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PROCESS FOR THE MANUFACTURE OF COMPLEX FERTILISERS BY
NITRIC ATTACK OF PHOSPHATE ROCK AND DOUBLE EXCHANGE
WITH POTASSIUM SULPHATE

By

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1. PREAMBLE

In the production of complex fertilisers from nitric attack it is well known that:

- It is not possible to obtain fertilisers from only nitric attack, since the solubilisation of P_2O_5 is necessarily accompanied by the appearance of hygroscopic calcium nitrate.
- Calcium must be eliminated as far as possible to such a minimum quantity as to ensure that the P_2O_5 present is stoichiometrically linked to the free Ca, which, in form of dicalcium phosphate remains citrate soluble.
- To obtain completely water soluble P_2O_5 it is necessary to push the elimination of calcium below the stoichiometric ratio of bicalcium phosphate: the elimination must be complete to have P_2O_5 almost fully water-soluble in the products.
- The elimination of calcium anyway does not mean its extraction from the attack slurries, but it may also mean its transformation into a salt other than nitrate, which is not susceptible of reacting in retrogradation actions.

On the other hand the extraction of calcium from the attack slurries may take place in the form of either calcium nitrate or calcium sulphate. The various industrial processes now in application fall under three groups:

- 1) Processes in which the calcium contained in the phosphate rock remains in full in the product, but not in the form of calcium nitrate;
- 2) Processes whereby calcium is partially removed in the form of calcium nitrate;
- 3) Processes in which calcium is removed either in part or in full as calcium sulphate.

The processes of the first group include the so-called sulphonitric, phosphonitric and carbonitric processes, whereby the calcium which has been taken away from the link with P_2O_5 is respectively transformed into calcium sulphate by adding sulphuric acid, into bicalcium phosphate by adding phosphoric acid or calcium carbonate by adding carbon dioxide. Through the above processes, fertilisers are usually obtained with a limited concentration (14.14.0 - 10.10.10 - 14.14.14) with a low percentage of P_2O_5 soluble in water (about 25%). The increase in concentration and in the content of water-soluble P_2O_5 makes these processes less convenient on an economic point of view, since they require a greater use of phosphoric acid.

The Odda process and derivatives belong to the second group.

These processes are based on the principle of the complete conversion of phosphate ore with nitric acid into phosphoric acid and on the partial reparation of calcium nitrate from the attack slurry performed through crystallisation of the same at low temperature and by centrifugation or filtration. The percentage of calcium nitrate to remove, and consequently the crystallisation temperature, depends on the content of P_2O_5 in the finished product which is intended to be soluble in water.

To obtain 50% of P_2O_5 in this form it is necessary to separate about 70% of the calcium introduced with phosphate ore, starting from Florida rock.

By these processes, binary fertilisers are obtained with N/ P_2O_5 ratio 1 : 1, from 20.20.0 to 23.23.0 according to the calcium separated.

The main obstacle of these processes is the forming of large quantities of calcium nitrate (or ammonium nitrate) as by-products which are to be sold together with the fertiliser. This in fact represents an association commercially undesirable, if we bear in mind that the by-product, which prevails in quantity, is selling with greater difficulty.

To the third group the most recent processes belong which generally make use of ammonium sulphate, recovered from organic processes, to precipitate as sulphate the calcium which is removed from the cycle.

By these processes fertilisers are obtained with a high concentration and a high content of water soluble P_2O_5 (more than 90%).

The N/P₂O₅ ratio in the products is 2 : 1 (grade 28.14.0), ie a little unbalanced towards nitrogen.

There are patents (Nad - Ussac) whereby it is possible to reduce such ratio by effecting a partial separation of ammonium nitrate.

No industrial applications in the sense have however been reported.

This third group includes the Montedison process, called DS process, which shows the peculiarity of replacing ammonium sulphate with potassium sulphate. This process allows the introduction of the third nutrient element at the same time as the ion SO₄ precipitating and consequently it is applicable to the production of the NPK fertilisers free from chlorine, which are the most valuable ones on an agronomical point of view. A convenient industrial integration is assured by using potassium sulphate obtained from the kainite ore mined in the Montedison deposits in Sicily.

By this process, only through nitric attack, a fertiliser N - P₂O₅ - K₂O is obtained with an approximate ratio of 1 : 1 : 2.

To modify this ratio, which is strongly unbalanced towards the K₂O content, one can attack the rock not only with nitric acid, but also with sulphuric acid or by extracting potassium nitrate through crystallisation during the working stage.

Montedison has chosen the latter way which permits either to obtain KNO₃ for agricultural application, or, through a simple process of refining, KNO₃ at high purity for industry.

2. MONTEDISON'S DS PROCESS

The first surveys have been made in 1961.

