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

USE OF CHEMICAL AND PHYSICAL DATA TO IMPROVE THE
QUALITY OF GRANULAR FERTILIZER PRODUCTION.

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This paper describes some of the most important improvements achieved by Montedison in the last years in the field of NPK compound fertilizers obtained by reaction phosphate rock with nitric acid.

This was achieved by simply improving the operating conditions of the plants with inexpensive modifications.

Such improvements have been achieved thanks to the information gained from physical chemical and technological tests (besides the usual tests at disposal of any laboratory operating in the field of fertilizer) such as: density, granule apparent density, porosity, specific external and total surfaces, critical relative humidity, hardness, powder content measurements, X ray and microscopical tests.

The availability of the information supplied by the tests and the interpretation of the results, allows a suitable operating condition change of the plants, both to improve the quality level of the products, and to increase the capacity and the process yields.

The present paper describes three different situations which occurred in NPK plants, in each of which, through the information given by the physical - chemical determinations and by the technological tests, it has been possible to obtain a significant improvement of the daily output.

The first example takes into consideration the improvement of the NPK fertilizers with reference to caking phenomena.

That was achieved through the investigation of physical-chemical data in the intermediary stages of the process and in the product by X ray and microscopical investigation.

Besides solving the caking problem, significant increases in the capacity of the plant and process yields have been obtained.

The second example concerns the improvement achieved in the capacity of a traditional rotary drier through the interpretation of the granule porosity data, and the consequent changes of the fertilizer formula and of plant operating conditions.

Lastly the example describes an interesting case of "ecological" improvement obtained by reducing the powder in the drier exit gases by the morphological modification of the crystals which constitute the granules, using surfactants.

The positive result was supported by the examination of hardness, porosity, specific surface and also by microscopical tests.

What described above justifies the space given in the paper to the treatment of three meaningful production examples, while a short description of the physucal-chemical procedures, and of the technological tests are given in the appendix.

EXAMPLE I.

The compound fertilizers of the type NPK are composed of multicomponent crystal systems whose greater or lesser stability can influence the greater or lesser tendency to caking.

The study of the salts constituting the fertilizers gives useful information on modification necessary for the plant operating conditions with the aim of improving the quality of the products as far as caking is concerned.

As previously metioned, sometimes such information allows the achievement of other objectives at the same time, such as, for example, an increase in the plant capacity and in the improvement of the process yields.

Below we describe two cases which demonstrate the importance of the study of the salt systems as a means of improving the operating conditions of compound fertilizers plants.

Theories and Considerations on Compound Fertilizer Caking.

The majority of theories on compound fertilizer caking tend to put the phenomenon down to the binding forces of the granules with each other generated either by crystallisation of the soluble salts following evaporation of the water (1), or by phase changing, or by chemical reactions, or by the formation of solid salt solutions (3), phenomena which lead to the formation of crystal bridges among the granules.

According to Thompson (4) the phenomenon of cementation of the granules by the formation of crystal bridges is not relevant part of the mechanism which leads to the caking of granular fertilizers.

He has proposed a theory based on the plastic deformation of the granules and on the binding force due to depression induced by capillarity (capillarity adhesion).

In our opinion the "capillary adhesion" of the fertilizer granule theory is valid, and can explain certain phenomena of caking otherwise inexplicable.

However, it is wise to say exactly that the transport of the material via saturated solution from the centre of the granules to outside, the transformation of the chemical systems to reach equilibrium, the phase changes generally lead to deformation and softening of the granules: which contributes to increase greatly the surfaces available to cause the "capillary adhesion" mechanism.

In other words, the "equilibrium of the granules" has always a relevant role in caking phenomena whether crystal bridges are formed or not.

One way of minimising the problems relating to caking could be that of reducing the moisture of the products to very low limits, thus making the possible reactions very slow, a technique used by many producers.

Montedison has preferred to produce fertilizers with a moisture between 0.8% and 1.5% to avoid possible self sustaining decomposition phenomena, which, as known, are higher with low moisture levels.

Below, some of the improvements made on our original process operating conditions are described, with the aim of obtaining products composed of solid phases as stable as possible. For this we have particularly made use of X Ray and microscopical examinations.

We shall discuss two cases in particular: the compound fertilizers 12-12-12 and 12-12-17S.

In the first case the potassium is supplied as KCl, and in the second as K₂SO₄.

KCl-NH₄NO₃ system and production of fertilizer 12-12-12

In Figure 1, the flow sheet of the NPK compound fertilizer Montedison's plant is given.

In the past, at the operating conditions used during the production of the compound fertilizer 12-12-12 the KCl feed was directly added into the granulator as crystals.

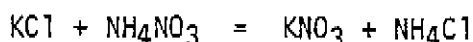
The granules of the fertilizer produced had a marked tendency towards caking during storage mainly because of exchange reactions between KCl and NH₄NO₃ since the products contained large amounts of free KCl.

We studied many articles existing in literature on KCl-NH₄NO₃ system, and made some specific checks on the system itself, in order to obtain practical information for improving the characteristics of the 12-12-12 fertilizer from the point of view of the stability of the solid phases constituting the granules.

Obviously such checks were carried out (especially by X Ray and optical microscopy) to control the different phenomena both qualitatively and quantitatively.

In addition reaction kinetics, especially affected by KCl crystal size were studied.

The KCl-NH₄NO₃ system is composed of two pairs of reciprocal salts, bound together by the reaction



Since K⁺ and NH₄⁺ ions can mutually replace each other, the formation of solid solutions of the type (K, NH₄)NO₃ and (K, NH₄)Cl are possible.

Janeke and Meyer-Hoffer (5, 6, 7) established the general principles for obtaining the phase diagram of the system composed by reciprocal salt pairs.

The phase diagram of the system KCl-NH₄NO₃ was studied by Janeke (8, 9) who gave the isotherms within the range 0-60°C.

A complete description of the binary NH₄NO₃-KNO₃ system is reported by Ando (3).

Janeke studied in particular the phase diagrams at 35°C and 65°C.

In Figure 2 the phase diagram at 120°C (temperature of slurries in the Montedison process for 12-12-12 production) we studied experimentally (the

