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THE CONVERSION OF CALCIUM NITRATE ORIGINATING IN A NITRO-PHOSPHATE PLANT WITH A VIEW TO IMPROVING THE EFFICIENCY, AS WELL AS A SURVEY OF THE POSSIBLE APPLICATIONS OF THE PRODUCTS

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ABSTRACT

The known processes used in the Hoechst conversion unit are described with the aid of a process diagram. The essential process steps with their specific equipment, the products and the economic aspects of the plant are discussed.

The plants of the FERTILIZER CORPORATION OF INDIA LTD. in Trombay and the PAKARAB FERTILIZERS LTD. in Multan, which are at present under construction, are used as examples to explain improved process steps based on a better method of washing out the  $P_2O_5$  which adheres to the calcium nitrate.

In conclusion it is pointed out which criteria are important for designing the Odda process with a conversion unit.

INTRODUCTION

The calcium nitrate conversion unit has now been in operation at the Hoechst works for ten years. This unit processes the calcium nitrate, which is obtained in the Odda plant, to ammonium nitrate and calcium carbonate. Both products are further processed in a calcium ammonia nitrate (CAN) plant. Part of the calcium carbonate produced is sold for special purposes. Any surpluses are also sold, so there is no "calcium problem" similar to the "gypsum problem" encountered when digesting phosphate rock with sulphuric acid. Thus, all components of the phosphate rock are utilized. The  $P_2O_5$  is converted to NP or NPK fertilizers and the CaO is converted to technically-pure calcium carbonate which is used for the CAN production together with ammonium nitrate.

The feedstocks required are: phosphate rock, nitric acid, ammonia, carbon dioxide and, if necessary, potassium salts, and traces of nutrients. This process does not require sulphuric acid for the production of fertilizers.

1. The Hoechst conversion unit

1.1 Process diagram

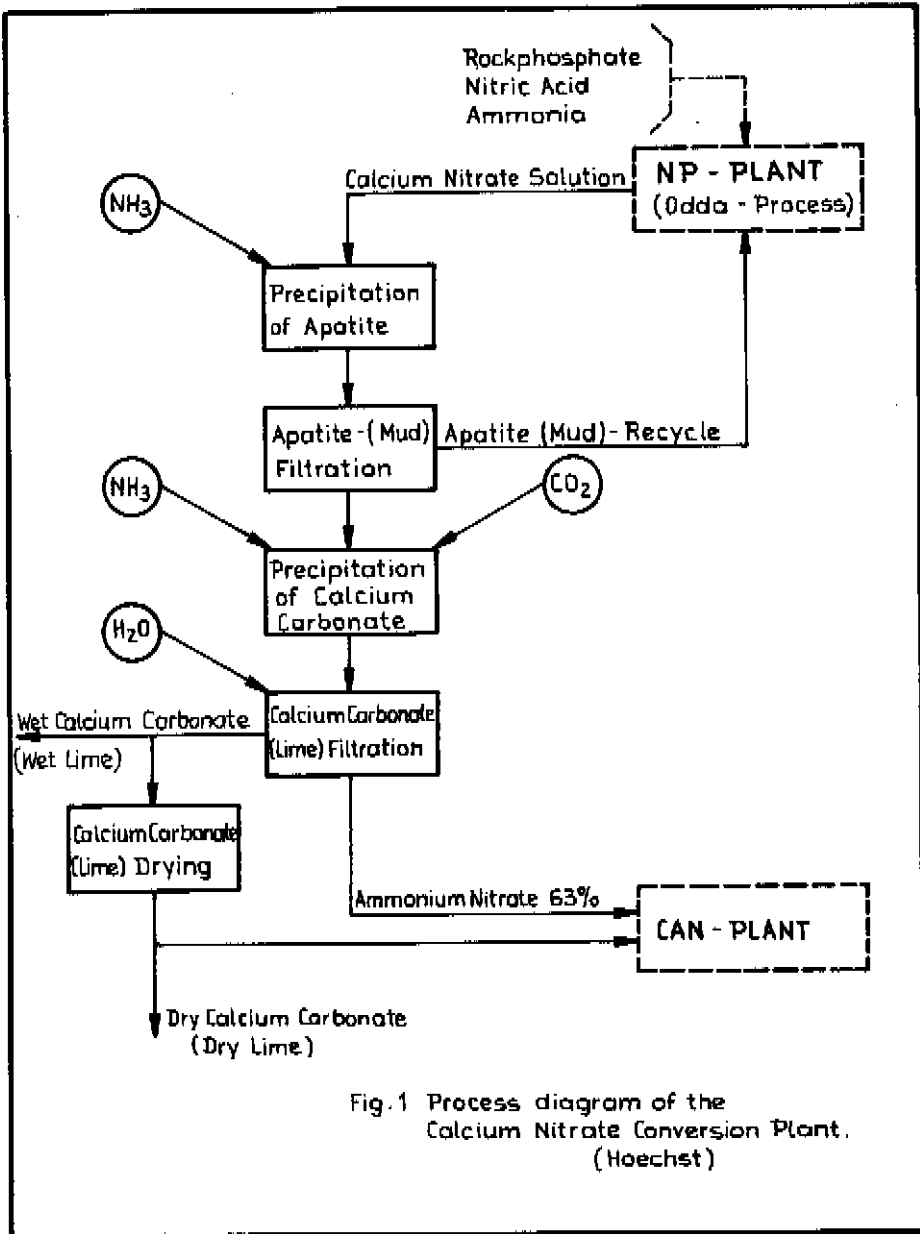
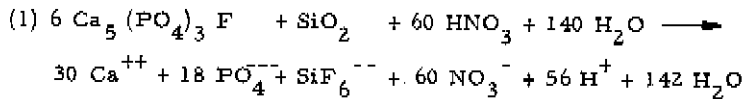