In 1963 at the Research Centre of Vercelli a pilot plant with a capacity of 0.5 t/h of 18/18/18 grade was set up.

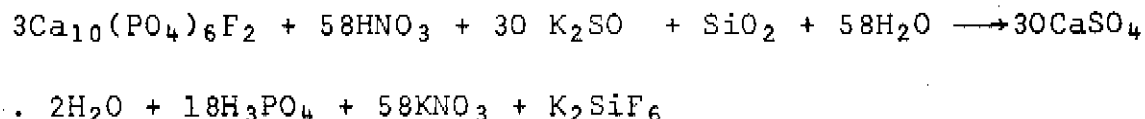
The perfectioning of the process, including the separation and the purification of the potassium nitrate covered about two years.

In 1968 the first plant came on stream, built in Sicily close to the site of the Porto Empedocle factory situated at about 30 Km from the kainite plants. The unit for the separation and refining of potassium nitrate went into operation in 1972.

The process is based on the solubility of phosphate ore with nitric acid and the precipitation of calcium through the reaction of double exchange between calcium nitrate and potassium sulphate.

The addition of sulphate is carried out during the stage of attack (the patent considers also the addition of potassium sulphate after the attack stage).

Consequently from fluoroapatite, considering the complete precipitation of calcium, the full reaction is as follows:



The slurry is filtered to remove calcium sulphate and the solution, neutralised with NH_3 , is conveyed to the production stage of the fertiliser.

Starting from Florida rock and executing the full exchange with K_2SO_4 , a basic fertiliser is obtained, mainly formed by di-ammonium phosphate and potassium nitrate with $\text{N}/\text{P}_2\text{O}_5/\text{K}_2\text{O}$ ratio 1.1 : 1 : 2.3 having the concentrations mentioned on the dry product: 14.6 : 12.7 : 30.

To modify the $\text{N}/\text{P}_2\text{O}_5/\text{K}_2\text{O}$ ratio the partial separation of potassium nitrate is performed.

It is easy to obtain a basic fertiliser with $\text{N}/\text{P}_2\text{O}_5/\text{K}_2\text{O}$ ratio 1 : 1 : 1 and with a nominal concentration 18 : 18 : 18.

In case one does not intend to obtain potassium nitrate as by-product it is always possible to modify the $\text{N}/\text{P}_2\text{O}_5/\text{K}_2\text{O}$ ratio by adding sulphuric acid in the attack stage or phosphoric acid or solid materials containing P_2O_5 in one of the subsequent steps.

This system has been worked out during the early years of the work.

The general scheme of the Montedison process is shown at Fig 1): it consists of the following operations:

- attack of the rock with nitric acid at 53% and simultaneous exchange with K_2SO_4 at 50% of K_2O , in reactors made of stainless steel provided with a stirrer. During the attack, the washing solutions of the gypsums are recycled. A system for the removal of heat has been devised in case of use of sulphuric acid, based on the prior mixing of H_2SO_4 with HNO_3 and cooling with liquified NH_3 .

The most serious problems which have arisen and which have been solved are the appearance of foams and the precipitation of double sulphates of calcium and potassium. The constant ratio of the numerous components, to keep the working conditions unchanged, is very critical.

- filtering of the attack slurry in view of the separation of gypsums and their washing on a tilting pan rotating filter.

The operation has required a difficult elaboration, the values of the liquid volumes being completely different from the ones concerning phosphoric acid and being subject to change according to the grades of the product.

Another problem, ie the very frequent clogging of the outlet pipes owing to crystallisation of K_2SiF_6 was solved by replacing steel with polypropylene resin (Moplen).

- pre-ammoniation of the slurry : needed to avoid considerable losses of HNO_3 or fluorine, with possible corrosion in the crystallisation of potassium nitrate; it is brought to a molar ratio $(NH_3) / (H_3PO_4) = 0.5$.
- pre-concentration of KNO_3 by cooling through adiabatic evaporation in vacuum. The two operations are to be performed in such a way as to ensure that the solution from which KNO_3 is separated has the ratio K_2O/P_2O_5 required by the manufacture of the fertiliser.
- separation of KNO_3 by means of a centrifugal machine by washing and drying the salt. The latter represents a fertiliser with the grade 13 - 0 - 44 and it can be obtained pure by a simple cycle of refining; the product has a concentration higher than 99% and it turns out to be practically free from chlorine and sodium, undesired in technical KNO_3 .
- concentration of the pre-ammoniated solution in double effect. Also this operation has raised considerable problems chiefly in connection with corrosion effects by the condensates: these problems have been cleared and solved.
- final ammoniation in the liquid phase;
- granulation with simultaneous ammoniation in the solid phase, by means of a rotating drum;
- drying, screening and crushing of the granules;

- cooling of the finished product;

At the moment of the granulation other solid products may be added, such as ammonium nitrate solution, micronutrients, etc.