NPK FERTILIZER PRODUCTION FLOW SHEET

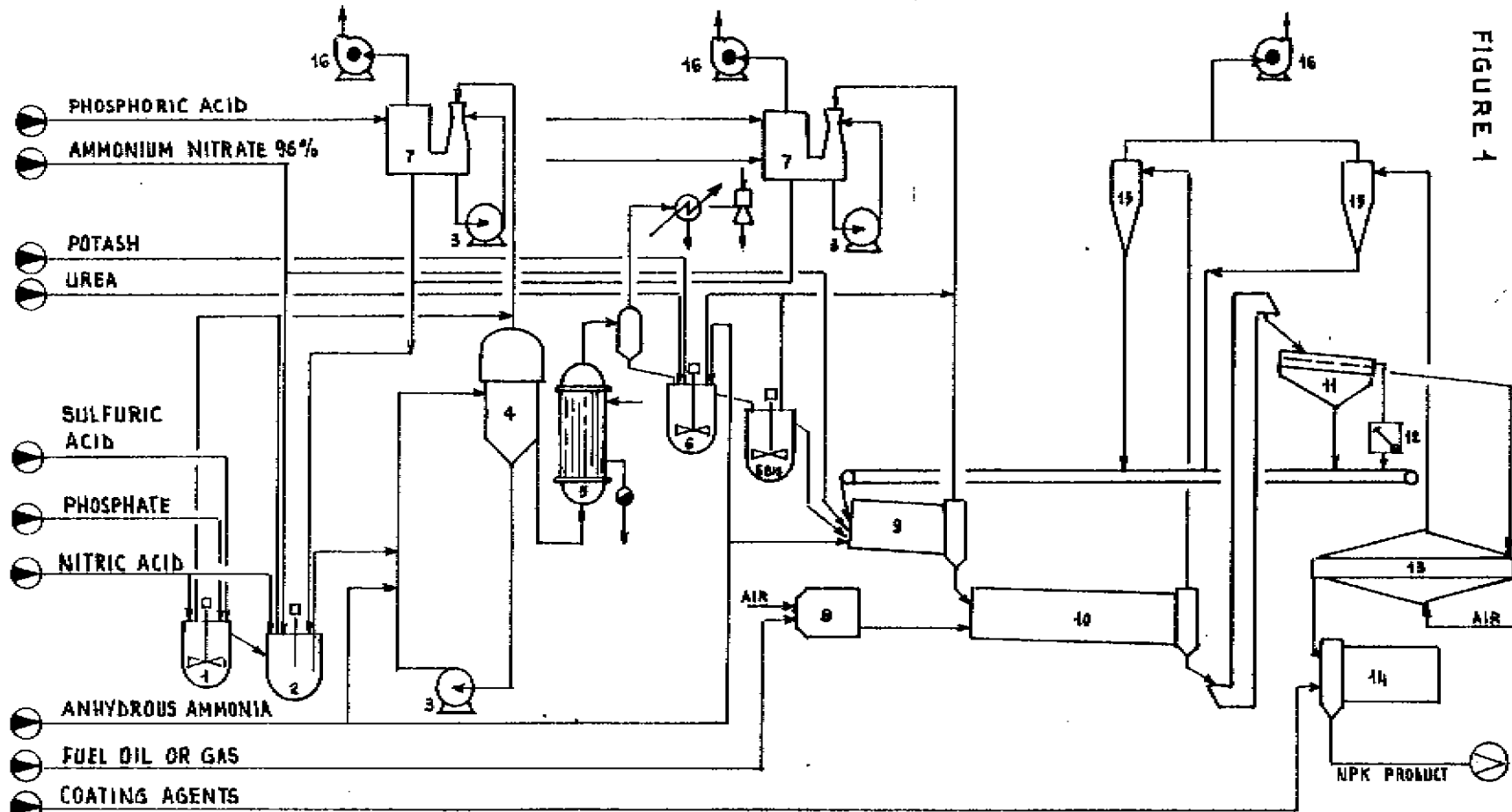
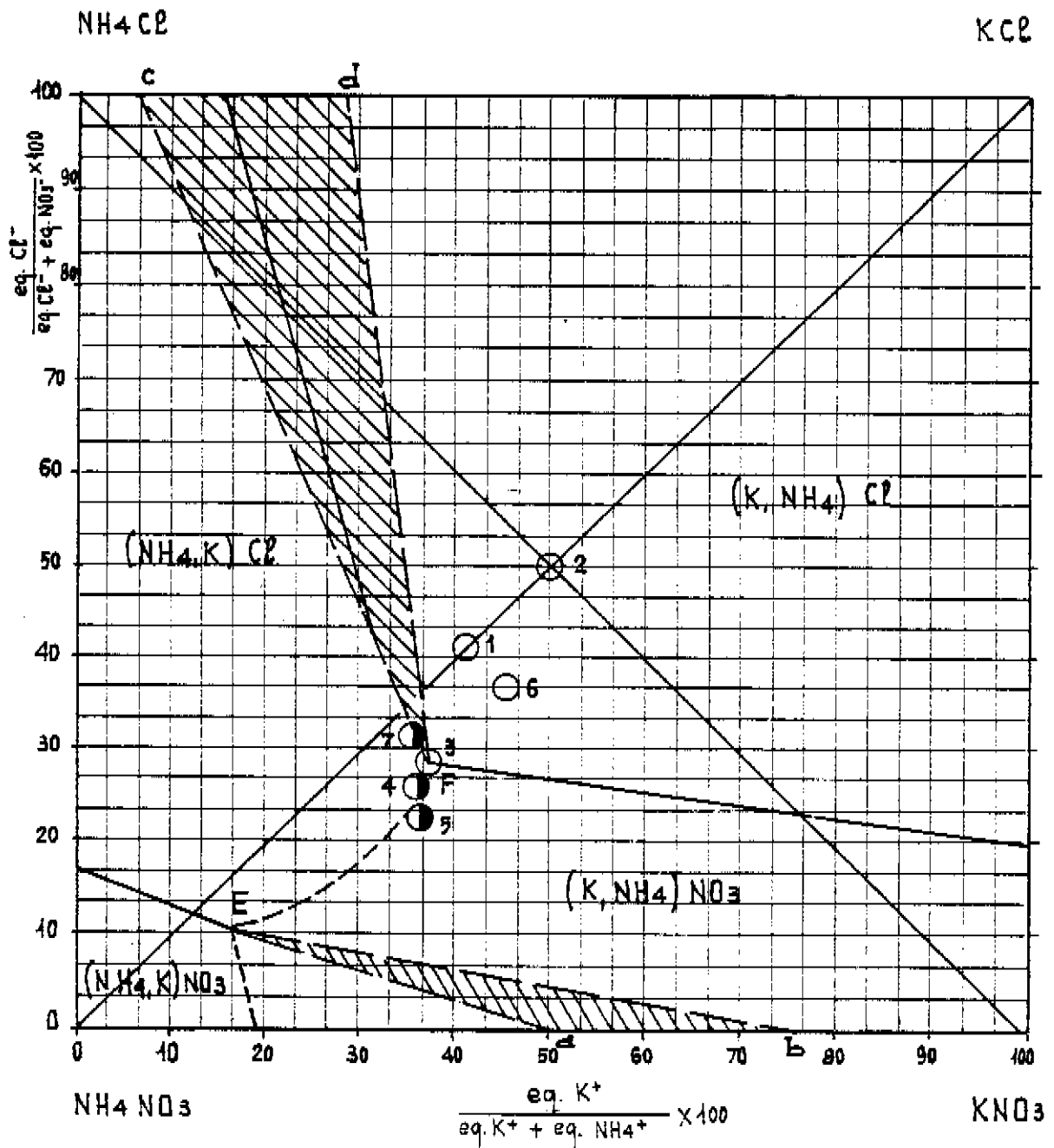


FIGURE 1

- | | | |
|---|---|---|
| <p>LEGENDA:</p> <ul style="list-style-type: none"> 1 - REACTOR 2 - REACTOR 3 - RECIRCULATING PUMPS 4 - HIGH EFFICIENCY AMMONIATOR (HEA) 5 - CONC 6 - 6 BIS - MIXER | <ul style="list-style-type: none"> 7 - SCRUBBER 8 - AIR HEATER 9 - GRANULATOR 10 - DRIER 11 - SCREEN 12 - CRUSHER | <ul style="list-style-type: none"> 13 - FLUIDIZED BED COOLER 14 - COATING DRUM 15 - DUST CYCLONES 16 - FANS |
|---|---|---|

EQUILIBRIUM SYSTEM $KCl - NH_4NO_3$ AT $120^\circ C$



AREA Eab : MISCIBILITY GAP OF $KNO_3 - NH_4NO_3$ SOLID SOLUTIONS

AREA Fcd : MISCIBILITY GAP OF $KCl - NH_4Cl$ SOLID SOLUTIONS

POINT E : LIQUID + 3 SOLIDS a, b, $(NH_4, K)Cl$

POINT F : LIQUID + 3 SOLIDS c, d, $(K, NH_4)NO_3$

FIGURE 2

dotted lines given in it have indicative value) is described. The system at the given temperature has the following solid solutions:

$(\text{NH}_4, \text{K})\text{Cl}$ solid solution of KCl in NH_4Cl

$(\text{K}, \text{NH}_4)\text{Cl}$ solid solution of NH_4Cl in KCl

$(\text{NH}_4, \text{K})\text{NO}_3$ solid solution of KNO_3 in NH_4NO_3

$(\text{K}, \text{NH}_4)\text{NO}_3$ solid solution of NH_4NO_3 in KNO_3

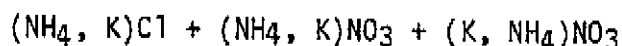
Two triple points are possible with the following solid solutions:

$(\text{NH}_4, \text{K})\text{Cl} + (\text{K}, \text{NH}_4)\text{Cl} + (\text{K}, \text{NH}_4)\text{NO}_3$ point F on the 120°C diagram

$(\text{NH}_4, \text{K})\text{Cl} + (\text{NH}_4, \text{K})\text{NO}_3 + (\text{K}, \text{NH}_4)\text{NO}_3$ point E on the 120°C diagram

Point I of the diagram gives the ratio $\text{KCl}/\text{NH}_4\text{NO}_3$ in the 12-12-12 fertilizer.

In equilibrium conditions at 120°C , total evaporation of solution having composition of point I gives the following three salts,



According to Janeke, at temperature below $55-60^\circ\text{C}$ one obtains the above mentioned three salts and $(\text{K}, \text{NH}_4)\text{Cl}$ never appears.

On the other hand at temperature above $55-60^\circ\text{C}$, the evaporation follows a different pattern: $(\text{K}, \text{NH}_4)\text{Cl}$, $(\text{NH}_4, \text{K})\text{Cl}$ and $(\text{K}, \text{NH}_4)\text{NO}_3$ initially precipitate.

The system then undergoes a transformation with redissolving the $(\text{K}, \text{NH}_4)\text{Cl}$: the final solid is once more $(\text{NH}_4, \text{K})\text{Cl}$, $(\text{NH}_4, \text{K})\text{NO}_3$ and $(\text{K}, \text{NH}_4)\text{NO}_3$

In conclusion in the solid phase with $\text{H}_2\text{O} = 0$ at the temperatures taken into consideration, the evaporation of liquids of composition corresponding to Point I must give solids containing neither KCl nor $(\text{K}, \text{NH}_4)\text{Cl}$.

Moreover at the studied temperature inversion of the stable salt pair does not occur. This is due to the effect of the solid solutions on the stability of the simple salts.

Taking into consideration what has been stated so far, the plant was equipped with a reactor (6 bis of Figure 1) so as to feed the KCl into the ammoniated slurry. The modified process operating conditions (followed in different experiments by X Rays and optical microscopy) allowed us to obtain solid mixtures of salts very close to the equilibrium at the drying temperature. The 12-12-12 fertilizer thus obtained shows only weak caking tendency during storage.

The obvious action so produced was that of allowing the crystal phases to reach stable equilibria through dissolution and precipitation mechanism: when the KCl was added to the granulator, here it remained partially unreacted, continuing to react with ammonium nitrate, as forecast by the phase diagrams, during storage.

Similar studies were carried out on other NPK fertilizers using KCl as raw material.

The granules were always free flowing and the anticaking agents use was reduced: money was saved.

In Table I the running conditions achieved by adding KCl into ammonia - ted slurry are given. The results obtained with the two different conditions

are also given.

In the first case, a large amount of free unreacted KCl was observed, while in the second the potassium was completely found in the solid solution $(\text{NH}_4, \text{K})\text{NO}_3$ and $(\text{K}, \text{NH}_4)\text{NO}_3$. Figures 3A, 3B and 3C, show the photographs of thin sections of the granules obtained in the two different running conditions.

The most interesting result was supplied by the caking test (10): the fertilizers produced adding KCl in the ammoniated slurry, proved free flowing with a caking index value below 30.

An interesting application of this information has enabled us to replace the KCl normally used in the past (screen analysis in Table 2 column A) with a KCl having larger particle content (screen analysis in Table 2 column B).