Fig.1 Process diagram of the Calcium Nitrate Conversion Plant. (Hoechst)

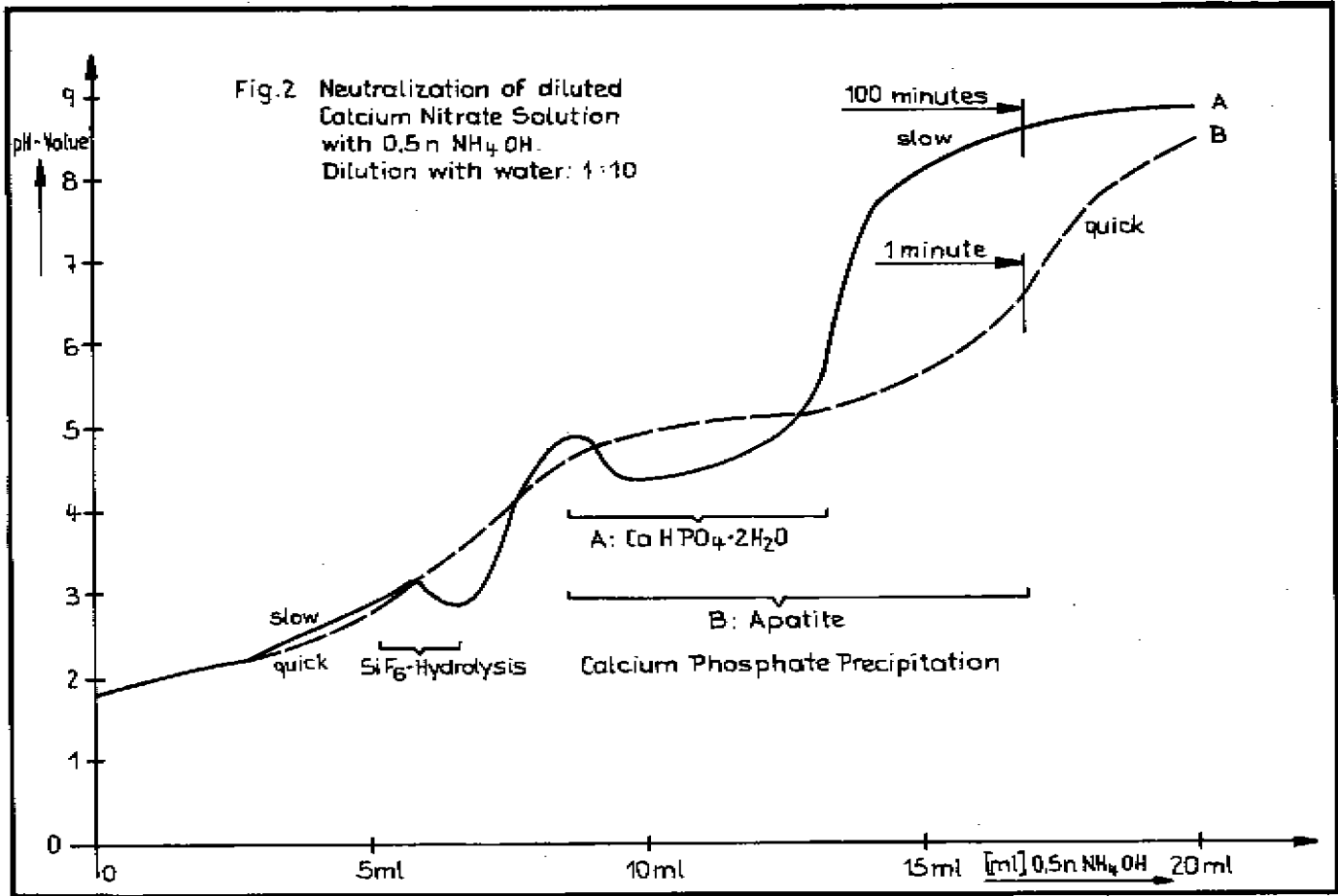
### 1.2 Apatite precipitation by neutralization with ammonia

In the Odda part of the nitrophosphate (NP) plant the calcium nitrate tetrahydrate crystals ( $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ ) are separated in single-stage pusher centrifuges. When the tetrahydrate has been removed from the NP solution, the tetrahydrate is still contaminated by small quantities of NP solution. After the tetrahydrate has been melted with steam, the approx. 60 % calcium nitrate solution contains approx. 2 %  $\text{P}_2\text{O}_5$ , because the NP solution is not washed out in the centrifuges.

Before the actual conversion, the adhering  $\text{P}_2\text{O}_5$  is precipitated mainly in the form of calcium phosphate with apatite structure under defined conditions. Apart from the  $\text{P}_2\text{O}_5$  that means  $\text{PO}_4^{--}$  the acid CN solution is polluted to a considerable extent by fluorine in the form of fluorosilicates. This is formed during the digestion of phosphate rock.

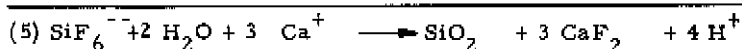
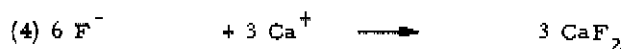
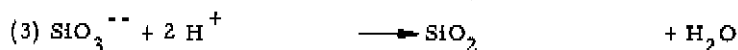
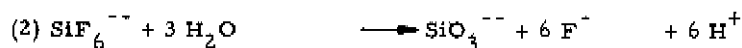


During neutralization with ammonia, the two main impurities,  $\text{PO}_4^{--}$  and  $\text{SiF}_6^{--}$ , should react in such a manner as to produce a precipitate which can be easily filtered. In order to understand why a continuous, single-stage neutralization process under strict observance of a certain pH value produces the best results, this process will now be explained in more detail with the aid of Fig. 2.

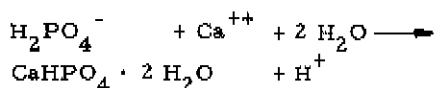


The pH value will change as shown by curve A when an acid CN solution is diluted with water in a ratio of 1 : 10 and slowly neutralized with ammonia.