The part of the plant concerned with the crystallisation of KNO_3 , long tested in a pilot unit, has regularly come on stream only recently.

At the Porto Empedocle factory, besides potassium sulphate, as precipitation agent of calcium, also ammonium sulphate has been used as residue of organic processes, obtaining the grades 28 - 14 - 0/25 - 10 - 0/, 20 - 10 - 10 etc. Of course in this case it is not possible to obtain KNO_3 as by product.

3. PRODUCTION OF COMPLEX FERTILISERS WITHOUT OBTAINING KNO_3 AS BY-PRODUCT.

The Porto Empedocle factory has been on stream for about four years operating with the DS cycle, without the by-production of KNO_3 , which has been decided later on.

The long period of operation has permitted the elaboration of the most economic chemical and physical working conditions.

As for the various plant sections they have been determined as follows:

3.1 Attack and precipitation conditions

To keep the most favourable working conditions, the check-up of the following parameters is very important:

equivalent ratio of attack

$\text{REA} = \text{equiv. H} / (\text{Equiv. CaO} - \text{Equiv. SO}_3 \text{ of rock})$

equivalent ratio of precipitation

$\text{REP} = \text{Equiv. SO}_3 / \text{Equiv. CaO} - \text{Equivalents of SO}_3 \text{ of rock}$

The two values which are related to the raw materials vary according to the rock analysis or the particular types of product desired and they are strongly critical to the crystallisation of gypsums and the losses of P_2O_5 and K_2O .

The following recommendations are to be observed:

temperature : 74 - 78° C
 water content in the slurry ≥ 42%

The values are maintained by adjusting the feeders and by checking the analyses of the slurries.

The capacity obtained in the step of attack and exchange is fundamentally conditioned by the gypsum crystallisation and it turns out to correspond to 1000 kilograms of P₂O₅ per day and m³ of the reactors.

3.2 Filtration and washing

The filtration formerly was effected on the basis of criteria drawn from the experience of working with phosphoric acid.

Since the ratios between filtrate, gypsum and washing water proved to be completely different, it was necessary to revise these criteria with the subsequent need to modify the filter and - at the end - the washing systems of the panel.

The problems have been well solved obtaining also, through the modification of the washing criteria, an extension of the filtration capacity to be evaluated in 30/40%.

The present specific filtration capacity is 8 t/d of P₂O₅ per m³ of filtrating surface starting from a filtrate containing 10% of P₂O₅. The water content of the gypsums is, on the average, lower than 20%.

Losses of P₂O₅, K₂O and N through the gypsums

At table 1) the losses are shown expressed as parts per 100 parts of nutrient elements.

The P₂O₅ yield is 98.5%, corresponding to a loss of 1.5 units in percentage. The loss of P₂O₅ soluble in ammonium citrate (co-crystallised) is 0.6 units i.e. particularly low in respect of the similar values for phosphoric acid. This is due in particular to the low concentration of P₂O₅ in the solution, which performs a favourable action in avoiding the co-crystallisation of P₂O₅ in the gypsum lattice.

This is valid, of course, with the proper control of the conduction parameters mentioned above.

The available K_2O is 96.5% accounting for a loss of 3.5 units. Out of these, as much as two units correspond to the forming of K_2SiF_6 and consequently they depend on the content in F and SiO_2 subject to attack of rock, particularly unfavourable with the Florida phosphate.

The loss in K_2O can be described in detail, as follows:

- inevitable loss due to K_2SiF_6
- loss in form of KNO_3 dissolved in the soaking water of gypsum
- losses due to the forming of double salts of the type $m CaSO_4 \cdot K_2SO_4 \cdot n H_2O$ among which pentasalt prevails ($5 CaSO_4 \cdot K_2SO_4 \cdot H_2O$) little soluble in water.
- the forming of pentasalt is favourably influenced by the decrease in the water content of the slurries, by the increase in temperature and by the time of retention in the attack and exchange reactors.

Thence the need to check these parameters avoiding to the stopping of the plant before conditioning the slurries.

The total K_2O yield amounts to 96.5%.
The loss of nitric nitrogen - a very small one - is due to the KNO_3 soaked up by the gypsums.
The yield of nitric N is 99.8%.

It is evident that such production can be obtained in a regular operation and they are particularly sensitive to the change of the reaction conditions, i.e. of the raw materials, which are at least one more than the case of phosphoric acid production.

The other working stages, if we exclude the concentration which, having a twofold effect, permits to save steam and has raised some corrosion problems, do not present any difficulty and they are similar to those of the normal processes for complex fertilisers.

