4,
HAmSO4, H2SO4

We established both their chemical analysis and their diffraction spectra.

Furthermore, as certain of our fertiliser production processes involved the reaction of salt solutions with a mixture of phosphate rock and sulphate of potash, we also drew diagrams of the equilibrium K2SO4, H2SO4, H2O, at various temperatures, demonstrating the presence of potassium salts similar to the ammonium salts mentioned above.

Diagram No. 1 represents the equilibrium of the system:
NH3, H2SO4, H2O, at 25°C.

Seven domains of existence can be observed in respect of pure salts or binary mixtures of these salts.

At higher temperatures these domains are obviously depressed towards the base, the homogeneous liquid zone becoming increasingly important. The equilibrium at ordinary temperatures is the only one considered in this paper, for, after all, the object of our interest is the fertiliser after it has cooled to these ordinary temperatures.

In fact, some calcium carbonates persist for a relatively long time and the evolution of CO_2 tends to cause the mass to expand (causing it "to rise" as our works say). This takes place when the product is already beginning to set, and even continues in the fertiliser after cooling.

It should be pointed out, moreover, that during superphosphate production the calcium fluoride is mostly reacted, whilst in the case of a salt solution reaction, the hydrofluoric acid is scarcely displaced at all. This feature is very marked when the salt solution is in zone 3, or when ammonia saturates at least half the sulphuric acid.

In addition, these solutions do not attack potassium chloride, which, in the case of certain fertilisers, is mixed with the phosphate rock before the reaction.

The curves established by Nunn and Dee show that the free sulphuric acid disappears in less than one hour. The second phase, comprising the attack produced by the liberated H_3PO_4, then continues at a decreasing rate, the maximum amount of free phosphoric acid coinciding with the disappearance of the sulphuric acid.

In the case of a reaction with a salt solution, the first stage of the reaction is faster at the start, because a very hot solution is used; the amount of free sulphuric acid decreases very rapidly, but the reaction slows down when the phosphoric stage is reached.

We did in fact observe that the reaction occurs in two stages, as in the case of superphosphate. There is no direct reaction, as some authors claim, between the phosphate rock and the acid ammonium sulphate. The salt solution acts in this case as a sulphuric solution of ammonium sulphate. The formation and evolution of phosphoric acid can be easily followed by means of acetone extraction of samples taken in the course of the reaction.

The Formation of Ammonium Phosphate

If one follows the progress of the free phosphoric acid, one notes that it disappears less rapidly at the start than in the case of superphosphate, but that it takes less total time to disappear. This can be explained by the formation of ammonium phosphate, which eliminates the monocalcium phosphate as soon as it is formed, according

Depending on the fertiliser formulation to be produced, our salt solutions fall into either zone 3 or zone 4. This might lead one to think that, if the reaction is incomplete and if any salt solution remains, once the fertiliser has cooled to ordinary temperatures one ought to find either the acid salt $HAmSO_4$, Am_2SO_4, in respect of solutions in zone 3, or the acid salt $HAmSO_4$ in respect of those in zone 4, these salts comprising the measured acidity of these fertilisers.

In fact, these salts cannot and have never been detected in our fertilisers.

Naturally, the residual salt solution would not have the same composition as it had before the reaction, because the three components do not remain in the same ratio one to another. There is a big loss of water, and the sulphuric acid disappears very quickly, so that if any salt solution does remain, the point on the diagram representing its composition would not be in the same zone as at the start of the reaction but would have moved towards the zone of neutral sulphate.

We shall see later that other reactions take place rendering it most unlikely that these acid sulphates might be found in our fertilisers, even if they had been accidentally blocked.

The x-ray diffraction diagrams have in fact never shown the characteristic rays of the salts, even in exceptionally acid fertilisers. This acidity is thus due to other salts, which we shall study later.
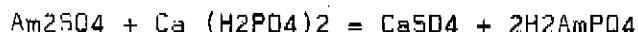
The phosphate reaction

Although the reaction between sulphuric acid and phosphate rock in the manufacture of superphosphate has been thoroughly studied and many times described, the reaction with a salt solution has not been the subject of much work as far as we know. In the case of the sulphuric acid reaction, for example, Nunn and Dee have established curves of variation of H_2SO_4 and H_3PO_4, as well as those of water soluble, citrate soluble and insoluble P_2O_5, as a function of time. It is interesting to compare these curves with those we have established in respect of the reaction with a salt solution.
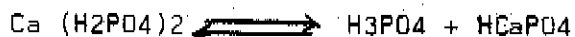
Without entering into detail, we should like to summarise the main points.

Apatites contain varying amounts of calcium carbonate. One might think that this would disappear entirely very early in the reaction.

to the following reaction:

Am2SO4 + Ca (H2PO4)2 = CaSO4 + 2H2AmPO4

whereas in superphosphate one has the equilibrium reaction:

Ca (H2PO4)2 $\rightleftharpoons$ H3PO4 + HCaPO4

This allows a free phosphoric acidity to persist for a relatively long time, and it can be extracted with a solvent. In the case of our fertilisers, it is not possible to extract free acid, even after a relatively short time.

The reaction resulting in monoammonium phosphate is complete if the salt solution is so rich in ammonia that there will be in the finished fertiliser at least two parts N for one part soluble P2O5, so that the weight ratio is:

$$\frac{\text{Nitrogen}}{\text{Phosphoric Anhydride}} = \frac{1}{5}$$

where the available P2O5 is in water soluble form as mono-ammonium phosphate. According to our theory, there should be no monocalcium phosphate in these fertilisers. This is, in fact, demonstrated by selective solvent analysis and, incontest-ably, by x-ray diffraction analysis, an example of which is found in diagram No. 2.

The spectrum of a random sample of this fertiliser clearly shows the characteristic rays of ammonium phosphate - both the strong rays situated at $16^{\circ}36$, $23^{\circ}45$, and $33^{\circ}40$, as well as the weaker rays. None of the characteristic rays of either mono-calcium phosphate or dicalcium phosphate are apparent, even the most intense rays of these two compounds, i.e. those found respectively at $7^{\circ}30$ and $11^{\circ}36$[1].

This is true for all our fertilisers manufactured from salt solutions, and we have been able to confirm that, in these fertilisers, <u>all the water soluble P2O5 is in the form of mono-ammonium phosphate</u>.

Diagram No. 2a clearly shows this.

<u>Free phosphoric acid.</u>

Unlike superphosphate, our fertilisers do not contain free phosphoric acid. The reason for this is explained above. Never-theless, certain products do have a certain acidity which can

[1]   In order to include all the diagrams of the pure salts on the same figure, we have had to cut off the main peaks in certain cases.

be titrated with methyl orange, but which cannot be extracted with
a solvent like acetone or ethyl formate. This is explained below.

Sulpho-phosphate

It is well known that reactions continue within superphosphate
for some time and that there is a gradual increase in the soluble
P2O5 content; this curing is due to the slow action of the free
phosphoric acid on the tricalcium phosphate.

In our fertilisers, on the other hand, particularly with
regard to certain formulations, this continued evolution is not
observed. Yet if one determines the acidity of these fertilisers,
it is found to be fairly strong, particularly, for example, if the
reaction has been accidentally blocked. Despite this acidity,
reactions in the fertiliser are either non-existent or negligible,
or at least much less than in superphosphate.

As mentioned above, this acidity, unlike that of superphosphate,
cannot be extracted by means of a solvent such as acetone or ethyl
formate. This suggests that this residual acidity consists, in fact,
of acid salts. Naturally, we might suppose that these salts are
the acid sulphates mentioned above, but, as we have seen, their
presence is very unlikely since the sulphuric acid disappears very
rapidly, leaving practically no free acid except phosphoric acid
after 30 minutes. But a certain amount of ammonium sulphate remains,
for in our fertilisers the ratio:

Phosphoric anhydride
        Nitrogen

is always less than 5. This gives rise to an excess of ammonium
sulphate in relation to the amount necessary for the formation of
ammonium phosphate.

Similarly, there is also potassium sulphate.

Do these two neutral salts combine with the phosphoric acid?
We think they do. They give rise to acid salts.

We studied the equilibria: H3PO4 - Syngenites, and noted what
seemed to us to be certain anomalies. We observed th t, in this
case, certain mixed acid salts were f rmed.

We studied the systems:

Am2SO4 - H3PO4 - H2O
and K2SO4 - H3PO4 - H2O

We determined the solubility of these salts at various temperatures and for various acid concentrations, and, in certain zones, we were surprised to isolate salts which, in spite of being washed with an appropriate solvent to free them from impregnated acid, showed firstly a strong acidity with methyl orange and, secondly, an equal acidity with phenol phthalein, just as if the phosphoric acid had been retained within these salts.