The hydrolysis of  $\text{SiF}_6^{--}$ , which proceeds according to the following equation, starts at a pH value of 3.2



The  $\text{H}^+$  ions which are formed during hydrolysis cause the pH to drop to 2.9, despite the supply of  $\text{NH}_3$ . After hydrolysis has been completed, the pH rises and then falls again to 4.9. This is caused by the  $\text{H}^+$  ions which are formed during the precipitation of the dicalcium phosphate dihydrate (Brushite-structure)



Curve B, fig. 2 shows the trend of the pH value during rapid neutralization. It is hardly recognizable at this point that two reactions take place. More ammonia is required during slow neutralization until the pH reaches 6.5. The reason for this is, that an increased alkaline precipitate, with apatite structure is obtained. During continuous neutralization  $\text{SiF}_6^{--}$  hydrolysis and calcium phosphate precipitation inevitably take place simultaneously. The  $\text{F}^-$  ions primarily produced during hydrolysis as shown in equation (2) can be incorporated in the apatite. By this process the precipitation of the calcium phosphate in the form of apatite  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})$  is favoured. The apatite can obviously also include some of the impurities which are contained in the CN solution, such as Si, Al, Fe and Mg.

The following conditions must be met in order to obtain an apatite precipitate which can easily be filtered:

- low viscosity of the solution (below 10 m Pa.s)
- high temperature (above 80 °C)
- vigorous stirring
- constant pH value (approx. 4.5), depending on the kind of rock phosphate

If the pH value is exceeded even slightly from the pH value found favourable by testing, this will result in a precipitate which is extremely difficult to filter. Therefore there are always two pH meters in operation so that the pH-measurement can be changed over immediately in the event of a disturbance.

### 1.3 Apatite mud filtration

The precipitated apatite and other impurities are filtered out of the CN solution by means of rotary drum filters. The following figures represent a typical mud analysis:

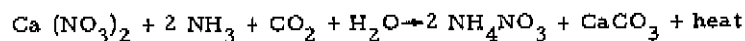
32 % w/w apatite, 10 % w/w  $\text{NH}_4\text{NO}_3$ ,  
30 % w/w  $\text{Ca}(\text{NO}_3)_2$ , 26 % w/w  $\text{H}_2\text{O}$

and the rest are inerts.

The apatite content can vary between 28 % and 35 %. As this quantity is 10-12 % of the  $\text{P}_2\text{O}_5$  feedstock introduced, used in the Odda plant, the apatite mud is fed back to the phosphate rock digester of the Odda plant. There, the apatite is digested again with nitric acid.

### 1.4 Precipitation of calcium carbonate

Calcium nitrate is converted to ammonium nitrate by means of carbon dioxide according to the equation:



As the formation of the two calcium carbonate modifications vaterite and aragonite is undesirable due to the slow growth rate, calcium carbonate is precipitated as coarse-grained calcite under the following conditions:



pH value: 7.8 - 8.2  
temperature: 60 - 90°C  
CO<sub>2</sub> excess: approx. 10 %

The stoichiometric ratio of ammonia to calcium nitrate is continuously checked by means of analyses.

Calcite is precipitated in the form of spherulites. Fig. 3 shows a specimen of a spherulite with a diameter of approx. 0.1 mm.