4. MANUFACTURE OF COMPLEX FERTILISERS OBTAINING KNO_3

Of this production, at the beginning on an industrial point of view, we have already seen and worked out the parameters in a pilot plant.

Obtaining good crystals of KNO_3 , does not raise any problem, if the normal crystallisation requirements are observed.

The presence of P_2O_5 , within ample limits, does not affect the habit of crystals and the possibility of separating and washing the product.

Fig. 2 shows the isothermal lines of the solubility of KNO_3 in the ternary diagram $\text{KNO}_3 - \text{H}_2\text{O} - \text{H}_3\text{PO}_4$ with the industrial impurities of the Florida rock in the liquid phase. These isothermal lines can be expressed with an approximation to straight lines, through the following expression:

$$t = - 97.69 \log K + 67.5$$

where K is the weight ratio $\text{H}_2\text{O}/\text{KNO}_3$ and t is the temperature in C degrees.

The vapour pressures of the solution saturated with KNO_3 have also been determined, drawing the following expression:

$$\log p = a \frac{1}{T} 10^4 + b$$

where p = vapour pressure in torr

T = temperature kelvin degrees

$$a = - R . 0.0255 - 0.1984$$

$$b = - R . 0.5539 + 8,0339$$

$$R = \text{weight ratio } \text{P}_2\text{O}_5/\text{free water}$$

Fig. 3 shows an experimental diagram from which the above expressions have been drawn.

The optimum crystallisation temperature is comprised between 40 and 50°C based on the final $\text{K}_2\text{O}/\text{P}_2\text{O}_5$ ratio, which is desired.

During the production of KNO_3 the following fertilisers have been produced in the pilot plant:

17 . 17 . 17
11 . 22 . 16

with two different final $\text{P}_2\text{O}_5/\text{K}_2\text{O}$ ratios.

5. ECONOMIC CONSIDERATIONS

As mentioned, the fertiliser plant is in a condition to manufacture either products through double exchange with potassium sulphate or products through double exchange with ammonium sulphate. In the former case KNO_3 can be produced and the fertilisers are of the type free from chlorine, particularly suitable for tobacco, fruits, sugar-cane, rice, cotton, etc.

As an economic comparison, let us consider a plant with a capacity of 300,000 t/y of fertilisers, operating at double exchange with only potassium sulphate, in a condition, or not, to produce potassium nitrate, to be compared with a factory manufacturing 300,000 t/Y of similar fertilisers, with traditional raw materials.

The grades selected for the comparison are 17.17.17 through DS and 16.16.16 through the traditional process.

The costs are compared of :

- 17.17.17 through double exchange with by-production of KNO_3 (553 kilograms per 1000 kilograms of product)
- 17.17.17 through double exchange and use of sulphuric acid.
- 16.16.16 from phosphoric acid and ammonium nitrate + K_2SO_4 .

Table 2 shows the specific consumptions per industrial yield (chemical + mechanical losses starting from feed-stock raw material up to bagged product) for the grades mentioned above (and the other ones obtained from K_2SO_4).

KNO_3 is estimated at the value of Nitric Acid and of the K_2O from sulphate therein contained. In this way only the equipment for the crystallisation and separation of crystal is evaluated as part of the plant.

The intermediates have been evaluated at the total cost from a plant of an economic size with capital charges of 20%.

The rock phosphate is evaluated at the cost at which it is available in Italy, stored in a factory provided with harbour facilities. A plant with a capacity of 300,000 t/y calculated in Italian lire, can be evaluated at the present costs, erected, but with the exclusion of stores and factory facilities.

3,400 MLit	if fit to produce with traditional systems
5,100 MLit	if fit to produce complex fertilisers through double exchange, without producing KNO_3
5,600 MLit	if fit to produce complex fertilisers and KNO_3 .

The costs, excluding bagging and shipment, are shown at Table 3), more precisely:

column A)	fertiliser 17.17.17 through double exchange plus Nitrate
B)	fertiliser 17.17.17 through double exchange
C)	fertiliser 16.16.16 through traditional process.

From the comparison between the columns C) and B) and referring to an annual production of only 250,000 tons, it is possible to see that against a greater cost of a plant of 1,700 MLit, there is a lower working cost of 820 MLit/y accounting for 48% of the invested capital.

From the comparison between the columns C) and A) it appears that against a greater cost of the plant of 2,200 MLit there is a lower working cost of 1,400 MLit, corresponding to 64% of the invested capital.

The latter percentage should further go up, if we consider the equipment for the production and the possible granulation and refining of KNO_3 which, in this case, should be evaluated on the proceeds and not on the costs of the raw materials.

The above data appear to be of considerable commercial interest.

6. CONCLUSIONS.

An interesting industrial process has been set up in Sicily by Montedison to obtain fertilisers with water-soluble P_2O_5 .