In order to stabilize the final crystal phases it was necessary to increase the retention time of the KCl in the slurries and the dissolution temperature. The plant was equipped with another dissolution reactor (reactor 6 Figure 1) and part of NH_3 was put into this reactor to increase the thermal level of the slurry. In Table 2 the new running conditions and achieved results are given.

The fertilizer is free from unreacted KCl and the caking test gives the same value as the product obtain with the KCl at smaller size.

$\text{K}_2\text{SO}_4 - \text{NH}_4\text{NO}_3$ system and production of compound fertilizer 12-12-175

For the compound fertilizers where there is the salt pair $\text{K}_2\text{SO}_4 - \text{NH}_4\text{NO}_3$ the problems relating to caking are much greater than those deriving from the salt pair $\text{KCl} - \text{NH}_4\text{NO}_3$ because of the greater system complexity.

The potassium sulphate ammonium nitrate system has been studied by several authors (3, 12, 13, 14, 15) both in water solution and in the melted state at different temperatures.

According to Osaka (15) the following salts can exist as solid solution at 25°C:

$(\text{NH}_4, \text{K})\text{SO}_4$ solid solutions of K_2SO_4 in $(\text{NH}_4)_2\text{SO}_4$

$(\text{NH}_4, \text{K})\text{NO}_3$ solid solutions of KNO_3 in NH_4NO_3

$(\text{K}, \text{NH}_4)\text{NO}_3$ solid solutions of NH_4NO_3 in KNO_3

$(\text{NH}_4, \text{K})_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$ solid solutions where the ion NH_4^+ bound to SO_4^{--} can be partially replaced by K^+

$(\text{NH}_4, \text{K})_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$ solid solutions where the ion NH_4^+ bound to SO_4^{--} can be partially replaced by K^+ .

When NH_4^+ replaces K^+ an expansion of the crystal lattice occurs since NH_4^+ has a slightly larger ionic radius than K^+ (Table 3).

K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ are isomorphous and mutually soluble in every proportions.

Solid solutions of NH_4NO_3 in KNO_3 III containing from 26% to 44% ammonium nitrate and solid solutions of KNO_3 in NH_4NO_3 III containing up to 30% of potassium nitrate were obtained.

It was found that, in disagreement on what Coates (11) stated, and in agreement with Ando (16), solid solutions of NH_4NO_3 in KNO_3 II containing up

Figure 3 A - Thin section micro-photograph of unreacted KCl.

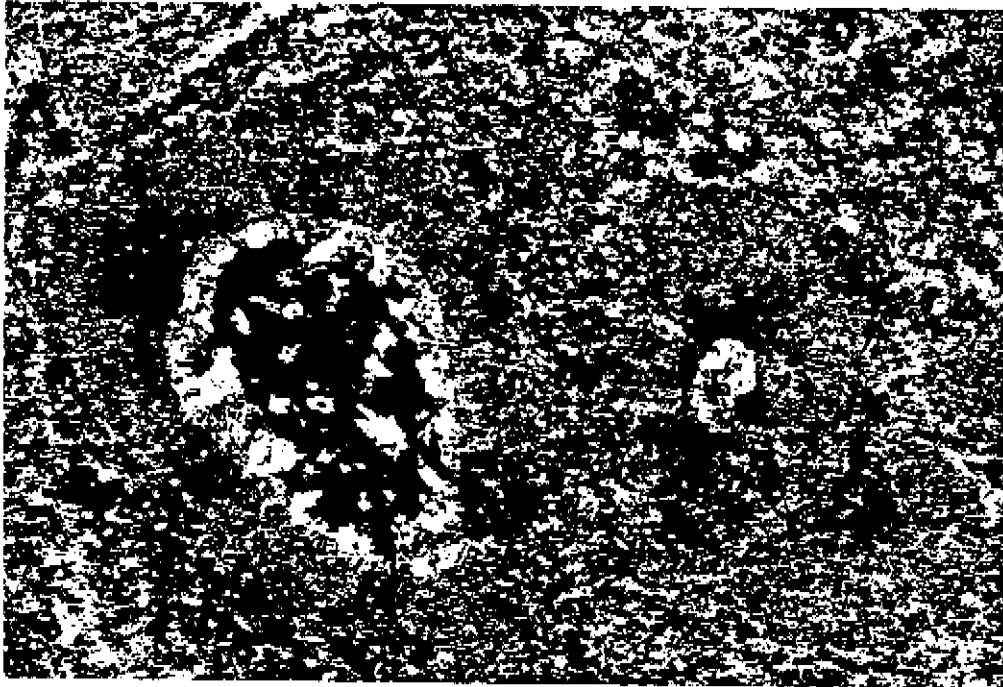


Figure 3 B - Thin section micro-photograph of reacted KCl during storage.

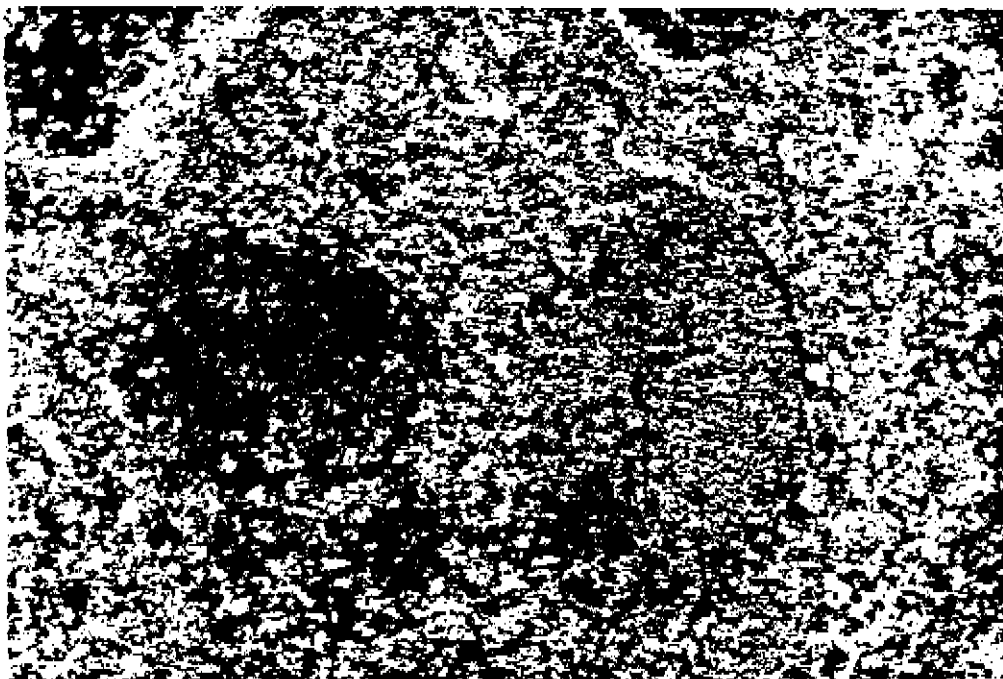
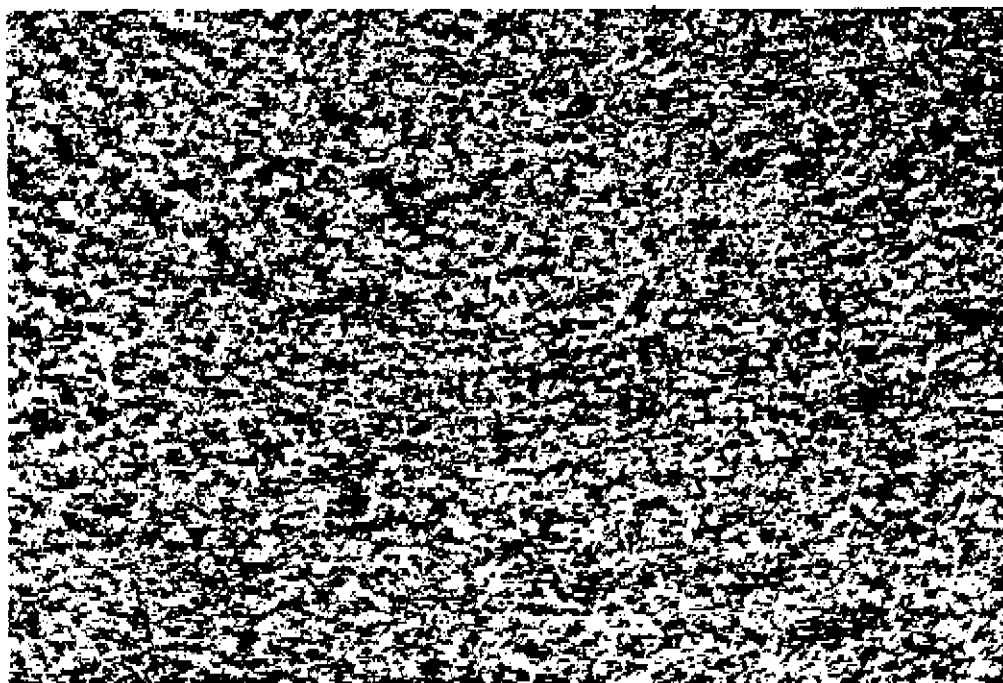


Figure 3 C - Thin section photograph of reacted salts during the process.
KCl added in slurry.

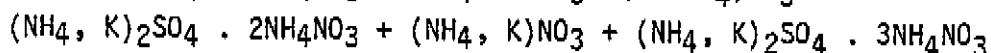
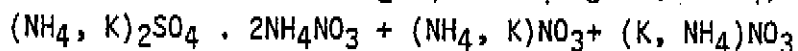
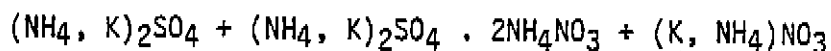


to 13.5% ammonium nitrate, can exist.