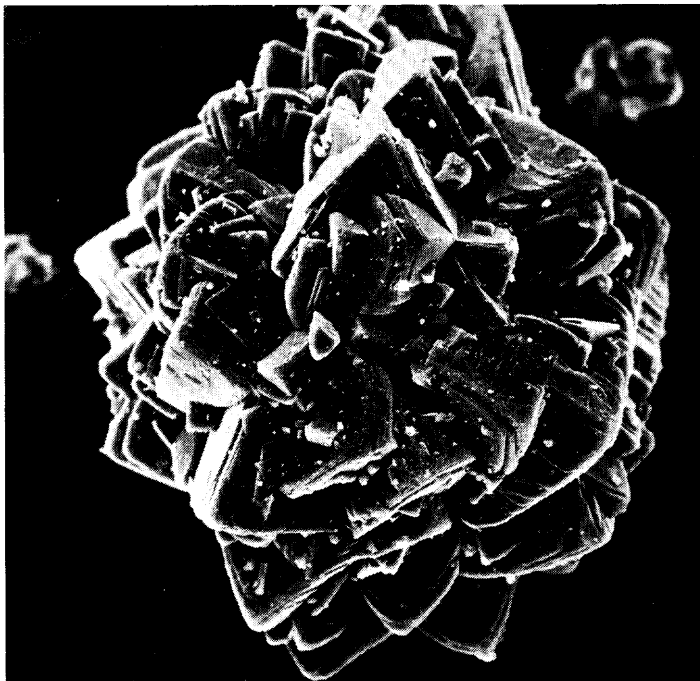


Fig. 3 Calcite spherulite, diameter approx. 0.1 mm

Suspension containing 24 % calcium carbonate in a 65 % ammonium nitrate solution is withdrawn from the conversion reactor. The reactor is of a special design developed by Hoechst AG, as shown in fig. 4. The gaseous CO<sub>2</sub> is introduced at the bottom, beneath the lowest cooling zone. Ammonia is fed to the reactor at three different levels, each one being situated beneath a cooling zone. In order to avoid NH<sub>3</sub> losses the CN solution is added at the top through the superposed scrubber.

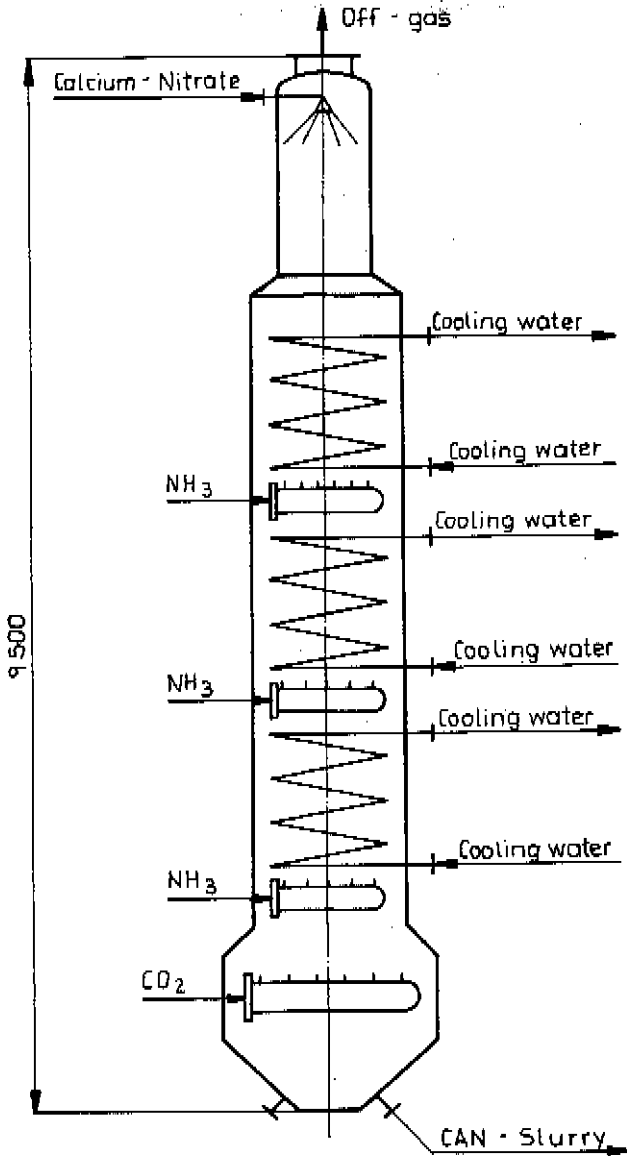


Fig. 4 Conversion Reactor  
with Scrubber

### 1.5 Calcium carbonate filtration

The filtration section consists of the first filter with two washing zones, a slurring vessel and the second filter which likewise has two washing zones. Rotary drum filters are used with chain removers for the filter cake. After it has been washed with fresh water, the filter cake contains a maximum of 13 % water and max. 0.15 % adherent ammonium nitrate. The ammonium nitrate solution produced contains 63 % ammonium nitrate.