One might imagine them to be a combination of the neutral salts and the phosphoric acid, corresponding to the formula:

$M2SO4, H3PO4$ (M being the alkaline metal).
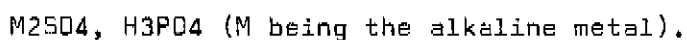
However, after studying these salts, we preferred to describe them by analogy with other acid salts, by means of the formula: $HM SO4, H2M PO4$, and we called them sulpho-phosphates.

The strong acidity determined with methyl orange corresponds to the first term.

The weak acidity determined with phenol phtalein corresponds to the second term.

These salts are definitely compounds and not mixtures. Their diffraction spectrum is very different from that of the two salts: $HM SO4$ and $H2MPO4$, taken separately, and also from those of the neutral salts, as is shown in Diagram No. 3.

These compounds are probably identical to those that Berndt Meppen encountered, without identifying them, and which he reported in his paper to ISMA in September, 1955, when he stated that "these abnormal salts have an acidity which cannot be extracted by means of solvents", although in this case calcium salts seem to be involved, which we have not been able to obtain, at least in the form stated above.

One form of calcium sulphophosphate was characterised by HALLE, but it is different from our compounds and is the neutral salt: $HCaPO4, CaSO4, 4 H2O$.

The existence of this latter salt is possible (and its spectrum has been characterised), but we have not been able to prepare the salt: $Ca (H2PO4)2, Ca (HSO4)2$.

Potassium and ammonium sulphophosphates can be prepared very easily by grinding the sulphates in 65% phosphoric acid, for example, and then centrifuging and washing with acetone.

The formation of these salts is exothermic and we have measured the amount of molecular heat given off.

We shall not describe all the work done on these compounds. We shall merely give the solubility curve and the equilibria at $22^{\circ}C$ for the potassium and ammonium salts (Diagrams Nos. 4 and 5).

Reverting now to the phosphate reaction, we mentioned how quickly the sulphuric acid disappears, leaving a phosphoric medium. As evaporation is intense, a very concentrated acid is obtained. The full sulphophosphate zone is very quickly reached, and any stoppage of the reaction by cooling or lack of water will inevitably lead to sulphophosphate deposition.

Graph No. 6 shows the variation of water and citrate soluble P_2O_5 and P_2O_5 in the form of free H_3PO_4 (expressed as percent of total P_2O_5) as a function of the reaction time for phosphate rock and one of our salt solutions.

After two hours, the free phosphoric acidity remains virtually constant, whilst solubilisation gradually continues. This is because the mass still contains a certain amount of water, sufficient for the crystallised sulphophosphate to hydrolyse, thus giving rise to free acid which disappears in reaction with the phosphate rock and destroys the equilibrium. Thus the reaction continues for as long as there is sufficient water.

After sixteen hours, 10% water was added. The sulphophosphate then became totally hydrolysed, and a marked increase in the amount of water-and citrate-soluble P_2O_5 was noted. This was due to the sharp increase in the amount of H_3PO_4, liberated by the hydrolysis of the sulphophosphate.

If we study the variation of the point of composition of the salt solution on the triangular diagram No. 4, we see that, after the first few moments, when the H_3SO_4 disappears, we can determine the composition of the salt solution as follows.

It is represented by the point S of the coordonnates:

Am2HSO4	68.7
H3PO4	18.6
H2O	12.7

We are, of course, considering only the salt solution.

If, at this moment, we were to cool the mass to $22^{\circ}C$, we should obviously obtain a crystallisation of a mixture of sulphate and sulphophosphate.

But we are, in fact, still operating in the zone of homogeneous liquid. The reaction continues, and H3PO4 disappears as it reacts with the phosphate rock. The diagrammatic point of composition is displaced towards M, but as a certain amount of water evaporates simultaneously, this point is in fact displaced into the zone MSN. The more water we lose, the greater will be the tendency to remain in the zone of the sulphate-sulphophosphate mixture, and, as a result, there will inevitably remain some sulphophosphate, constituting a residual acidity in the fertiliser. If water is added, however, acid will be liberated and this acid will react with the phosphate rock, causing the point of composition to move into the zone of neutral sulphate.

Finally, we might consider whether the sulphate of potash added to the phosphate rock before the reaction reacts with the phosphoric acid.

We vigorously stirred potassium sulphate of varied particle sizes into a phosphoric salt solution (that at point S) at $100^{\circ}C$. After cooling, we examined the x-ray diffraction spectrum of the solid phase. Obviously, we revealed the presence of ammonium sulphophosphate, but not the corresponding potassium salt. However, the spectrum of potassium sulphate was in fact present, but its rays were displaced towards the right, indicating the inclusion of a larger ion in the lattice, characteristic of a solid solution of $(KAm)^2 SO4$. We shall refer to this later.

To conclude the discussion of the sulphophosphates, we should mention that our products are regulated in such a way as to avoid

the presence of these acid salts, which are normally only found
in very small quantities in our fertilisers.

Syngenites

We shall now consider the main constituent of our fertilisers:
Syngenites. From the very start of our work on the diffraction
spectra, we were surprised not to find the characteristic rays
of potassium sulphate, nor, for that matter, those of ammonium
sulphate (the excess over and above the amount necessary for the
formation of ammonium phosphate), nor even, finally, those of
the anhydrite or semi-hydrate forms of calcium sulphate such as,
for example, gypsum, or as found in superphosphate. In fact, we
found very different rays. We then thought of syngenites, and we
prepared these compounds, which have been well known for a long
time. They can be very easily obtained with an exothermic reaction
by stirring gypsum in a solution of an alkaline sulphate.

We shall not dwell on the work carried out on this subject,
which covers the same ground as much older work, by Ditté in
particular.

We determined the spectra of the syngenites:

CaSO4, K2SO4, H2O

CaSO4, Am2SO4, H2O

and those of the bi- and penta-calcium syngenites. It was then
easy to identify them in all our fertilisers.

Here again, however, the rays were found to be displaced by
comparison with those of the pure compounds, and this indicated
that the compounds in our fertilisers were present in a state of
solid solution.

We should, incidentally, indicate that these salts stabilise
the alkaline sulphate to a certain extent, in the sense that in
a mixed fertiliser containing only potassium or ammonium sulphate,
without calcium sulphate, these salts obey their solubility law
and will be very quickly leached by rain, producing concentrated
solutions of these salts.

On the other hand, if these sulphates are incorporated in
the form of syngenites, they will produce only solutions in equi-
librium with these complexes, i.e.:

- a solution of about 3% potassium sulphate for potassic syngenite.

- a solution of about 35% ammonium sulphate for ammoniacal syngenite.

and less still if these syngenites are in solid solution.

The syngenites in our fertilisers thus act as fixing agents for the nitrogen and potassium.

The spectra in diagram No. 2b clearly show the presence of these compounds in the fertiliser analysed, and it can be seen that the spectrum of the ammonium syngenite is clearly displaced towards the left.

Solid Solutions

Some of our fertilisers are manufactured by reacting the salt solution with a mixture of phosphate rock and potassium chloride. The following equilibrium reaction can thus be anticipated: $Am_2SO_4 + 2KCl \rightleftharpoons K_2SO_4 + 2 AmCl$
The poor solubility of K_2SO_4 causes it to proceed mainly in the direction of left to right.

We studied this reaction and found that 75 to 80% proceeded in this direction in our fertilisers. However, this reaction takes place only when there is an excess of ammonium sulphate. over and above what is needed, in the first place, for the formation of ammonium phosphate; and the amount of sulphate formed depends, moreover, on the proportions of ammonium sulphate and potassium chloride. The equilibrium Am_2SO_4, KCl was also studied in a phosphoric acid medium.

In this medium, practically no HCl is displaced.

Salt solutions which are low in nitrogen can displace a very little HCl at the start of the reaction, when there is still free sulphuric acid. But solutions containing at least equimolecular quantities of Am_2SO_4 and H_2SO_4 or H_3PO_4 do not react with the chloride, whatever their concentration or temperature, at least in our manufacturing conditions.

In this work on the formation of potassium sulphate we observed a continuous displacement of the rays of this sulphate, characteristic of solid solutions. We had already previously

noted, during a study on the preparation of potassium sulphate from gypsum, the secondary reaction of which was the double decomposition of Am2SO4/KCl, that the potassium sulphate obtained was always contaminated by ammonium sulphate, despite fairly intensive washing. It is very difficult to extract with water this ammonium sulphate in solid solution, and we were able to establish that the solubility of the ammonium sulphate thus "dissolved" in the potassium sulphate was much less than for ammonium sulphate taken seperately or even when simply mixed with potassium sulphate.

The displacement of the rays of the diffraction spectra enable us to analyse the composition of these solid solutions. Graph No. 7 shows the displacement of rays towards the left for a series of solid solutions.

$$(Am_{1-x}K_x)2 \quad SO4, \text{ where } x \leqslant 1$$
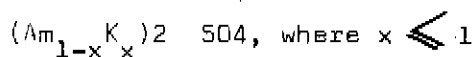
and where x is varied and the composition determined by chemical analysis.