It was not found possible to prepare solid solutions of the type $(\text{NH}_4, \text{K})_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$ despite many attempts at different temperatures and concentrations according to Coates (11).

Table 4 gives the X Ray powder diffraction data found for the double salts $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$ and $(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$. The data for $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$ agree with those of Smith (17) and Coates (11) while those found for $(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$ agree at the most with those given by Coates (11).

The $\text{K}_2\text{SO}_4\text{-NH}_4\text{NO}_3$ system admits according to Osaka (15) three triple points made up of the following solid solutions:



By carrying out isothermic evaporation of mixtures at different temperature and conditions, the existence of the three triple points were confirmed while in the place of the solid solution $(\text{NH}_4, \text{K})_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$ the double salt $(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$ was always found.

In the production of granular fertilizers NPK type containing potassium sulphate and ammonium nitrate, it is important to find the best operating conditions for obtaining a stable product in order to avoid caking phenomena during storage.

With reference to the production of the compound fertilizer 12-12-17S whose flow sheet is shown in Figure 4, four different K_2SO_4 feeding conditions were adopted. That in order to establish the best conditions for obtaining a product stable during storage. The four feeding conditions, which differ mainly in the point of the plant where the potassium sulphate was added, can be grouped as follows:

Feed A K_2SO_4 added in 6 (Figure 4)

Feed B K_2SO_4 added in 4 (Figure 4)

Feed C K_2SO_4 added in 1 (Figure 4)

Feed D K_2SO_4 added in stoichiometric ratio to CaO in 1 to form CaSO_4 and the balance in 6.

The fertilizer produced according to feed A (Table 5) gave a product which in storage showed a strong caking tendency even when coated with great amounts of anticaking agents. Moreover the yields of water-soluble P_2O_5 (45.8% w/w) were very low.

Using feed B, the quality of the product is slightly improved, but however with a reduction of capacity due to bad working conditions of the concentrator positioned after the feeding point of K_2SO_4 .

As compared with feed A the water soluble P_2O_5 yields are greatly improved (from 45.8% to 75.0%) while the water soluble K_2O yields are reduced quite a lot.

With feed C at the same capacity as feed A a stable product in storage was obtained and as compared with feed A the water soluble P_2O_5 yields were double, although the water soluble K_2O yields were less again.

The best feeding conditions from the economical point of view proved to

12-12-17 S PRODUCTION FLOW SHEET

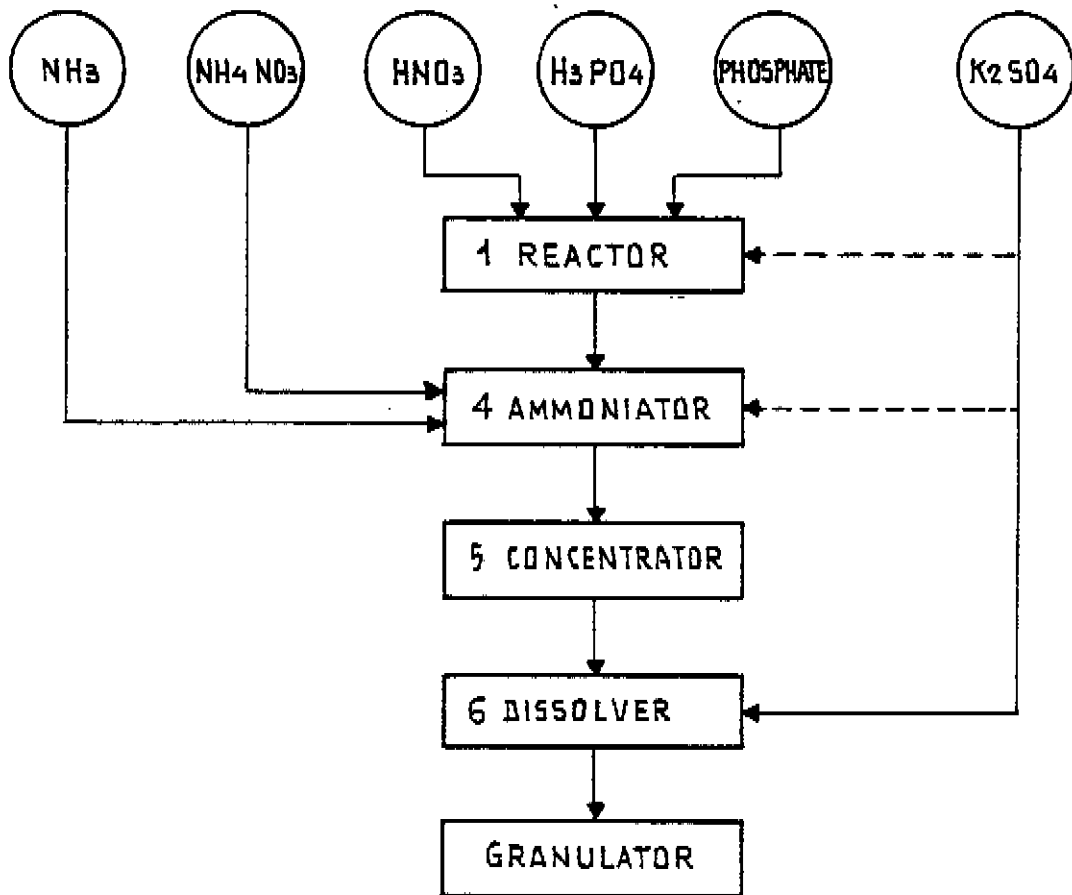


FIGURE 4

be feed D (18). As compared with feed A, the water soluble P_2O_5 yields had an increase from 45.8% to 78.7%, the K_2O yields were practically the same while the plant capacity had an increase from 35 tons/hr to 38 tons/hr.

However, with feed A, the product was by no means acceptable as far as caking tendency was concerned.

The fertilizer produced with feed D did not show caking tendency. The different salts of the fertilizer were in equilibrium at drying temperature and did not show caking problems during storage.

The great increase in the water soluble P_2O_5 yields can be put down to the fact that the feeding conditions D led to the formation of ammonium phosphates and calcium sulphate rather than dicalcium phosphate.

The examination of X Ray lines of the products obtained with the feeding conditions B-C and of A-D showed that in the first case $K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$ was present.

The double salt has a lower solubility than that of $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ present in the products obtained with the feeding conditions A-D. That is why the products obtained with the feeding conditions B-C had a lower yield of water soluble K_2O than that of the products obtained with the feeding conditions A-D.

EXAMPLE 2

The most important phenomena of the drying operation can be summarized as follows:

- the water diffuses as vapour in the vacuum (porosity) in the solid (19). This was demonstrated by Garside (20) who also supplied the most recent mathematical model of drying
- the slow stage of mass transfer is the diffusion of water-vapour in the solid (21)
- the slow stage of heat transfer is outside the granule (22) in the transfer from air to the surface of the granules
- the exact solution of mass transfer equation studied by Garside leads to the following observations:
 - a) in an industrial rotary dryer the drying takes place, keeping the other factors constant, at the same rate as in a fluidized bed. In fact the time during which the granules are out of air contact is not lost: diffusion goes on inside the granules.
 - b) the diffusion takes place in such a way that a portion of wet material exists in the centre of the granule, which shrinks little at a time as water evaporates.

A simplified expression of the general equation considering what has been reported above, can be so derived

$$(C/C_0)^{-2/3} - (C/C_0)^{-1/3} - (C/C_0)^{1/3} + (C/C_0)^{2/3} = \frac{3K (p - p_a) D t}{C_0 q \xi^2 T} \quad 1)$$

where:

- C and C_0 water contents at the time t and t_0 (gr/gr)
- p and p_a vapour pressures of the water into the granule and outside (bar)
- D diffusivity of the water (cm^2/sec)
- ρ density of the solid (gr/cm^3)
- r granule radius (cm)
- T absolute temperature ($^{\circ}\text{K}$)
- t time (sec)
- K constant dimensional which has the value 0.2193 with the units chosen above.

The relationship 1 can be used considering D constant during the drying.

Actually there is an interaction between diffusivity D and the structure of the granules which has not yet been studied completely.

What has been stated above is because any direct measurement of diffusivity D has been carried out. Only indirect measurements of the diffusivity D are available using relationship 1 or similar equations where the other variables are known. However it is known (20) that calculating the diffusivity through the relationship 1, D values are obtained exponentially bound to the porosity.

From the practical point of view, it is therefore in particular the porosity which conditions directly the drying rate. One must also stress that, with the present experience, at least, the link between porosity and diffusivity is independent from the nature of the solid, and thus valid for every granular products.

The characteristics of the solid affect the drying "via" the vapour pressure p in solution which wets the solid.

A study in laboratory and an in industrial ammonium nitrate plant was undertaken in order to correlate the diffusivity D to the porosity for this product.

The porosity was modified by using increasing amounts of an anionic surfactant.