### 1.6 Lime drying

The filter cake is dried in a drying tube by means of hot gas of a temperature of approx. 550°C. The gas outlet temperature and the calcium carbonate temperature are approx. 130°C. The fine-grained calcium carbonate is removed from the exhaust gas by means of two cyclones. The exhaust gas is finally purified by wet scrubbing.

### 1.7 Products

#### 1.7.1 Ammonium nitrate

The 63 % ammonium nitrate solution contains approx. 0.01 % calcium carbonate that was not retained by the filter and approx. 50 ppm dissolved  $\text{Ca}^{++}$  ions.

The quantity of organic impurities which originate from the phosphate rock, flotation aids and from anti-foam agents is so small that this ammonium nitrate is perfectly suitable for the production of calcium ammonium nitrate and other fertilizers containing ammonium nitrate.

#### 1.7.2 Calcium carbonate

The conversion section is operated in a manner as to ensure that the lime produced is very suitable for the production of calcium ammonium nitrate.

The physical and chemical data of the lime produced are as shown in table 1:

#### Table 1

Physical and chemical data of the calcium carbonate obtained in the conversion of calcium nitrate.

calcium carbonate, dry (dry lime)

|  |   |
|--|---|
| crystal structure:                         | calcite   |
| shape of particles:                        | spherulite  |
| size of particles:                         | 35 - 55 %, larger than 63 $\mu\text{m}$   |
| screen analysis:                           | approx. 10 % larger than 100 $\mu\text{m}$<br>approx. 40 % between 63-100 $\mu\text{m}$<br>approx. 25 % between 40-63 $\mu\text{m}$<br>approx. 25 % smaller than 40 $\mu\text{m}$ |
| bulk density:                              | 1.2 $\text{g}/\text{cm}^3$  |
| specific surface:                          | 0.6 $\text{m}^2/\text{g}$   |
| blaine test:                               | 900 $\text{cm}^2/\text{g}$  |
| degree of whiteness                        |   |
| compared to MgO (blue filter R 46):        | 78 - 88 %   |
| pH value (1 g + 10 g demin. water):        | 9.5-11.5  |
| humidity:                                  | less than 0.05 %  |
| soluble salt as per DIN 55918:             | approx. 0.18 %  |
| components insoluble in hydrochloric acid: | approx. 0.01 %  |
| CaO:                                       | approx. 54.5 %  |
| adherent ammonium nitrate:                 | approx. 0.15 %  |
| nitrate-N occluded:                        | approx. 0.15 %  |
| ammonium-N occluded:                       | approx. 0.15 %  |
| $\text{P}_2\text{O}_5$ , F, Na, Mg, Sr     | approx. 0.05 % each   |
| Fe, Si, S                                  | less than 100 ppm each  |
| Mn, Al, Cr, Ba, Cu:                        | less than 10 ppm each   |
| Cd, Pb, Se, Mo:                            | less than 1 ppm each  |
| As, V:                                     | less than 0.5 ppm each  |
| Hg   | less than 0.1 ppm   |

These data depend on the origin of the phosphate rocks treated and the quantity of matter insoluble in the calcium nitrate, handled in the plant. It should be mentioned that the occluded nitrate and ammonium nitrogen cannot be removed by washing and that their quantity cannot be determined until the dry lime has been dissolved in acid. The adherent ammonium nitrate can be almost completely washed out, but this requires a greater effort.