This process permits to obtain on one hand NPK fertilisers free from Chlorine, on the other hand potassium nitrate for agricultural and industrial use.

The process appears to be economically convenient as compared with the traditional processes and we can consider the same effective in all its parts.

The economic convenience is strictly linked to the production of KNO_3 , which is advisable to push to the maximum, seeking the most suitable grades.

DISCUSSION

MR. I. MINI (Montecatini Edison, Italy):
One of the methods of eliminating calcium after nitric attack of phosphate rock for the production of complex fertilisers is that of precipitation as calcium sulphate and ultimate separation. In the case of separation of the calcium sulphate, ammonium sulphate, possibly deriving from organic processes, is generally used. The Montedison double exchange process belongs to this type of treatment. It was developed industrially at Porto Empedocle in Sicily. The new factor is that potassium sulphate is used instead of ammonium sulphate in precipitating the calcium. If the simple process of nitric attack and double exchange is used without further addition, products which are rich in potassium, as compared with the other fertilising elements, are obtained, i.e. a product titrating 14-3.3-20. Following pilot-scale tests, a double exchange industrial plant was built in 1968 very near the potassium sulphate production works. In 1972, this was supplemented by a potassium nitrate extraction unit. After attack and double exchange, carried out simultaneously, the gypsum is washed and the slurry conveyed to the fertiliser production units. In order to reduce too high a K_2O/P_2O_5 ratio either the phosphate rock may be attacked with nitric acid plus sulphuric acid, producing in practice phosphoric acid mixed with the slurry, in which case cooling is necessary or else the potassium nitrate must be separated from the filtered solution. With this system, the ratio can be reduced to a figure of less than one. Using each process, the product obtained is 18-18-18 or 17-17-17. Naturally other additives may be introduced, such as superphosphate, triple superphosphate, ammonium nitrate etc.

The process comprises the following operations: attack, with cooling if required, filtration of gypsum, pre-ammoniation, pre-concentration of the filtered solution and cooling, separation of the crystallised potassium nitrate, double-stage concentration of the solution, final ammoniation in slurry form, granulation and ammoniation with additives, drying and cooling of the product. To ensure smooth operation there must be clearly established values and therefore some parameters, i.e. the equivalent ratio of attack, which is the

ratio between the hydrogen ions and CaO in the phosphate rock, the equivalent ratio of precipitation, i.e. the ratio between the SO_4 and the CaO in the phosphate rock. The temperature is between 70 and 75°C while the water content of the solution should be a minimum of 42%. We have experienced several problems as a result of the ratio between the gypsum and the filtered solution differing from that of the phosphoric acid. These problems were solved by changing the original distribution between filtration and washing surfaces, and changing the washing system, i.e. modifying the filters.

We had a loss of yield in attack and double exchange of 1.5 for the P_2O_5 , including 0.5 as co-crystallised. The losses of K_2O were 3.0, including 2 as fluosilicate. The losses of nitric nitrogen were 0.2%. Of course these losses do not represent those of the whole production system.

From the economic standpoint, if we produce 17-17-17 with or without the production of KNO_3 , and if we compare it with chlorine free 16-16-16, we find that the product of double exchange is much more acceptable. If, on the other hand, we wish to compare it with a product containing chlorine, assuming again that the double exchange product is chlorine-free, the product with chlorine is almost comparable, but in this economic study we considered the value of the co-produced potassium nitrate as the sum of the value of the nitric acid and potassium sulphate. However, the potassium nitrate we produce is of a very high grade, i.e. one better suited to technical uses than as fertiliser, particularly as it is pure and contains absolutely no sodium or chlorine. If we also consider the plans for production and refining of potassium nitrate, we can see that the system we have studied is much more suitable, in comparison with products obtained by the normal system and with potassium chloride.

MR. L. K. RASMUSSEN (Superfos a.s., Denmark):
In recent years we have observed tremendous developments in the fertiliser industry. New technology and new processes have been introduced for reasons of competition.

To mention but a few:

1. The new phosphoric acid hemihydrate processes.
2. The application of solvent extraction methods to the production of phosphoric acid and potassium nitrate.
3. The introduction of spherodizer and prilling techniques.
4. The application of the ion-exchange technique to the production of complex fertilisers.
5. SO_4 -recirculation-processes applied to the production of complex fertilisers.

The DS-process developed by Montedison adds itself nicely to the above mentioned methods. Therefore I think Messrs. Mini and Monaldi deserve credit for their work.

The preamble describes excellently the removal and elimination of calcium. To complete the matter I should like to include, in the group of industrial processes, a fourth group: processes in which calcium is removed partly or completely, as calcium chloride.