In Figure 5 the values of the diffusivity calculated by the 1 against the measured porosity are reported. The derived relationship existing between the diffusivity D expressed in cm^2/sec and the porosity V expressed cm^3/cm^3 is given by:

$$D = 0.48 V^{3.60}$$

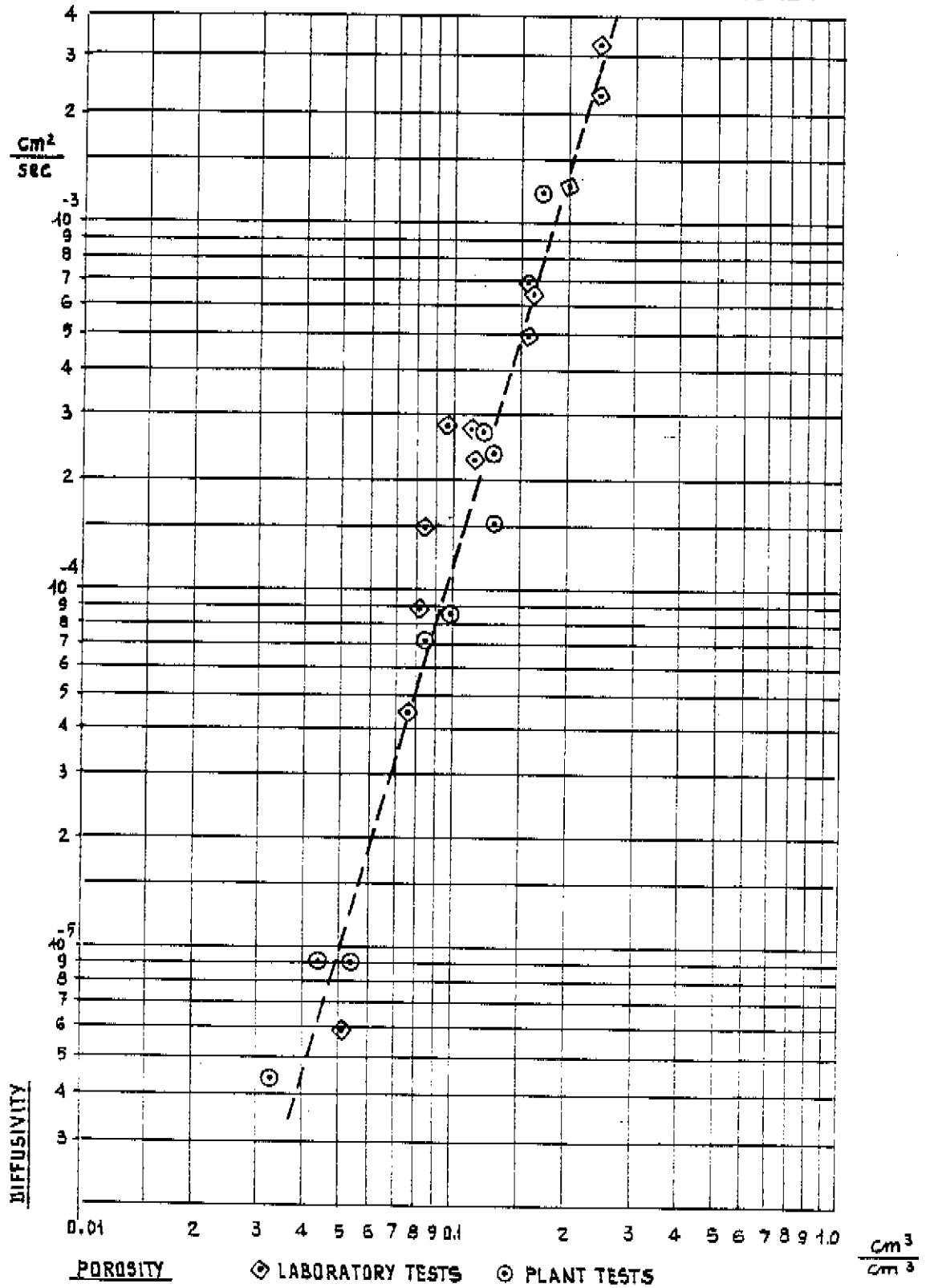
The influence of the porosity (and granule size) on the capacity of the rotary drier was studied at the NPK plant for the 25-10-0 fertilizer.

The factor which conditions the capacity of the plant is the evaporating capacity of the drier. At the hourly capacity of 30 tons the moisture of the product was equal to 1.2% and this result is to be considered unacceptable. The situation was improved through a change of the formula which could determine an increase of the granule porosity.

Here after two different operating conditions are described, which for the sake of brevity, we shall name A and B.

Formula A differs from formula B in a higher feed of phosphate rock, while in the B formula superphosphate is used, adding it directly to the rotary granulator. In both formulae the ammonium nitrate (96% conc) is

CORRELATION BETWEEN DIFFUSIVITY FOR AMMONIUM NITRATE
DRYING ON ROTARY DRUM FIGURE 5



produced in a separated reactor and added to ammoniated slurry before going into the granulator.

The flow sheet of the process is given in Figure 1. In Table 6 the most important values of the two different operating conditions are given. In particular, the more significant data found in the drying stage to test the drier capacity in the two different operating conditions are reported.

Finally the chemical and physical characteristics of the products are given in Table 7.

The granules of the two fertilizers seem quite different in porosity and size.

The granules obtained with formula B, in particular, have more than twice the porosity value than those obtained with formula A, and the internal specific surface values appear quite in line with the porosity values.

The higher porosity of product B and the different granule size (average diameter of product on entering the drier, mm 2.7 against mm 3.4) is due to the highest capacity reached by the driers. In fact, with the operating conditions A, for a production rate of 30 tons/hr, 2000 kg/hr of water were evaporated in the drier, obtaining a product with residual moisture of 1.2%.

With formula B it was possible to raise the production rate to 35 tons/hr, evaporating 3000 kg/hr of water with a residual moisture in the product of 0.8%

The influence of porosity (and granule size) on drying capacity is so confirmed.

EXAMPLE 3

An ecological problem present in the production of compound fertilizer is that of the powder inside the plants, and above all, the problem of powder going into the air from the chimneys of driers and coolers especially if the plants are not equipped with wet washing system. The dust problems, which arises from the undesired flaking of the granules varies from one product to another.

The theory which best explains the phenomenon (23) relates this flaking of the granules to a localized loss of mechanical resistance especially on the granule surface due to the shape and bond type of crystal which determine the strength of cohesion of granule surface.

The formation mechanism of granules is based on a coating of recycling granules by the fresh slurry: a cooling, crystallising happens; while the residual liquid phase penetrate in the original nucleos.

The external zone has not therefore enough liquid to fill the interstices between the new crystals.

During the drying, surface crystals are subject to a flaking whose intensity depends on surface structure.

The variable which directly or indirectly can influence the flaking of granules are:

- a) composition of liquid phase (solubility). The low viscosity of the liquid phase simplifies its separation from the solid part on the growing granules. From this point of view ammonium nitrate granulation shows a disadvantage as compared to the slurries of ammonium phosphate.

The impurities present in the phosphoric acid, especially iron and aluminium, have a coagulating effect and thus prevent dust;

- b) the temperature (affects both solubility and viscosity);
- c) the presence of large crystals and aggregates (greater than 20 - 30 microns) which form more permeable layers and which make aggregates with less points of contact;
- d) the presence of surfactans which reduce surface pressure of the liquid phase in the granulator and facilitate the percolation in the underlying porosity. Some non-ionic surfactans, have proved to have a limited action on porosity, although they had a positive effect on hardness of the granule, giving them a greater resistance in the flaking phenomena.

Microscopical investigation have been carried out, first on granular ammonium nitrate and then on 25-10-0, which can be defined as the most powdery of our NPK fertilizers: they showed that these surfactans modify the morphological characteristics of the crystals, which become thinner and thus adhere more easily to the surface of the granules.

Although having the same average diameter, the granules have, in fact, a greater external specific surface and hardness.

These surfactans also proved to have a positive influence on granulation.

In fact reducing the size range of the product leaving the granulator, the efficiency of granulation is improved, and also the working conditions of both screens and crushers are improved.

Table 8 gives the results obtained during the 25-10-0 production both with and without surfactans (conditions A and B).

The amount of dust in the gases leaving the drier were compared with the screen analysis of the product leaving the drier, and with the physical characteristics of the granules.

As can be noted, the use of non-ionic surfactans allowed the amount of dust leaving the chimney by 5 times.

From the screen analysis it can be seen that without surfactans, about 3 kg of fines passing 100 mesh screen were found per ton. of circulating product, whereas adding the surfactant such amount was found to be less than 0.5 kg.

The physical characteristic show that the granules obtained with the surfactant are harder and have greater external specific surface at the same average diameter.

Such a value is not justified by the porosity value which proved to be slightly greater.

On the other hand the internal specific surface value is in agreement with the porosity.

Example 3 completes Example 2 and illustrates how, by suitable running conditions it was possible to achieve two aims at the same time: increasing the drier evaporating capacity reducing dust from chimney.

APPENDIX: equipment and methodology

Here after, the equipment and the different methods of investigation at disposal of Montedison's Fertilizer Research Centre are briefly described, attempting to emphasize the meaning and the use of each test for the improvement of the quality of fertilizer production.

X Ray Diffractometry and Optical Microscopy

An X Ray powder diffractometer equipped with a goniometer and proportional counter is available. It is possible to adapt to the sample camera a special device (made by us) which enables us to carry out tests in the temperature range 0-60°C. The routine tests are:

- 1) qualitative analysis
- 2) quantitative analysis
- 3) determination of lattice constants
- 4) determination of average crystallite size
- 5) changes in phase or composition within temperature range 0-60°C.

What described in points 1 - 2 - 5 was very useful in the study of the two salt pairs $KCl-NH_4NO_3$ and $K_2SO_4-NH_4NO_3$ both as far as concerns the equilibrium, and the reaction kinetics at the temperatures achieved in the plant.

The study of the reaction kinetics, in particular enabled us to establish the best operating conditions for the compound fertilizer production.

That allowed us to obtain products in equilibrium during storage, as described in Example 1, with low caking tendency.