This displacement towards the left is predictable, since the potassium ion is smaller than the ammonium ion whose place it comes to occupy.

Only a small section of the spectrum (the first three rays) was scanned, in order to amplify this zone and make the displacement of the ray more apparent.

The Végard relation is very distinct in this case. This relation permits the determination of a solid solution as a function of the reticular distance of the reflecting plane. In our example, the reticular distances were calculated for the third ray from the following:

$$2 \, d \, \sin \theta = \lambda \text{ (here } \lambda = 1.54 \, \overset{o}{A} \text{ (line } K\alpha_1 \text{ of copper)}$$

This was done for the pure salts K2SO4 and Am2SO4 and for each solid solution (Nos. 1 to 7 measured for the third ray where the steps are more legible) and these values are shown as ordinates on Graph No. 8. The abscissae are constituted by the molecular composition of the solid solutions ex mined (Nos. 1 - 7). It may be noted that all the points are on the line joining K2SO4 to Am2SO4. Thus the composition of a solid solution can be determined with good accuracy.

I do not wish to claim that it is easier to analyse the com-

position of a solid solution in this way than to do it by chemical analysis in the simple case with which we are concerned, where we have only the two common cations and one common anion. However, this method is very valuable in the case where one has other anions, as in our fertilisers which comprise a complex mixture of several salts. Chemical analysis would be absolutely incapable of differentiating the combinations and still less the division of ions in solid solution.

These particular solid solutions, (KAm)2 S04 or (AmK)2 S04 are encountered only in some of our fertilisers, but in almost all of them we find solid syngenite solutions. This is clearly indicated on diagram No. 2b, which shows a shift to the left of the rays of the ammonium syngenite, indicating that K ions have taken the place of Am ions.

Before discussing these mixed salts, we should point out that one can also find solid solutions of sulphophosphates, but only in very small amounts in our fertilisers.

Solid solution of Syngenites

The calcium sulphate formed in superphosphate remains mainly as anhydrite. We have seen above that, in our fertilisers, this anhydrite is converted into syngenite, and, since potassium and ammonium sulphates are present, a solid solution of syngenites is formed. Depending on which fertiliser is concerned, one can obtain a syngenite (KAm) or (AmK).

The displacement of the rays enabled us to discover the presence of these syngenites in our fertilisers, and the measurement of this displacement is the only way of determining their composition, since a chemical analysis of the fertiliser would give only the total amount of K and Am ions without indicating the combination in which they are arranged.

As in the case of solid solutions of (AmK)2 S04, we are able to determine the composition of these syngenites from the displacement of the rays observed by x-ray diffraction. For example, we can determine the composition of the syngenite present in the fertiliser described in diagram No. 2b. It is a syngenite containing 35% by weight of Am2 S04 and 13% of K2S04,

with the formula:

$$CaSO_4, (Am_{0.78}K_{0.22})2, SO_4, H_2O.$$
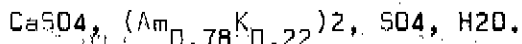
Other Constituents

Some of our fertilisers are made with potassium chloride instead of potassium sulphate, and as we have seen, the reaction is as follows:

$$2KCl + Am_2SO_4 \rightleftharpoons K_2SO_4 + Am\ Cl$$

- a reaction almost complete in the direction of left to right.

In addition to the constituents already mentioned, the spectrum of these fertilisers indicates the characteristic rays of ammonium chlorhydrate. As these fertilisers contain considerably more nitrogen and potash than is necessary to satisfy the formation of ammonium phosphate and syngenite, solid solutions of KAm sulphate are found. These salts are well characterised in the diagrams of these fertilisers.

Diagram No. 9 is that of a 10-12-14 fertiliser. The lower diagram is that of the same fertiliser washed in alcohol, which eliminates AmCl.

Ammonium nitrate is added in certain products, and this also produces the following double equilibrium decomposition with KCl:

$$AmNO_3 + KCl \rightleftharpoons KNO_3 + Am\ Cl$$

Potassium nitrate is, in fact, found to be present, and this reaction proceeds to 80% completion if there is an excess of KCl.

In order to observe certain constituents present in only small quantities it is often necessary to make a first diagram of the sample and then a second after treatment with a selective solvent which eliminates one or several salts, in order to concentrate the minor components.

Finally, we should mention that our fertilisers contain 5 to 10% apatite and 1 to 2% unreacted calcium carbonate.

We need not mention the minor constituents originating from the raw materials involved or certain elements added deliberately during manufacture.

The constituents we have mentioned are those which are found in a normally reacted fertiliser, i.e. in a fertiliser where all the reactions have reached their final equilibrium.

It may happen, however, that this final equilibrium is not reached at the time of bagging. Then, as the reactions continue,

hardening takes place due to crystallisation. This caking may also be due to variations in humidity or temperature, but there is also another cause which has not been adequately emphasised: pressure. If a fertiliser, which normally does not cake, is stored in bags piled in stacks above a certain height, it can cake very strongly as a result of reactions and crystallisation promoted by the joint effect of humidity and pressure. We know that it is a fact that certain reactions are promoted by pressure. We were able to make solid solutions in this way.

Tc conclude, the following are the main constituents of two of our fertilisers:

7 - 8 - 5   %

Free H_2O 3

$H_2Am\ PO_4$ 13.1

Syngenite AmK
- Ca SO_4 — 33.5
- $Am_2\ SO_4$ — 25.5
- $K_2\ SO_4$ — 9.3
- H_2O of crystallisation — 4.4

72.7

Apatite   6

10 - 12 - 14

Free H_2O 2

$H_2Am\ PO_4$ 16.2

Syngenite KAm
- Ca SO_4 — 16.3
- $K_2\ SO_4$ — 16.3
- Am_2SO_4 — 3
- H_2O of crystallisation — 2.1

37.70

Solid Solution AmK
- $Am_2\ SO_4$ — 10.8
- K_2SO_4 — 4.1

14.9

Am Cl   16

K NO_3 6.5

Apatite   5.5

This completes our account of the constitution of our fertilisers. Our purpose was to show what were their main constituents, and we apologise for any omissions or lack of precision. We wished to show how we established the presence of certain mixed salts and to describe the methods which allowed us to define their composition. We have had to summarise a large part of our work.

We should like to emphasise, that, owing to their initial passage through a homogeneous liquid phase, our fertilisers contain salts or complexes which cannot be found in simple mixed fertilisers. The mere contact of the constituents with each other in the latter does not enable the ultimate equilibria to be achieved.
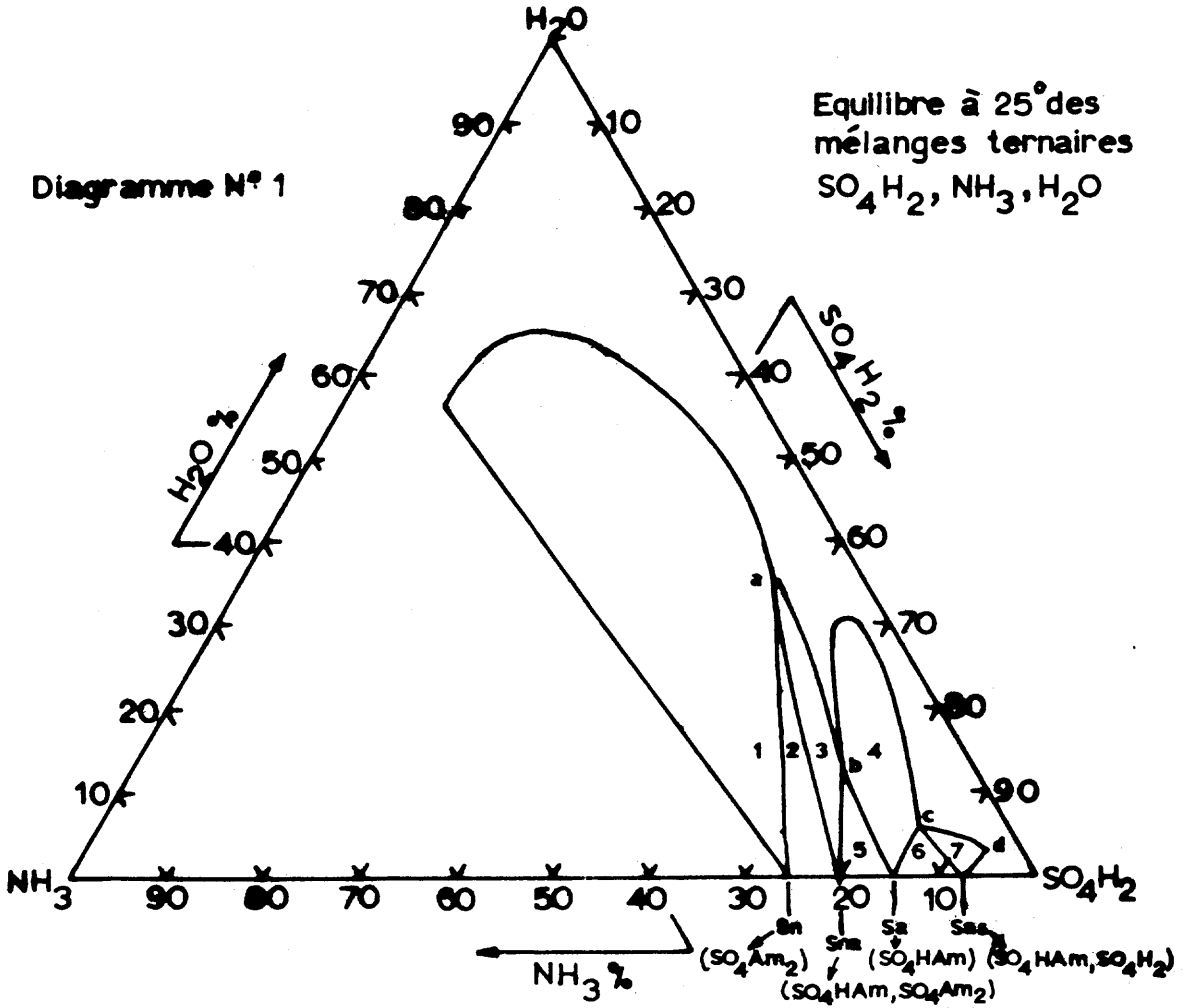
Diagramme N° 1