Delegates heard yesterday two interesting contributions about processes in this category. With regard to the DS-process, let us immediately acknowledge that the basic chemical reaction is not an unknown one. This reaction takes place in the process belonging to group 1 known as the nitro-sulfolpotassic process. The principal difference between this and the DS-process is that the latter includes the removal of the gypsum resulting from the reaction whereas the gypsum remains within the fertilisers as a result of the nitro-sulfo-potassic process. The advantage of this removal is, of course, higher concentration of the desired components in the final product.

The potassium sulphate necessary for the DS-process is expensive. The price to be paid for equivalent quantities, expressed as K_2O , is 50 - 60% higher when obtained from potassium sulphate than with potassium chloride as a source.

As a means of producing chloride free NPK-fertilisers the DS-process appears to be very attractive indeed. Highly concentrated fertilisers with a high content of water soluble P_2O_5 are obtained apparently at a lower cost than is feasible in processes based on

the use of phosphoric acid. The problem of flexibility is avoided skilfully by means of the separation of potassium nitrate.

It would be natural to raise the question whether by using the DS-process it would be possible to produce chlorine-free NPK-fertilisers at a price lower than the production costs relating to a corresponding NPK-fertiliser containing chlorine. In my opinion the answer to this question is as follows: by using potassium sulphate as a potassium source we obtain in addition a means of removing the calcium as calcium sulphate.

When we produce NPK-fertiliser in the traditional way based upon potassium chloride and sulphuric acid we have to substitute the potassium sulphate with equivalent quantities of potassium chloride and sulphuric acid. As both processes involve removal of gypsum by filtering (the traditional NPK-process employs sulphuric acid for the production of phosphoric acid) and as the investments and running costs in both cases will be of the same order, the chances of the DS-process producing NPK-fertiliser more cheaply than the traditional method utilising potassium chloride will depend on whether the price of potassium sulphate is lower than the combined cost of the equivalent quantities of potassium chloride and sulphuric acid.

Assuming the following prices:

K_2SO_4	\$55/t
H_2SO_4	\$15/t
KCL(60%)	\$40/t

It appears that the combination of potassium chloride and sulphuric acid is approximately 25% lower in price than the equivalent quantity of potassium sulphate.

Therefore I must conclude that the DS-process can only be economically advantageous if we compare the costs with the production costs for chlorine-free NPK-fertilisers. However, I am of the opinion that chlorine-free NPK-fertiliser can only be produced at a price equal to or lower than that of traditional NPK-fertiliser containing chlorine if the production is based upon the cheaper potassium chloride.

Concluding these remarks I would like to have your comments on the following questions:

1. Why do you call your process "double exchange"?
2. What is the maximum chloride content of the potassium sulphate which you allow?
3. Would you be kind enough to state the REA and REP proportions for Florida and Kola phosphates?
4. What percentage of the calcium from the phosphate rock remains with the gypsum?
5. What construction materials did you use for the evaporation plant?
6. What is the production capacity of your industrial plant (expressed as tons K_2O /day)?
7. You have succeeded in convincing your readers that the process conditions have to be maintained within very narrow limits. In this connection, could you indicate to us the plant availability expressed as a percentage of total time for the industrial plant?
8. Referring to 2b, we should like to have your opinion on the consumption of raw materials in relation to the analysis of the final product. The figures indicate losses as follows:

Florida

N : 5,5%, P_2O_5 : 7,0% (34,0% P_2O_5), K_2O :8,0%

MR. MINI:

1. The title "double exchange process" was devised by chemists, who referred to the reaction between potassium sulphate and calcium nitrate, to give gypsum and potassium nitrate, as a double exchange. Now, of course, it is a traditional name which has remained as it was first used and is merely a question of history.

2. The maximum quantity of Cl. We use the potassium sulphate produced by one of our plants. The chlorine content of this potassium sulphate is 0.1%. But we had some infiltration of sea water in the washing of the gypsum, because the plant site is very short of water. For this reason we

found in practice that if we have a content of 0.2 it is quite acceptable. We have no further knowledge of higher contents.

3. In answer to question 3 on the ratio of attack and the ratio of precipitation of Florida and Kola phosphates, we tested only Florida phosphates. And we can say that the equivalent ratio of attack and the equivalent ratio of precipitation may change and there are some variations if they do change. We found that a good value was 1.04 for both.

4. On the fourth question about the quantity of calcium from the phosphate rock found in the gypsum, this percentage depends on the equivalent ratio of attack and the equivalent ratio of precipitation, i.e. if we have a very high equivalent ratio of attack we have a large quantity of gypsum in the solution. If we have a high ratio of precipitation, we have a smaller quantity of gypsum in the solution. With the above values, i.e. 1.04 for the two, we know that the quantity of gypsum remaining in solution in the filtered solution, i.e. the quantity of calcium, is 5% of the calcium in the phosphate rock.