By suitable computing programs, lattice constants and average crystallite constants are calculated using both interplanar spacing data and profile examination of diffraction lines.

The data are particularly important for deriving the composition and the reactivity of phosphate rocks.

By computing unit cell dimensions of the solid solutions which are present in the compound fertilizers, the cationic ratio K/NH_4 can be derived.

After the X Ray investigations have been completed, the optical investigations are performed.

As a matter of fact, for the quali-quantitative investigation of multi-component mixtures composing the compound fertilizer granules, the X Ray diffraction data are mostly used.

The optical microscopy is used especially to examine the mutual arrangement of the crystals inside the granules, their morphology and to reveal the possible mechanisms of reaction in the solid phase.

This is basically done by studying thin sections of the granules, whose preparation is particularly accurate.

The microscopes, for documentary purposes, are equipped with devices for macro and micro photography.

However the optical microscopy is not always (and only) a support technique for X Ray diffractometry. It can become a primary technique and often proves indispensable.

By the examination of the thin sections, quantitative analyses can be carried out for specific cases, such as, for example (to refer to examples

reported in the text) the determination of the free KCl and K₂SO₄ in the compound fertilizers.

The optical microscopy has allowed us to carry out important morphological studies.

Such studies have in particular, for example, enabled us to modify the crystal shape of the KNO₃, separated as intermediary product from a particular process of compound fertilizer production (24) obtaining rhombohedral shaped crystals instead of thin flat crystals, thus avoiding filtration problems.

Finally (using optical microscopy) specific techniques were studied for determining the nucleation and growth rates of crystals in continuous flow crystallizers, under specific experimental conditions.

The last possibility has opened up a great research field, since the results of the determination of the nucleation and growth rates as a function of the operating conditions, can be suitably applied even in the fertilizer industry.

Interesting applications have been made in the production of wet phosphoric acid to improve the morphology of the crystals with the use of non-ionic surfactants.

Critical relative humidity

Part of the caking phenomena can be related to the mechanism of absorption and desorption of water which occur on the granule surface: in such a way crystal bridges can form among granules (by precipitation of the most soluble salts) causing caking of fertilizers.

The absorption of water on the granule surface occurs when the partial pressure of the water in the air is superior to the vapour pressure of the saturated solutions on the surfaces of the granules themselves.

The opposite effect occurs, on the other hand, when the vapour pressure is superior.

Finally it is obvious that when the vapour pressure of the saturated solutions of the sample is equal to the partial pressure of the water in the air there is neither absorption nor desorption of water.

It is defined as "Critical Relative Humidity" the relationship between the vapour pressure due to saturated solution of the granule surface and the vapour pressure of water at the same temperature.

Practically the CRH represents the relative humidity of the air at which the substance neither absorbs nor desorbs water.

When pure salts are involved the CRH measurements are simply performed measuring the vapour pressure of a saturated solution prepared in any way.

In this case the CRH is independent of the water content.

In the case of granular compound fertilizers, the CRH depends on the water content and on the salts presents as impurities, which can be more soluble than the main compounds constituting the fertilizers themselves.

In this case, it is necessary to know the behaviour of the CRH with respect to the water content of the fertilizer.

The apparatus used in our laboratory is described in Figure 6.

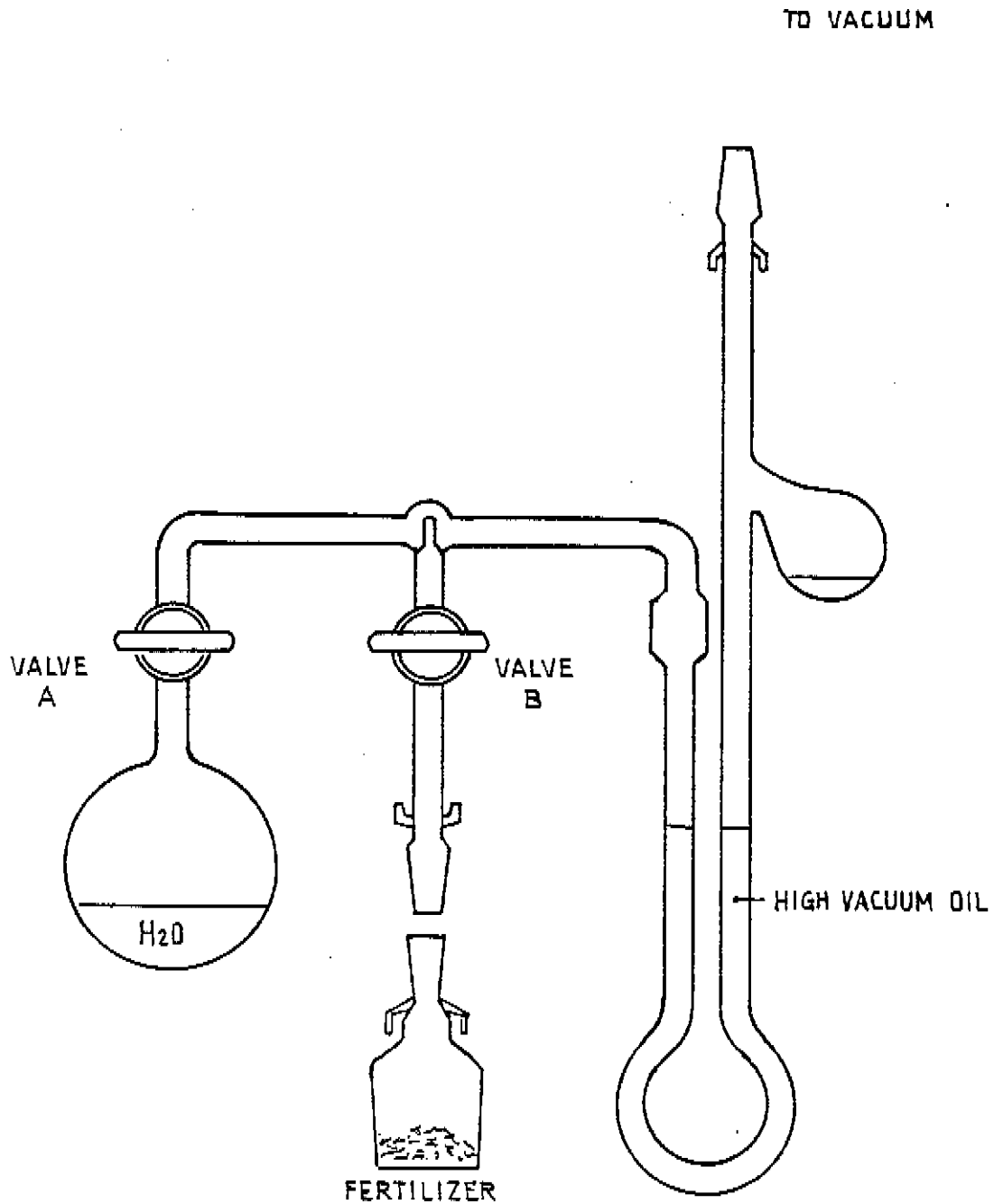
APPARATUS FOR CRITICAL RELATIVE HUMIDITY DETERMINATION
AT DIFFERENT WATER CONTENT

FIGURE 6

Basically, it is modified Menzi's Isoteniscope immersed in a thermostatic bath where it is possible to humidify the fertilizer, to control the water absorbed, measure the vapour pressure of the fertilizer.

It is very important to know the values of CRH for the different fertilizers, because, as mentioned, the mechanism of water absorption and desorption, and therefore possible caking phenomena depend on that values.

It is to be observed that the phenomena are also directly connected to the type of solid phases present in the fertilizers.

For example, in the case where a fertilizer containing the salt pair $K_2SO_4 - NH_4NO_3$ is stored far from the thermodynamic equilibrium at the storage temperature it can contain great amounts of free unreacted NH_4NO_3 which lowers the CRH and thus makes easy water absorption.

The Example given above, clearly demonstrates the interdependence of the microscopical and diffractometric investigations on the CRH measurements.

The integrated examination of the results clarifies the phenomena of water absorption on the surface of fertilizers during storage.

Besides measuring the Critical Relative Humidity, it can sometimes be important (and our laboratory carries out such determination) to measure the water absorption rate.

Such a rate depends on the relative humidity of the air and on the CRH, on the ventilation, on the particle size of the product and on the amount of water already present, in the fertilizers.

The results of such tests supply information on the storage conditions of the products and on the bagging.

Real density, apparent density, porosity, external specific surface, total specific surface, powder content of fertilizers, granule hardness

We shall describe below only the principles of these measurements, briefly, because the practical use of the data taken from these measurements, has already been shown in Examples 2 and 3.

The real density expresses the weight in grams per cm^3 of the material composing the solid under examination (without empty spaces). The determination is made by measuring the actual volume of a known sample weight. In our laboratory, a picnometer with gas pressure balance is used to measure it.

The granule apparent density represents the ratio between the weight and the known volume of the granules. The volume of the granules includes the empty spaces within the granule (porosity). The determination of the proper volume of the granules is made by putting the sample into a container (dilatometer) with a known volume, and by filling the empty spaces between the granules with mercury. From the weight of mercury used, its volume is calculated, and by difference, the proper volume of the granules.

The external specific surface of the granules of a fertilizer is defined as the extension of the surface area of 1 gram of the product and is expressed in cm^2/g . At Fertilizer Research Centre this measurement is made by determining the value deriving from the pressure drop of a gaseous fluid passing through a porous medium. The fluid used is anhydrous air with known viscosity. Measuring the different pressure drop values that occur when anhydrous air is made to flow at different rates, with laminar flow, the calculation of external specific surface is possible by means of Koreny's formula.