Equilibre à 25°des
mélanges ternaires
SO_4H_2, NH_3, H_2O

H_2O

SO_4H_2 %

H_2O %

NH_3

NH_3 %

SO_4H_2

ôn
(SO_4Am_2)   Sna   Sa   Sas
              (SO_4HAm) (SO_4HAm,SO_4H_2)
    (SO_4HAm,SO_4Am_2)

DIAGRAMME N°2	
PHOSAMO 7-8-5	
PHOSPHATE MONO-AMMONIQUE	
SYNGÉNITE POTASSIQUE	
SYNGÉNITE AMMONIACALE	
PHOSPHATE MONO-CALCIQUE	
PHOSPHATE BI-CALCIQUE	
SULFATE DE POTASSE	
SULFATE D'AMMONIAQUE	

50°   40°   30°   20°   10°   4°
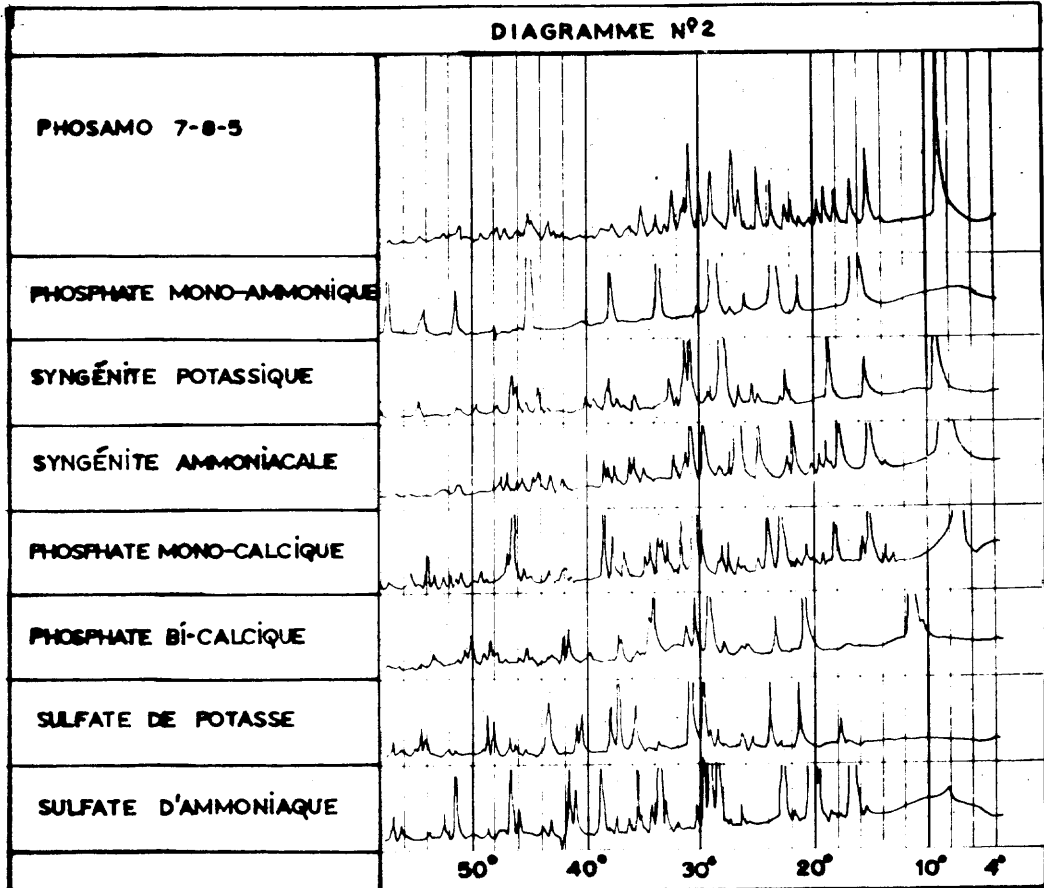
DIAGRAMME N° 22
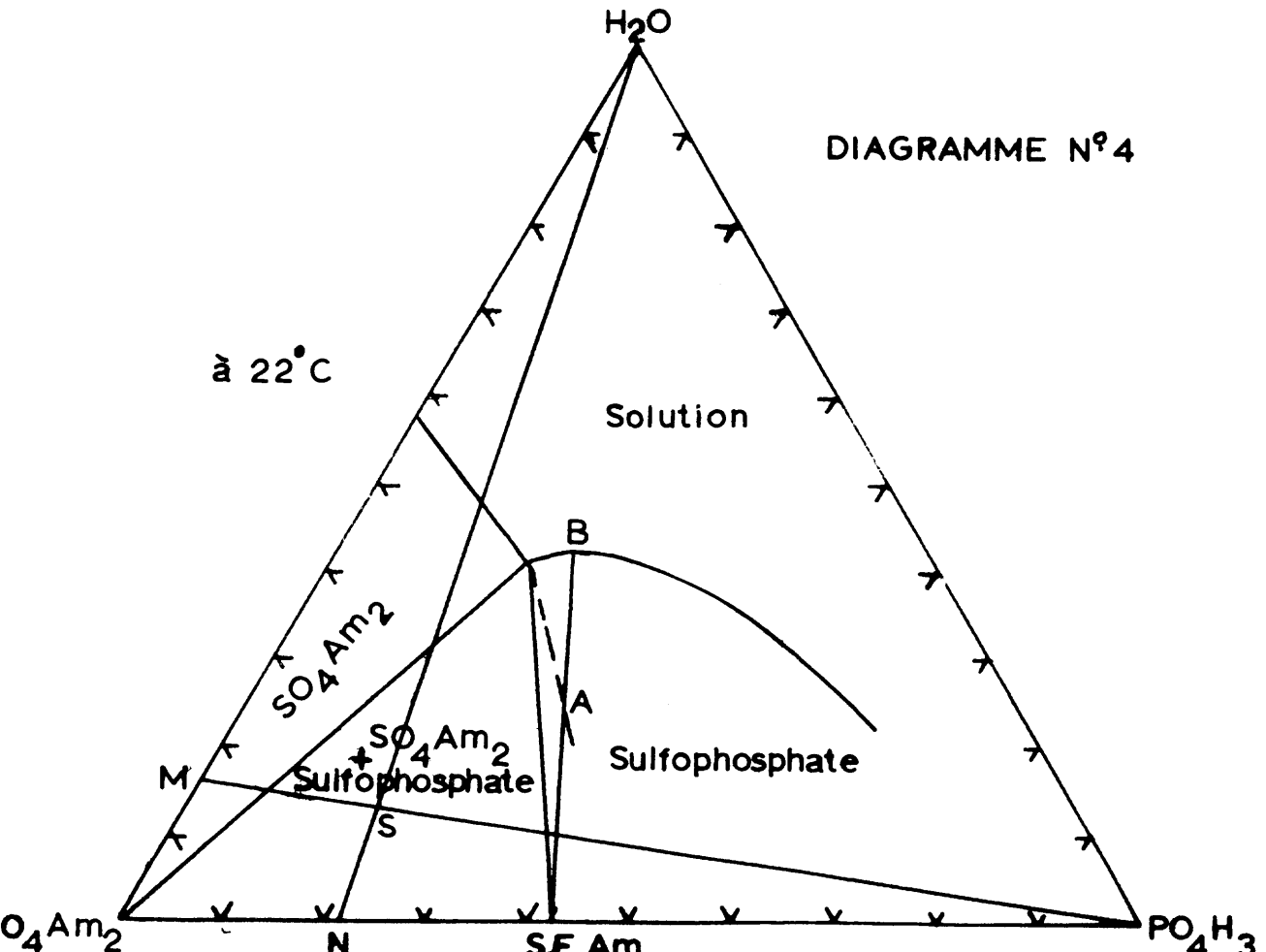
PHOSAMO   7-8-5