5. On the question of construction materials for the evaporation plant, we used 316 L steel with welded tubes. We did experience corrosion, but have now found a system of preventing it almost entirely.

6. We produce 100 tonnes K_2O daily. Our bottleneck is availability of nitric acid.

7. On the subject of yield, this is virtually unrelated to the production unit because it is limited only to the effect on the yield of raw materials. In general, we may consider that the yield in terms of time is 95% over the year, including of course the change virtually every 20 days of the grade produced.

8. The losses we have considered are only the filtration losses. But we also have losses through having a grade higher than that shown, because Italian law requires that the guaranteed content must be maintained in respect of all nutrients. Then there are the actual physical losses, since the consumption figures considered are reckoned from the stored raw material to the bagged product, ready for despatch.

MR. O. H. LIE (Norsk Hydro a.s., Norway):

My question is about table No.7 in the paper, where the losses of P_2O_5 , K_2O and N in the gypsum amount to 7% of feed raw materials. It seems to me that one of the basic problems both in this process and in the ion exchange process we discussed yesterday is the fact that K is present in the digested liquor where most of the fluorine is also found. So K is tied to the fluorine component. This simply means that the amount of K lost as potassium fluosilicate is proportional to the fluorine, and consequently it is proportional to the P_2O_5 present. Now this is relevant to table 1 where you should have shown the K_2O/P_2O_5 ratio used in production. In other words if you have a material very rich in K_2O and low in P_2O_5 , the percentage loss of K_2O as K fluosilicate is going to be much lower because the part made up of K fluosilicate will be very small. To make the answer simpler, in table 1 what was the K_2O/P_2O_5 ratio used when you had these particular numbers?

MR. MINI: You are right in saying that the largest loss of potassium is in the form of fluosilicate. Of course this depends not only on the fluorine content of the phosphate rock but particularly on the form of silica in the phosphate rock, and the Florida phosphate we used contains a form of silica which is not particularly favourable to the production of phosphate, i.e. the formation of fluosilicates is favoured. I think that with other types of phosphates we can reduce this loss, but I do not as yet know. And of course if we use sulphuric acid these losses will rise. They are regarded as loss from the nitric attack. Account needs to be taken of this.

MR. G. MIDGLEY (Foster Wheeler, U.S.A.):

I have two questions. The first one: I should like to know whether you had any corrosion problems in the reactor due to the presence of the chloride contained in the potassium sulphate? In your paper you specify a very low chloride content, but the potassium sulphate which is commercially available usually contains 1 to 1.5%

The next question: Is it necessary to wash out the filtration section from time to time? On a conventional phosphoric acid plant, you have to wash out at different points at intervals of one or two weeks.

MR. MINI: On the subject of corrosion in the reactor, we have had no corrosion at all at any time whatsoever. I do not know whether this is the result of the low chlorine content of our potassium sulphate but, in practice, we have had no trouble in this area. All corrosion has been associated with the concentrators.

In answer to the second question, I said that we had had considerable problems with filtration. One was the formation of potassium fluosilicates; not gypsum, but potassium fluosilicates in the pipework. We have in practice solved this problem by replacing the original stainless steel pipes with polypropylene pipes and, in present circumstances, a weekly wash of a few hours is sufficient.

DR. W. BOOS (Gewerkschaft Victor, Germany): I find it very surprising that Mr. Mini should say that potassium losses in the gypsum are so low and they are to be explained partly by the fact that the greatest part is present in the form of potassium silico fluoride.

We too have been operating a similar reaction process in our plant for the past 20 years, in which calcium nitrate is reacted with potassium sulphate. We have never succeeded in obtaining such low potassium sulphate losses. Apart from losses in the form of potassium silico fluoride further potassium sulphate losses may also occur as a result of the formation of double salt syngenite or pentasalt.

I should be very pleased to hear your explanation of these low potassium sulphate losses. In addition lm^3 reaction volume per ton P_2O_5 per day seems to me to be extremely small, i.e. the exchange of potassium sulphate into potassium nitrate must take place in a remarkably short time.

My question is, therefore, how finely do you grind the potassium sulphate?

Furthermore, we have been able to establish that in the presence of chlorides the formation of pentasalt is considerably accelerated. Can you tell me how much chloride there is in your potassium sulphate, or how much chloride is present during the conversion to potassium sulphate in the reaction solution?

MR. MINI: I do not recall the exact degree of fineness of grinding. I could send you the granulometry diagram, but at the moment I cannot recall the granulometric analysis. About the chlorine I cannot in practice say anything. We did formerly have considerable losses in the form of double sulphate, a complex salt of potassium and calcium sulphates, but we reduced it simply by adjusting the equivalent ratio of attack and the equivalent ratio of precipitation to bring it to a minimum. We were able to reduce the losses of potassium in the gypsum to a minimum.