The total specific surface of a product is the sum of the external surface area and of the surface area of the inside holes. It is determined by making the sample cooled in liquid nitrogen. A monomolecular layer of nitrogen (from a mixture of nitrogen and helium) is adsorbed on the surface area (external and inside). The gas is then desorbed and analyzed by a conductivity detector which determines the amount of nitrogen absorbed. Since the surface which can be covered under normal conditions of T and P ($4,39 \text{ m}^2$) is known, it is possible to calculate the total specific surface.

The porosity of a granular product is by definition, the volume of the empty spaces of 1 g of granules. To determine the value of the empty spaces inside the granules, the technique of mercury penetration under pressure (2000 kg/cm^2 maximum) inside the granules. On the basis of theoretical laws it is possible to correlate the pressure used with the size of the filled spaces. The volume of the filled space is equal to the volume of mercury used, which in our equipment is followed automatically (by a needle in contact with the mercury put into a capillary with a constant diameter) versus the pressure increase. It is possible to derive the volume of the pores on the basis of their diameter.

The powder content measurement of a granular fertilizer is based on the evaluation of the weight of the dust which is given off by the fertilizers submitted to stress of an air flow under controlled conditions.

The granule hardness is carried on the granules which represent in size the average diameter of the granules of the product to be examined. The method is based on the measurement of the mechanical stress of compression necessary to break the fertilizers.

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TABLE 1 - 12.12.12. production with addition of KCl in granulation or in slurries

		<u>KCl</u> in granulator	<u>KCl</u> in slurry
<u>MATERIALS FEED</u>			
- Phosphate rock	kg/ton of product	309	309
- 100% H ₂ SO ₄	"	120	120
- 100% HNO ₃	"	271	271
- P ₂ O ₅ from H ₃ PO ₄	"	26	26
- NH ₃	"	85	85
- KCl	"	208	208
- Coating agent	"	4	4
<u>PRODUCTION RATE</u>	tons/hr	48	48
<u>AMMONIATED SLURRY</u>			
- Water	%	19	19
- NH ₃ : H ₃ PO ₄ mole ratio	-	0.97	0.97
- Temperature	°C	110	110
- Viscosity at 110°C	cP	90	90
<u>SLURRY AFTER KCl ADDITION</u>			
- Water	%		16
- Temperature	°C		103
- Viscosity at 110°C	cP		63
<u>GRANULATION</u>			
- Recycle ratio	-	4.0	4.5
- Product moisture	%	4.8	4.6
- Temperature	°C	71	75
<u>PRODUCT</u>			
- Moisture	%	1.4	1.5
- Water soluble P ₂ O ₅	"	6.0	6.1
- Water and cytrate soluble P ₂ O ₅	"	12.0	12.1
- NH ₃ -N	"	6.4	6.4
- NO ₃ -N	"	5.7	5.6
- Soluble K ₂ O	"	12.0	11.9
- Free KCl	"	4.0	0
- Total porosity	ml/ml	0.0932	0.0798
- Hardness	kg	2.0	2.5
- Caking index	-	55	15

TABLE 2 - 12.12.12 production by two different types of KCl in reference to screen analysis

		A small size KCl	B large size KCl
<u>KCl SCREEN ANALYSIS</u>			
* + 2.000 mm	%	0.0	0.0
* 2.000 ÷ 1.000 mm	"	2.7	1.9
* 1.000 ÷ 0.500 mm	"	2.0	23.7
* 0.500 ÷ 0.200 mm	"	11.3	46.8
* 0.200 ÷ 0.075 mm	"	72.3	21.8
- 0.075 mm	"	11.7	5.8
<u>FORMULA (See TABLE 1)</u>			
<u>AMMONIATED SLURRY BEFORE KCl ADDITION</u>			
- Water	%	19.0	19.8
- NH ₃ : H ₃ PO ₄ mole ratio	-	0.97	0.92
- Temperature	°C	110	110
- Viscosity at 110°C	cP	90	47
<u>SLURRY AFTER KCl ADDITION</u>			
- Dissolution rate	min	30	60
- Free KCl in the dried slurry	%	4	4
- NH ₃ : H ₃ PO ₄ mole ratio	-	0.97	0.97
- Water	%	16.0	16.3
- Temperature	°C	103	103
<u>PRODUCT</u>			
- Free KCl	%	0	0
- Hardness	kg	2.5	2.5
- Caking index	-	15	15

TABLE 3 - Major line shifts of solid solutionsSOLID SOLUTION OF $(\text{NH}_4)_2\text{SO}_4$ IN K_2SO_4

<u>% $(\text{NH}_4)_2\text{SO}_4$</u>	<u>d_A°</u>
10	4.190
25	4.210
50	4.250
75	4.310
90	4.349

SOLID SOLUTION OF $(\text{NH}_4)_2\text{SO}_4$ IN $\text{K}_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$

<u>% $(\text{NH}_4)_2\text{SO}_4$</u>	<u>d_A°</u>
10	3.255
20	3.270
30	3.275
40	3.300
45	3.380

SOLID SOLUTION OF NH_4NO_3 IN KNO_3 II

<u>% NH_4NO_3</u>	<u>d_A°</u>
5	3.784
10	3.789
13.5	3.792

SOLID SOLUTION OF NH_4NO_3 IN KNO_3 III

<u>% NH_4NO_3</u>	<u>d_A°</u>
26	3.30
44	3.31

SOLID SOLUTION OF KNO_3 IN NH_4NO_3 III

<u>% KNO_3</u>	<u>d_A°</u>
10	3.21
20	3.20
30	3.19

TABLE 4 - X Ray diffraction data of ammonium sulphate nitrate double salts

<u>$(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$</u>		<u>$(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$</u>	
<u>d Å</u>	<u>I</u>	<u>d Å</u>	<u>I</u>
12.30	VW	9.93	MW
7.97	VW	7.52	VW
7.63	VW	6.70	VW
5.37	MW	5.45	VW
5.11	VW	5.22	VW
5.00	VW	4.95	S
4.76	MS	4.68	S
4.54	MW	4.21	VW
4.14	VS	3.78	W
3.99	W	3.46	VVW
3.96	W	3.30	VS
3.90	VW	3.19	VS
3.80	W	3.03	VVW
3.70	VW	3.00	VW
3.63	VW	2.93	M
3.41	VW	2.85	W
3.26	VS	2.65	VW
3.17	VS	2.59	VW
3.11	VS	2.51	VW
3.01	VW	2.48	S
2.98	W	2.40	VW
2.90	MS	2.32	VW
2.76	VW	2.25	VW
2.73	MW	2.12	VW
2.69	VW	2.00	VW
2.62	VS	1.98	VW
2.49	VW		
2.38	VW		
2.26	VW		
2.25	VW		
2.20	VW		
2.09	VW		

TABLE 5 - Results of experiments for compound fertilizer 12.12.17 production

		<u>Feed a</u>	<u>Feed b</u>	<u>Feed c</u>	<u>Feed d</u>
<u>PRODUCT</u>					
- Moisture	%	1.4	1.2	1.3	1.3
- NH ₃ - N	"	6.6	7.0	7.0	7.1
- NO ₃ - N	"	5.5	5.0	5.0	5.0
- Total N	"	12.1	12.0	12.0	12.1
- Water soluble P ₂ O ₅	(A) "	5.5	9.0	10.3	9.6
- Water and cytrate soluble P ₂ O ₅	(B) "	12.0	12.0	12.2	12.2
- Water soluble K ₂ O	(C) "	17.0	17.0	17.0	17.0
- Total K ₂ O	(D) "	17.2	18.4	18.4	17.3
- Water soluble P ₂ O ₅ yield	(A : B) "	45.8	75.0	84.4	78.7
- Water soluble K ₂ O yield	(C : D) "	98.8	92.4	92.4	98.3
- Hardness	kg	2.4	3.0	3.0	3.0
- Caking index	-	80	60	15	15
<u>CAPACITY</u>	tons/hr	35.0	25.0	35.0	38.0

TABLE 6 - 25.10.0 production

		<u>Operating conditions</u>	
		<u>a</u>	<u>b</u>
<u>MATERIAL FEED</u>			
- Phosphate rock	kg/ton of product	158	72
- 100% HNO ₃	"	75	80
- 100% H ₂ SO ₄	"	60	-
- P ₂ O ₅ from H ₃ PO ₄	"	60	50
- NH ₃	"	43	46
- NH ₄ NO ₃ 96%	"	605	625
- Superphosphate 18/20	"	-	162
<u>PRODUCTION RATE</u>	tons/hr	30	35
<u>AMMONIATED SLURRY</u>			
- Water	%	8.2	9.6
- NH ₃ : H ₃ PO ₄ mole ratio	-	0.97	0.97
- Temperature	°C	115	120
- Viscosity at 110°C	cP	28	19
<u>GRANULATION</u>			
- Recycle ratio	-	4.9	5.1
- Water content in input product	%	1.2	0.8
- Temperature	°C	80	79
- Slurry to granulation	tons/hr	37.5	22.5
- Recycle	"	150	180
- Water content in output product	%	2.3	2.2
<u>DRYING</u>			
- Water in input product	%	2.3	2.2
- Water in output product	"	1.3	0.8
- Input product temp.	°C	80	79
- Output product temp.	"	77	74
- Drier air temperature	"	78	74
- Evaporated water in the drier	kg/hr	2000	3000

TABLE 7 - Physical and chemical characteristics of 25.10.0 produced at two different operating conditions