PHOSPHATE MONO AMMONIQUE
PO⁴H²Am

DIAGRAMME n°2b

LH/63/5

PHOSAMO X.8-5

SYNCKNITE AMMONIACALE
80°C, 80'AM° H2O

DIAGRAMME N° 4

à 22°C

Solution

B

SO₄Am₂

SO₄Am₂
Sulfophosphate

M

Sulfophosphate

A

S

H₂O

O₄Am₂   N   S.E.Am   PO₄H₃

DIAGRAMME N° 5

LH/63/5

à 22°C
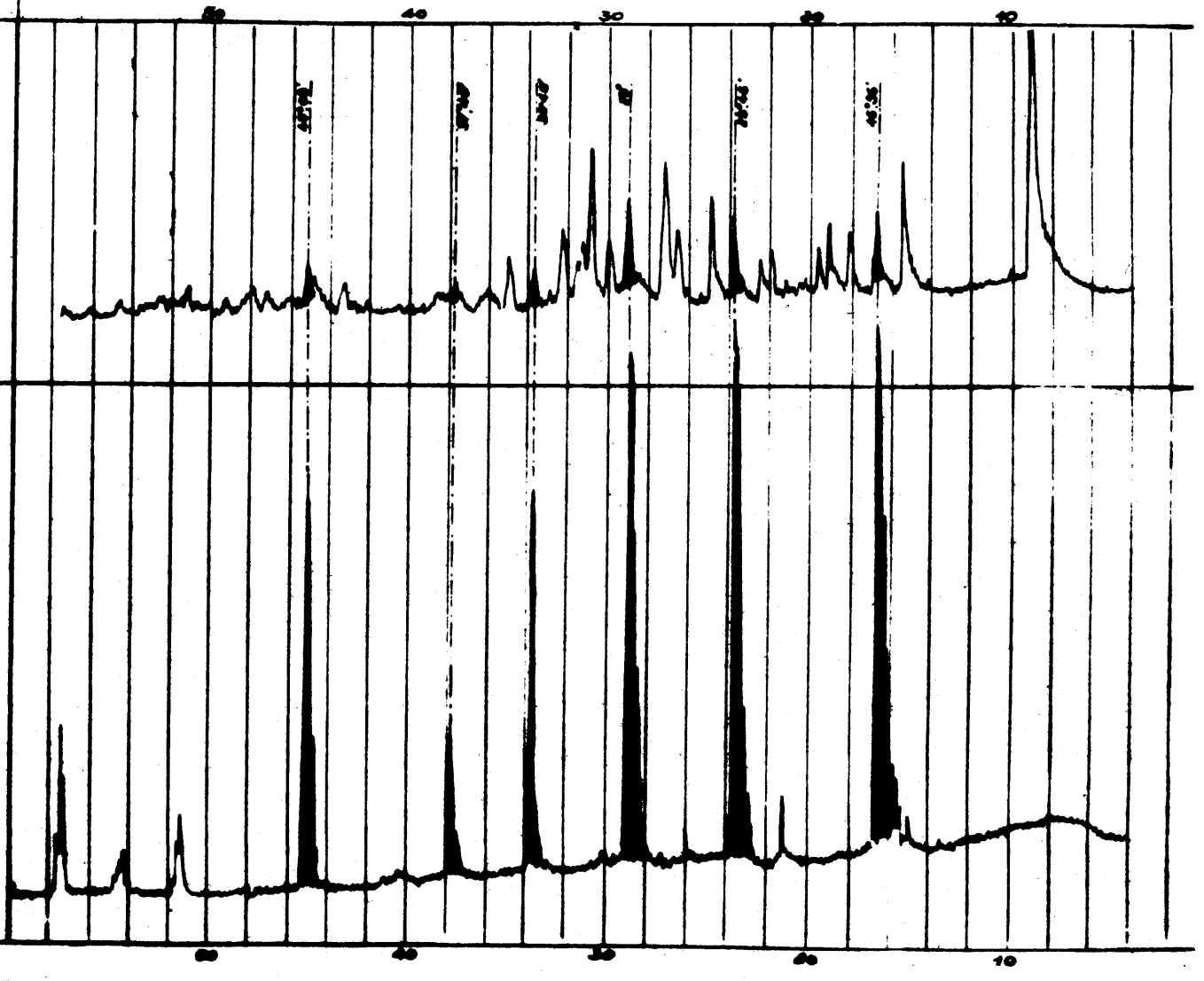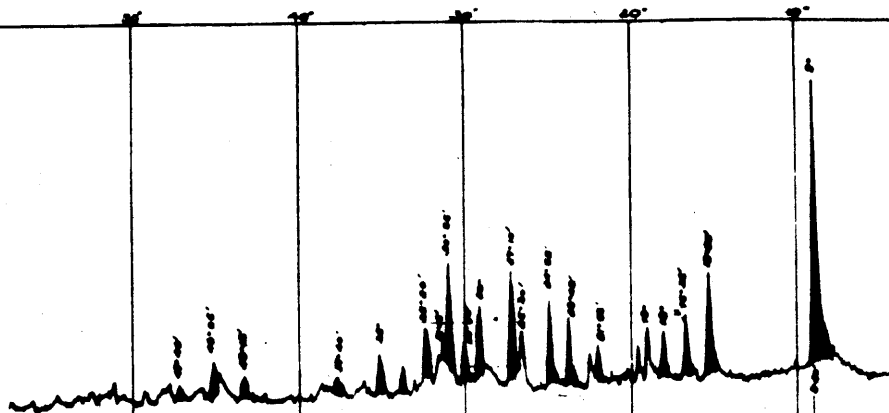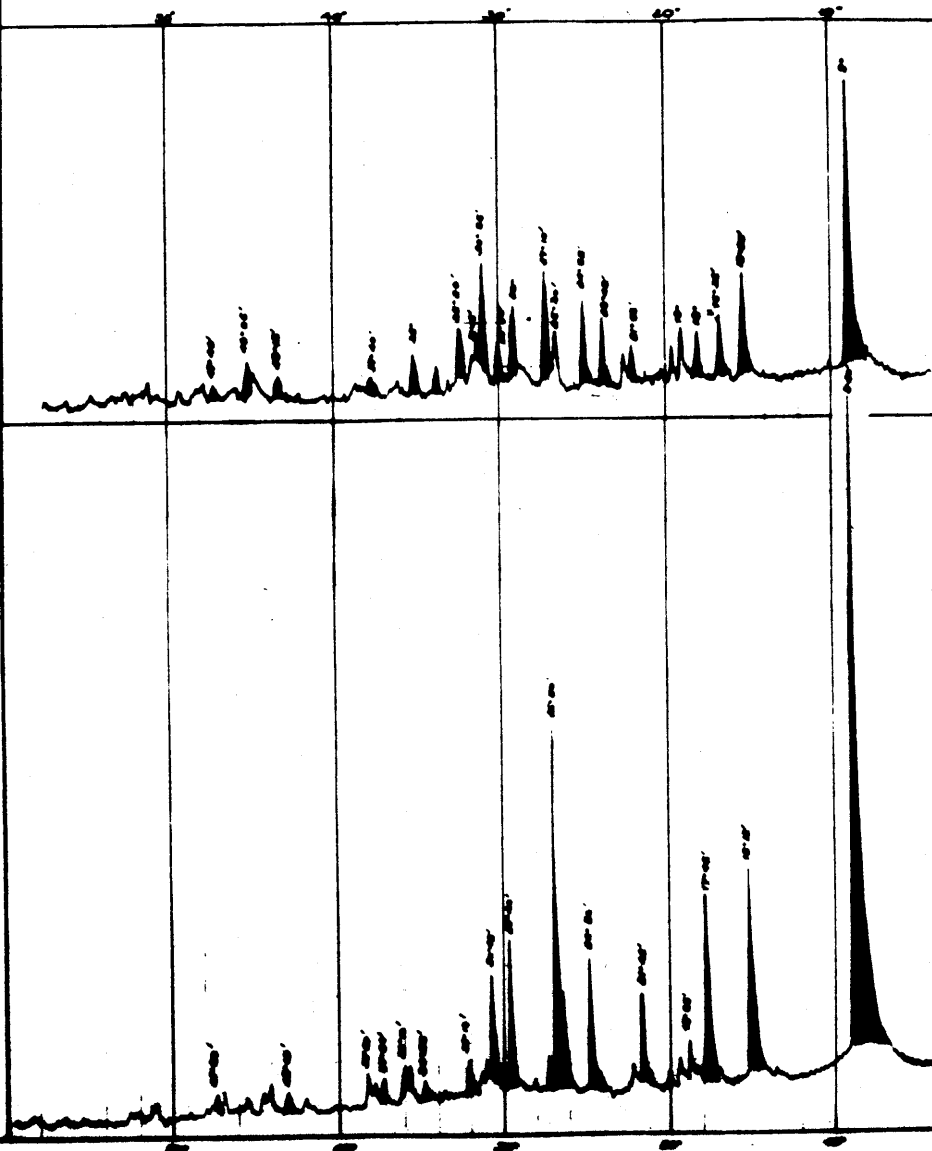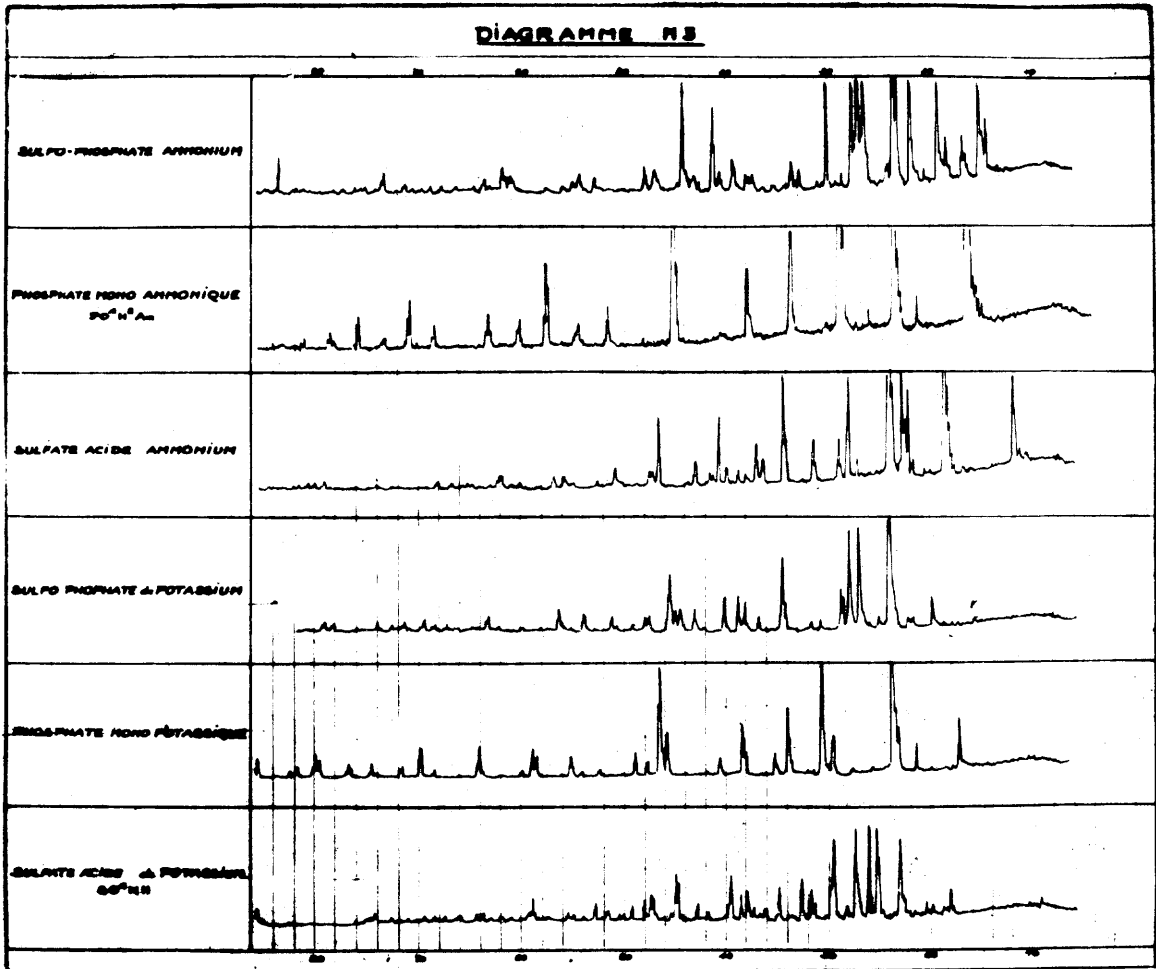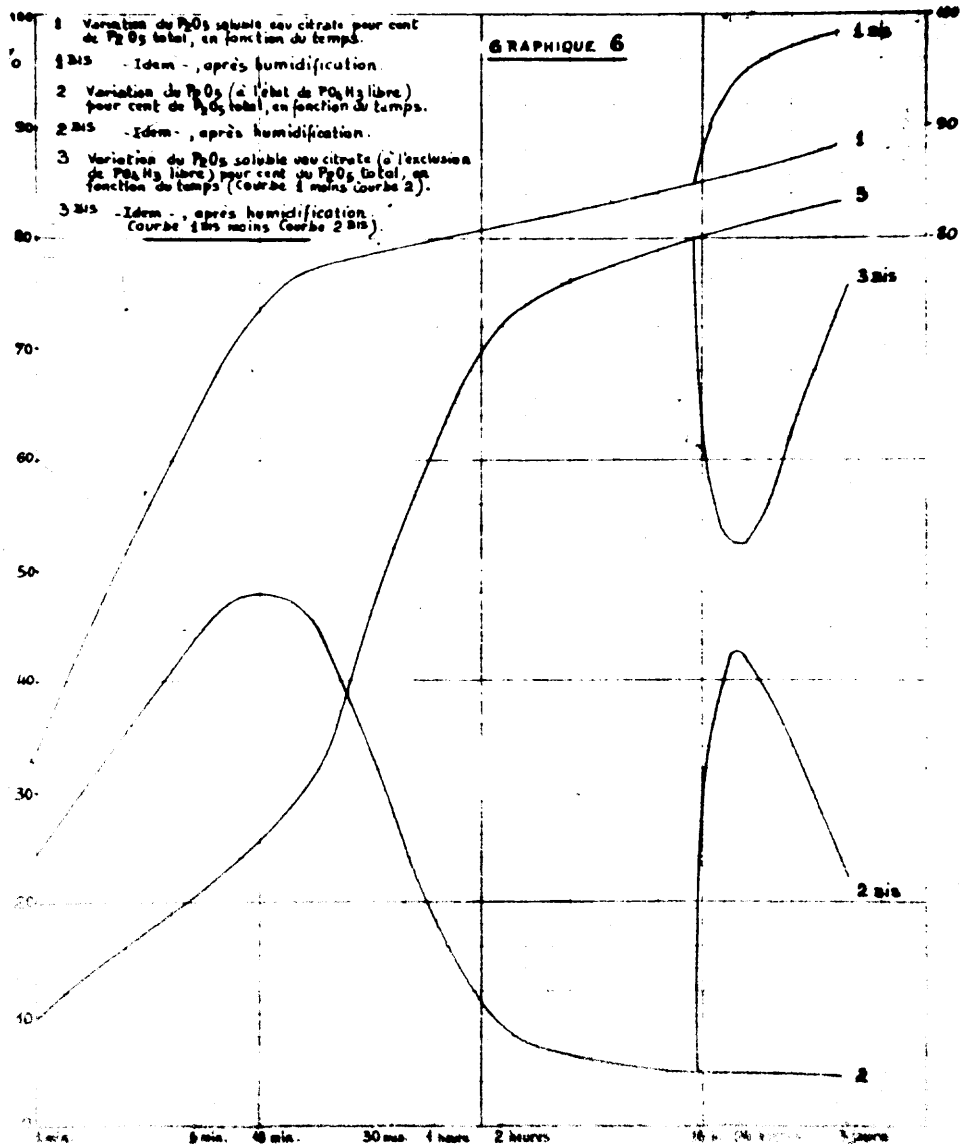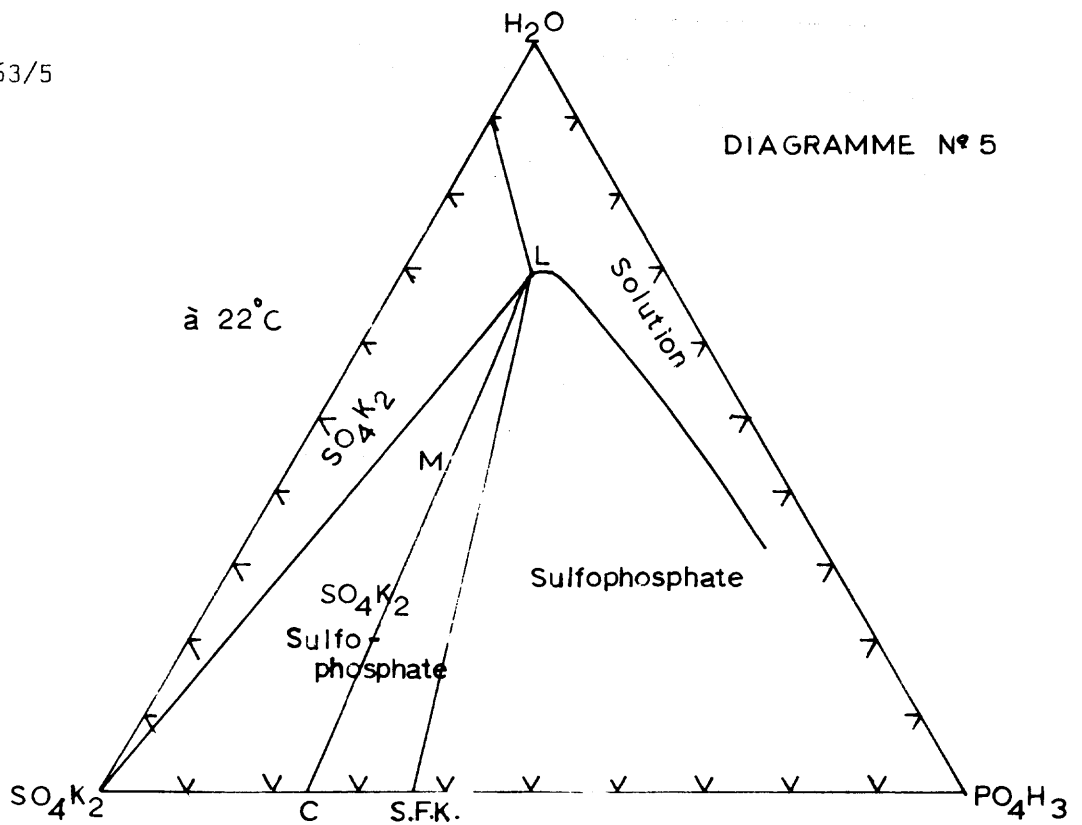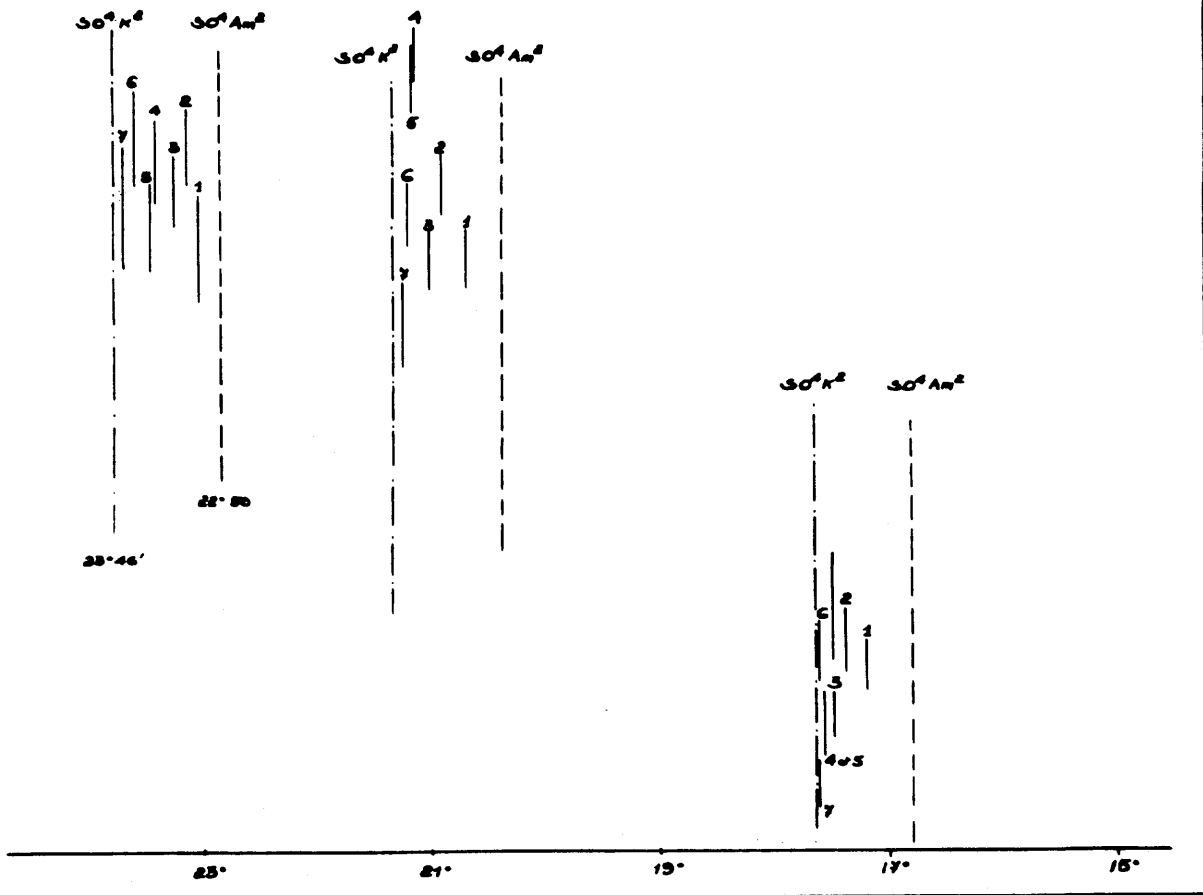
GRAPHIQUE N° 7