TABLE No 1

PROCESS FOR THE MANUFACTURE OF COMPLEX FERTILISERS BY NITRIC
ATTACK OF ROCK AND DOUBLE EXCHANGE WITH POTASSIUM SULPHATE.

Losses of P_2O_5 , K_2O and N in gypsum expressed as percentage
of feeded raw materials.

Fertiliser unit	Units	Values
P_2O_5 water soluble	% in weight	0,7
P_2O_5 insoluble	"	0,2
P_2O_5 co-crystallised	"	0,6
P_2O_5 total	"	1,5
K_2O water soluble	"	0,7
K_2O as K_2SiF_6	"	2,0
K_2O in double sulphates	"	0,8
K_2O total	"	3,5
N total	"	0,2

TABLE 2

		17.17.17 DS		16.16.16	11.22.16S	20.10.10 S	10.15.20S		
		(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Florida rock	t/t	0,569	0,543		0,562	0,306	0,326	0,326	0,273
Sulphuric Acid	t/t		0,259		0,290		0,151	0,019	
Nitric Acid	t/t	0,747	0,392	0,247	0,251	0,346	0,471	0,557	0,311
Ammonia	t/t	0,116	0,116	0,144	0,078	0,0525	0,135	0,112	0,049
P ₂ O ₅ in phosphoric acid	t/t			0,171					0,006
Superphosphate 0.18.0	t/t				0,256				0,345
Superphosphate 0.44,5.0	t/t					0,291			
K ₂ SO ₄ 50% K ₂ O	t/t	0,880	0,374	0,331	0,354	0,342	0,222	0,219	0,424
Anticaking	t/t	0,003	0,003	0,004	0,003	0,003	0,003	0,003	0,003
Filler	t/t	0,057	0,057	0,026			0,147		
Steam	t/t	0,52	0,4	0,16	0,4	0,4	0,4	0,4	0,4
Electric Power	kWh/t	95	80	65	80	80	80	80	80
Water	m ³ /t	50	37	25	40	40	40	40	40
Fuel oil	kg/t	20	20	20	20	20	20	20	20
KNO ₃ by product (100%)	t/t	0,537	-	-	-	-	-	-	-
Ammonia N	%	9,0	9,0	11,0	6,0	4,0	10,4	11,1	3,7
Nitric N	%	8,2	8,2	5,2	5,2	7,2	9,8	9,1	6,5
Total N	%	17,2	17,2	16,2	11,2	11,2	20,2	20,2	10,2
Water soluble P ₂ O ₅	%	15,6	15,6	15,3	18,2	16,0	9,2	3,5	12,2
Water citrate soluble P ₂ O ₅	%	17,2	17,2	16,2	22,2	22,2	10,2	10,2	15,1
K ₂ O	%	17,2	17,2	16,2	16,2	16,2	10,2	10,2	20,2

- (a) From nitric attack and KNO₃ crystallisation
 (b) From nitric attack plus K₂SO₄
 (c) From classical via H₃PO₄
 (d) From nitric attack plus H₂SO₄
 (e) From nitric attack and partial double exchange
 (f) From nitric attack plus H₂SO₄
 (g) From nitric attack and partial double exchange
 (h) From nitric attack and P₂O₅

TABLE No 3

17.17.17 S 16.16.16 S

		(a)	(b)	(c)
Florida Rock	8350 Lit/t	4.750	4.660	
H ₂ SO ₄ 100%	12000 "		3.100	
HNO ₃ 100%	16700 "	12.200	6.550	4.130
NH ₃	32500 "	3.750	3.840	4.680
P ₂ O ₅ da acido fosf.	75000 "			12.800
Pot. Sulph.50% H ₂ O	32000 "	28.150	11.950	10.600
Anticaking	50000 "	150	150	150
Steam	1680 "	1.000	750	300
Electric power	6,0 Lit/kWh	600	500	400
Water	4 Lit/m ³	200	150	100
Fuel oil	14 Lit/kg	300	300	300
KNO ₃ by product		21.600*		
		29.500	31.950	33.460

Fertiliser cost 16.16.16 referred to the grade 17.17.17:35.550 Lit/t.

Difference C - A 6.050 Lit/t

Difference C - A 1.512 MLit/year (250.000 t/year)

Difference C - A 1.412 MLit/year (considered fixed cost 100 MLit/year)

Difference C - B 3.600 Lit/t

Difference C - B 900 MLit/year

Difference C - B 820 MLit/year (considered fixed cost 80 MLit/year)

* Evaluated as K₂SO₄ and corresponding HNO₃ (5.550 + 16.100)