		<u>A</u>	<u>B</u>
<u>CHEMICAL ANALYSIS</u>			
- Moisture	%	1.2	0.8
- NH ₃ - N	"	12.4	13.5
- NO ₃ - N	"	12.8	11.5
- Total N	"	25.2	25.0
- Water soluble P ₂ O ₅	"	8.0	6.0
- Water and cytrate soluble P ₂ O ₅	"	10.1	10.0
<u>AVERAGE GRANULE DIAMETER</u>	mm	3.4	2.7
<u>PHYSICAL CHARACTERISTICS</u>			
- 75,000-38 A porosity	cc/cc	0.05950	0.1123
- 560,000-75,000 porosity	"	0.00140	0.0017
- Total porosity	"	0.06090	0.1140
<u>TECHNOLOGY TESTS</u>			
- Hardness	kg	2.8	2.7
- Caking index at 45°C	-	18	12

TABLE 8 - 25.10.0 production with and without surfactant

		A	B
		<u>without surfactant</u>	<u>with surfactant</u>
<u>POWDER LEAVING THE CHIMNEY</u>	kg/hr	100	20
<u>CIRCULATING PRODUCT</u>	tons/hr	207	210
<u>PRODUCT SCREEN ANALYSIS</u>			
- + 4,000 mm	%	15.40	15.40
- 4,000 ÷ 3,000 mm	"	18.00	14.70
- 3,000 ÷ 2,000 mm	"	26.80	33.90
- 2,000 ÷ 1,000 mm	"	27.70	30.70
- 1,000 ÷ 0,500 mm	"	9.00	9.20
- 0,500 ÷ 0,300 mm	"	1.80	0.70
- 0,300 ÷ 0,150 mm	"	0.98	0.15
- 0,150 ÷ 0,100 mm	"	0.12	0.05
- 0,100 ÷ 0,075 mm	"	0.10	0.00
<u>PRODUCT AVERAGE DIAMETER</u>	mm	2.50	2.50
<u>PRODUCT PHYSICAL CHARACTERISTICS</u>			
- 75,000-39 Å porosity	cc/cc	0.105	0.118
- 560,000 ÷ 75,000 porosity	"	0.018	0.017
- Total porosity	"	0.123	0.135
- External specific surface	cm ² /gr	14.27	19.23
- Internal specific surface	m ² /gr	0.6286	0.69781
- Total specific surface	"	0.6300	0.7000
- Hardness	kg	2.7	3.3

TA/80/12 Use of chemical and physical data to improve the quality of granular fertiliser production by A. Barbera, R. Monaldi, Montedison SpA, Italy (Rapporteur F.G. Membrillera, S.A. Cros, Spain)

Q - Mr. B. AVENBERG, Supra, Sweden

You have an X-ray powder diffractometer that can carry out tests between 0-60° C temp. How did you study the system of $\text{NO}_3\text{NH}_4\text{-ClK}$ at 120° C?

A - There are two problems involved:

1) How to analyze equilibrium composition at 120° C.

2) How to make investigations on equilibrium solids. The first one is not a particular problem because once the solution at 120° C is taken away from the equipment, total ion content is analyzed.

With reference to the second one, once the solids have been collected on a filter (temperature of filtration 120° C), there is a step of drying with suitable solvents. Dried crystals are handled in a climatic controlled room in order to avoid water absorption, and in the same room X-ray diffractometry is performed. Without water, no (or little) reactions occur.

Q - Mr. C. HOEK, D.S.M., Netherlands

In table 2, you mention two particle sizes of potash. Have you ever done work with very small size KCl, e.g. 98% 100 ? With such fine potash we find with retention times 0.5 min. conversion of nearly 100%. Moreover if some potash does not react you will find no deterioration of the finished product.

A - We have never used such fine KCl crystals. It is obvious that dissolution rate can be related to crystal size. Thus for the 12-12-12 fertiliser dissolution rate must be very high.

Q - A practical figure of porosity seems to be $0.12 \text{ cm}^3/\text{cm}^3$. This means a porosity of 25% of the volume of the granules; this could be a great disadvantage to the bulk density and therefore to the cost of bags and transport.

A - Porosity of 12-12-12 compound fertiliser is 0.093 and 0.0798 in the mentioned two operating conditions and not $0.12 \text{ cm}^3/\text{cm}^3$. Porosity influences little bulk density which is more dependent on granule size.

Q - Mr. L.K. RASSMUSSEN, Superfos, Denmark

When producing 12-12-17s according to feed D, what will be your limitations on:

- 1) Chloride content in the K_2SO_4 and the final product.
- 2) Construction material for reactor 1?

A - We usually employ K_2SO_4 from Sicily which has a low Cl- content (less than 1%). We use SS AISI 316. KCl dissolution reactors are in Hastelloy-C.

Q - Mr. R. LOSTE, S.A. Cros, Spain

In page 16, you mention "the presence of surfactants has a positive influence on granulation". Please could you explain:

How much the granulation efficiency can be increased with surfactants and give some information about type of surfactant employed and quantity to be added to the granulator.

A - We must distinguish between products with an excessive granulation behaviour, and products with a bad granulation behaviour.

In the first case, the use of surfactants allow to reduce the recycle ratio while in the second case surfactants can be dangerous. The amount of surfactant added during granulation depends on the type of product. Usually the final product contains 150 ppm of surfactant.

Q - Mr. O.H. LIE, Norsk Hydro, Norway

When measuring the external specific surface area you pass anhydrous air across a bed of fertiliser particles. Since these particles have a finite water vapour pressure, you will obtain a certain amount of drying of the particles during the test. How does this affect the results? The correct way it seems to me should be to use air with a water vapour pressure equivalent to the Critical Relative Humidity of the fertiliser.

A - From our experience the result is not particularly affected by the drying of particles.

On the other hand what you suggest can well be done, but only after having measured the Critical Relative Humidity.

Q - Mr. L. THIRAN, Société Carbochimique, Belgium

Do you think that during sample manipulation for X-ray determination reactions can occur?

A - In order to avoid reactions during manipulation of products to be studied by powder X-ray diffractometry both slurries and fertiliser granules are first washed with alcohol-ether (water is thus taken off) and then dried under vacuum.

In addition manipulation is carried out under controlled air humidity. In the absence of water no further massive reaction takes place in the solids (except phase transitions of course).

Q - Do you prepare thin sections?

A - I talked about thin section preparation during the lecture and suitable slides have been shown. In this case too, manipulation of products is carried out under controlled air humidity.

Q - How do you perform caking tendency measurements?

Do you use fresh product or a conditioned one for the test?

A - During the lecture slides have been shown describing a fast method for caking tendency measurements.

For routine purposes caking tendency is measured on 24 hr. average samples. For research purposes instantaneous samples can be taken into consideration.

Samples are not conditioned before measurements which are performed under air pressure at two different temperatures (25° C and 45° C for 3 days). Results are of good value.

Q - Mr. A. CLAERBOUT, Société Carbochimique, Belgium

Can you say anything about crystal growth measurements?

A - Nucleation and growth rates can be well studied using a "continuous mixed suspension mixed product removal" crystallizer.

The kinetics of crystallization of calcium sulphate and ammonium nitrate have been studied by us, using a continuous laboratory crystallizer.

The crystallizer has to operate long enough to achieve steady rate. An analysis on the size distribution of crystals is made: screen analysis and/or microscopic analysis along well defined crystallographic directions.

A size distribution in terms of population density can be obtained (population density = $n = \lim_{L \rightarrow 0} \frac{N}{L}$ where $N =$ number of crystals in the range L).

If McCabe's L law applies (growth rate independent of crystal size) population density is given by $n = n^0 \exp(-L/rT)$.

Where n^0 is the population density of nuclei, L is a characteristic dimension of the crystal, r is the linear growth rate and T the holding time.

A semilog plot of data will give a straight line with the slope related by holding time to the growth rate, r . The intercept is the population density n^0 .

Effects of temperature, agitation, impurities can be studied.

References can be given on request.

Q - Mr. J.L. TORAL, S.A. Cros, Spain

The question refers to the study made in an industrial granulation plant of ammonium nitrate to increase the porosity of the granules.

You use anionic surfactants (organic matter) to modify the porosity during granulation. Which amount maximum?

What granulation temperature have you?

What grade of A.N. do you produce?

A - Anionic surfactants are used during the granulation of 26% NH_4NO_3 with a maximum amount of 100 ppm.
The granulation temperature is about 150° C.

Q - Do you think the equation shown in your paper establishing a relation between diffusivity and porosity can be applied to any grade of A.N. with the same granule size?

A - The derived relationship $D = 0.48 p^{3.60}$ between diffusivity D and porosity p was studied and found true for NH_4NO_3 26%, NH_4NO_3 34% and ammonium sulphate - nitrate 26%.

Generally speaking there is always a relationship like that. Actually there is an interaction between diffusivity and granule structure which has not yet been well studied.

Thus the derived constants must be verified for other products.

Q - Mr. A. HORNSHØJ-MOELLER, Superfos, Denmark

Has any work been done on NPK fertilisers containing for example 2% MgO? If yes, where do you add the magnesium, in form of kieserite to produce a fertiliser with only little tendency to caking?

A - Yes, we produced the 12-12-17 containing 2% MgO as kieserite. The salt is added to the reaction tank (reactor 1 of figure 4 reported in the paper). K_2SO_4 is added in stoichiometric ratio to CaO in the reactor and the rest in the dissolver before granulator.

Two ammoniation steps were used in order to control viscosity:

1) $\text{NH}_3 / \text{PO}_4\text{H}_3$ ratio = 0.7 - 0.8

2) $\text{NH}_3 / \text{PO}_4\text{H}_3$ ratio = 1.3

A free flowing product was obtained.