GRAPHIQUE N° 8

Solutions solides : $SO_4(Am_{1-x}K_x)_2$

DIAGRAMME N° 9.

CHLORHYDRATE d'AMMONIAQUE.

PHOSA·MO 10-12-14 (Echantillon II)

PHOSA·MO 10-12-14 LAVÉ à L'ALCOOL
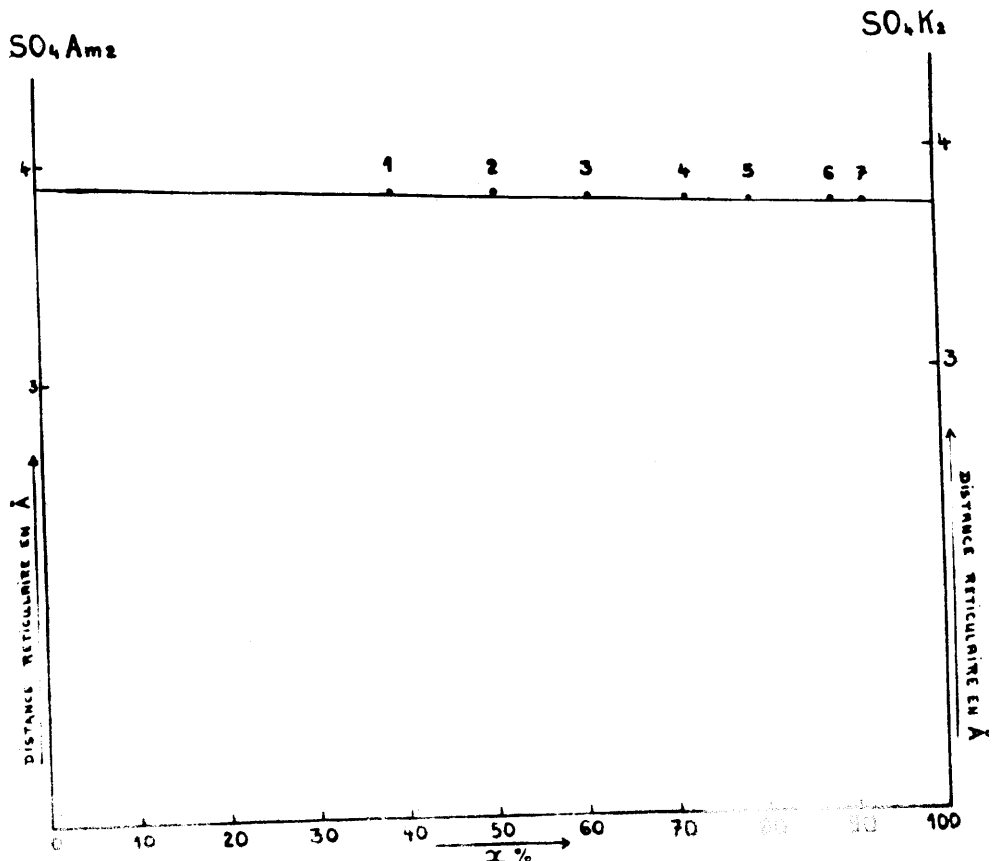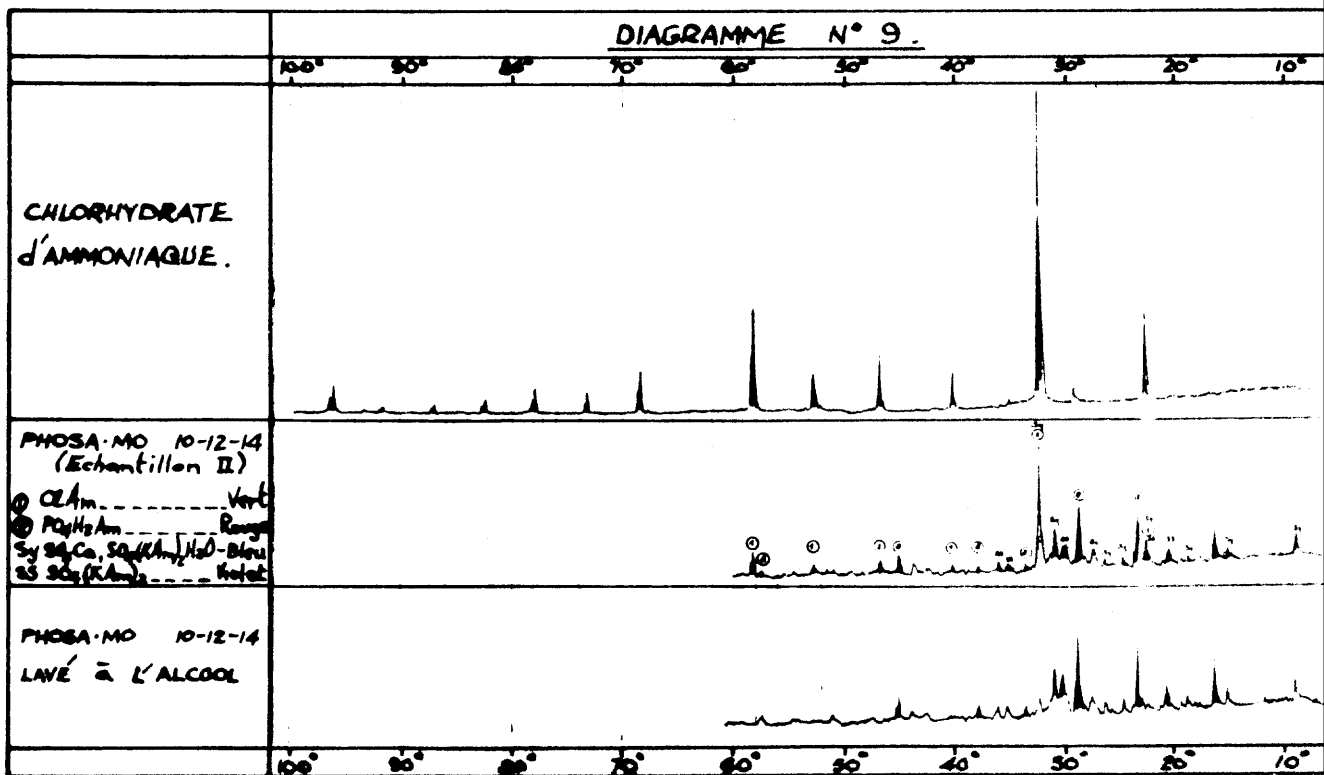
DISCUSSION

Mr. A. BEGHIN (France) : The paper I am now presenting is
a kind of digest of a lengthy study undertaken several years ago in
order to determine the constitution of our complex fertilisers.
Whilst the great majority of compound fertilisers still consisted
of mixtures, my company had for some time developed the production
of complex fertilisers by the chemical combination of the various
constituents. By this I mean that our products pass through a
homogeneous semi-liquid phase which allows processes of double
decomposition to achieve their final equilibria. Our agronomists
had, for their part, observed from the very outset of their crop
experiments the great effectiveness of our compound fertilisers in
comparison with mixed fertilisers of the same grade. Since we then
geared our propaganda to the slogan "Fertilisers obtained by chemical
combination of the constituents", we had to base this slogan on
irrefutable proofs. This was the pretext for this study. We were
able, for example, to confirm and note on our labels that all the
soluble P_2O_5 was combined with ammonia in the form of mono-ammonium
phosphate.

During this work, I discovered the existence of double salts,
to certain of which, the sulpho-phosphates for example, I was un-
able to find any allusion in the literature.

In this summary I have tried to express myself as clearly
as possible and I am ready to clarify any points which might seem
obscure to certain delegates at this meeting.

Dr. K.C. SCHEEL (Germany) : Mr. Beghin's paper relates to
ternary fertilisers apparently produced by a process described by
Mr. Dondin in his paper "Manufacture on a Kuhlmann conveyor of
ternary fertilisers based on superphosphate", which he presented to
the ISMA Technical Conference in Stockholm in 1959. According to
this process, sulphuric acid is ammoniated continuously to a certain
degree in a column; ground phosphate rock, or a mixture of ground
rock and potash, is acidulated by this acid in exactly the same
way as is done in the production of ordinary superphosphate. The
chief advantage of this process seems to be that equipment used for
the production of single superphosphate can be adapted at very low

capital cost to the manufacture of binary or ternary fertilisers. Apart from this, the additional uniformity obtained in these products, compared with the mixtures prepared from superphosphate, may be of additional importance. The main disadvantage of the process, pointed out during the discussion of the paper in Stockholm, is that only relatively low grades can be produced. Mr. Dondir mentioned a formula 5-8-10 as his main product, whereas Mr. Beghin describes formulas of 7-8-5 and 10-12-14. The latter one seems to be produced by additional use of ammonium nitrate.

Mr. Beghin gives us in his paper a profound analysis of the reactions involved in the production of these fertilisers and of the constitution of the finished products. For this purpose he makes use of X-ray diffraction analysis. Especially remarkable seems to me his method of determining the composition of solid solutions by measuring the displacement of certain lines of the diffraction patterns.

The sulfophosphates which Mr. Beghin found as a by-product of his research and which occur at an intermediate stage of the reaction seem to have been well-known compounds in former times. The potassium sulfophosphate was first described by a Frenchman called Jacquelain in Ann. Chim. Phy. 70,317 (1839). In a publication by Meyer in Zeitschrift angew. Chemie, 18,1389 (1905), the first technical production of the sulfophosphates by reacting potassium sulphate and ammonium sulphate with high grade phosphoric acid is reported to have been effected in Germany in 1886. One of the plants mentioned by Meyer was at Vienenburg and now belongs to our company (Guano-Werke A.G.) and is still in production. These sulfophosphates produced in former times contained 25 % P_2O_5 and 10.5 % nitrogen, or 24 % P_2O_5 and 27 % K_2O. They were specially produced for export purposes, for example to the former Dutch East Indies.

The main constituents found by Mr. Beghin in the finished products are monoammonium phosphate, formed by reaction between monocalcium phosphate and ammonium sulphate, and different types of syngenites, which originate from co-crystallisation of calcium sulphate with ammonium, sulphate and potassium sulphate combined with one mole of water per mole of sulphate. The formation of these syngenites seems to be instrumental in causing caking of

the fertilisers in storage. I should therefore like to ask
Mr. Beghin whether the formation of these syngenites is particularly
characteristic of the process first reported by Dondin, or whether
they are also responsible for the well-known caking of the old
superphosphate mixtures with ammonium sulphate. Has Mr. Beghin
analysed these mixtures also by his methods ?

Mr. BEGHIN :   I should like to thank Dr. Scheel for the
information he has just provided. I was unaware of any work
previous to that which I carried out fifteen years ago. But my
contribution - and this is what I think had never previously been
done - was to determine the domains of existence of these salts.

Before replying to the questions put by Dr. Scheel, I should
like to clarify one point which has given rise to confusion. Our
products are of two kinds. For our low grade fertilisers we use a
process similar to that used for superphosphates. We make a salt
solution by dissolving ammonia in sulphuric acid. This solution is
then agitated with the other raw materials, and the slurry is poured
into a den. For our high grade fertilisers, however, we have a
continuous process with a tower as described by Dr. Scheel, into
which we feed sulphuric and phosphoric acid. We partially neutra-
lise this mixture of acids by means of ammonia. It is this solution
which is poured on to the mixture of the other constituents in a small
mixer of the Kuhlmann type, and the reaction continues on conveyor
belts, at the termination of which a supplementary ammoniation is
carried out with gaseous ammonia. The granulation stage then
follows, and the whole process is continuous. We are now embarking
on the study of still more highly concentrated fertilisers.

In reply to Dr. Scheel's second question, I should simply like
to say that I have not analysed mixed fertilisers for the presence
of syngenites; but I have tried to determine compounds of this
material in our Phosamos, resulting from a double decomposition.
I was unable to find these compounds in certain mixed fertilisers,
because these fertilisers do not pass through a liquid phase
permitting ion exchange. For example, if we mix ammonium nitrate
with potassium chloride, it is said that potassium nitrate is formed.
This is partly true, but if one wants a more complete reaction which

will achieve a final equilibrium, one must have a homogeneous liquid phase such as applies to our own fertilisers. For syngenites, this certainly does not apply. In our fertilisers, calcium sulphate forms syngenites - solid solutions of ammoniacal and potassic syngenites - when it begins to crystallise. These reactions certainly occur to a certain extent in mixed fertilisers, but in a very incomplete manner, and I do not think that these salts are the cause of caking in mixed fertilisers.