The portion of  $P_2O_5$  and F and therefore the degree of whiteness depend on the quantity of matter insoluble in the calcium nitrate solution processed in the plant and which could, if necessary, be further purified. The heavy metal content in the lime is very low.

### 1.7.3 Possible applications of calcium carbonate

The major portion of the calcium carbonate produced is generally used for the production of calcium ammonium nitrate. It is mainly the cement industry that takes any surplus owing to the low proportion of  $P_2O_5$  and F, the lime can be used for the manufacture of white cement without the addition of natural lime.

Other practical uses have already been found for dry lime in the manufacture of scouring powders, fire-extinguishing powder and as calcium feedstock for producing dicalcium phosphate dihydrate which is used in the manufacture of tooth paste.

It is e. g. also suitable for producing so-called liquid scouring powder and filler for internal building work.

Pollution control is another sphere for which the lime can be used. Typical applications are deacidifying of waste waters and, due to its high degree of purity which thus prevents the formation of slag, the desulphurization of waste gases.

In agriculture, calcium carbonate can be used as lime fertilizer and processed to fodder. The low content of undesirable trace elements, such as F, As, Pb, Hg, Ca, Cr<sup>VI</sup>, Cu, Se, Mo and V is favourable for the preparation of fodder. Taste tests showed that there was no difference from the usual fodder- $CaCO_3$ .

There are many possible applications for calcium carbonate if it is in fine-grained form, which can be obtained by other precipitation conditions or by dry or wet grinding. The lime can then be used as filler, e. g. in the paper, paint and plastics industry.

The lime can also be burnt, the heat of the waste gases from the combustion section being used to dry the wet lime. During combustion, highly-active calcium oxide (CaO) is produced, which can be processed to standard grade calcium hydroxide ( $Ca(OH)_2$ ) according to DIN 1060 in a lime slaking machine.

## 2. Improved equipment and better efficiency of conversion units

Taking as an example the plants of the FERTILIZER CORPORATION OF INDIA and of the PAKISTAN FERTILIZERS LTD., which are designed in collaboration with STAMICARBON BV as licensor for the NP-fertilizer plants, with HOECHST-AG as licensor for the CN-conversion plants and with UHDE as engineering company, we would like to illustrate the latest developments in regard to conversion units.

### 2.1 The fertilizer complex of FCI/Trombay

The complex comprises a NP fertilizer plant with an Odda plant and a calcium nitrate conversion unit. The capacity of the NP plant is 1200 tpd NP of the grade 1:1. The  $P_2O_5$  water solubility in the fertilizer product is 60 %.

The products of the conversion unit are: ammonium nitrate solution, of which two thirds are supplied to the NP unit, one third after concentration to 80 %, to an existing NP plant, and 330 tpd calcium carbonate. We would now like to describe the improved process steps in more detail.

#### 2.1.1 Improvement of the filtration of apatite mud

The NP solution which adheres to the tetrahydrate is washed out by cooled nitric acid to a  $P_2O_5$  content of 1.1 %. This is done by using a two-stage pusher centrifuge with one washing zone and an extended drying zone. In contrast to the Hoechst plant, the apatite mud obtained during the filtration of neutralized calcium nitrate solution is not fed back to the digestion section, but into the NP solution upstream of the neutralization section. The mud must be washed with water, in order to prevent the water solubility of the NP product from being reduced by the calcium nitrate which is returned with the apatite mud. The apatite itself is digested again in the NP solution by means of the available nitric acid.

Tests have shown that a belt filter with a four-stage counter-current wash system is suitable for reducing the nitrogen content of the mud to below 2 %, of this, 1.8 % N is present in the form of  $Ca(NO_3)_2$  and 0.2 % N is present in the form of  $NH_4NO_3$ .

We used the Pannevis belt filter for the first time in the mud and lime tests with good results. The operating principle of this belt filter is shown in fig. 5.

The filters installed by us are approx. 22 m long and 2 m wide.

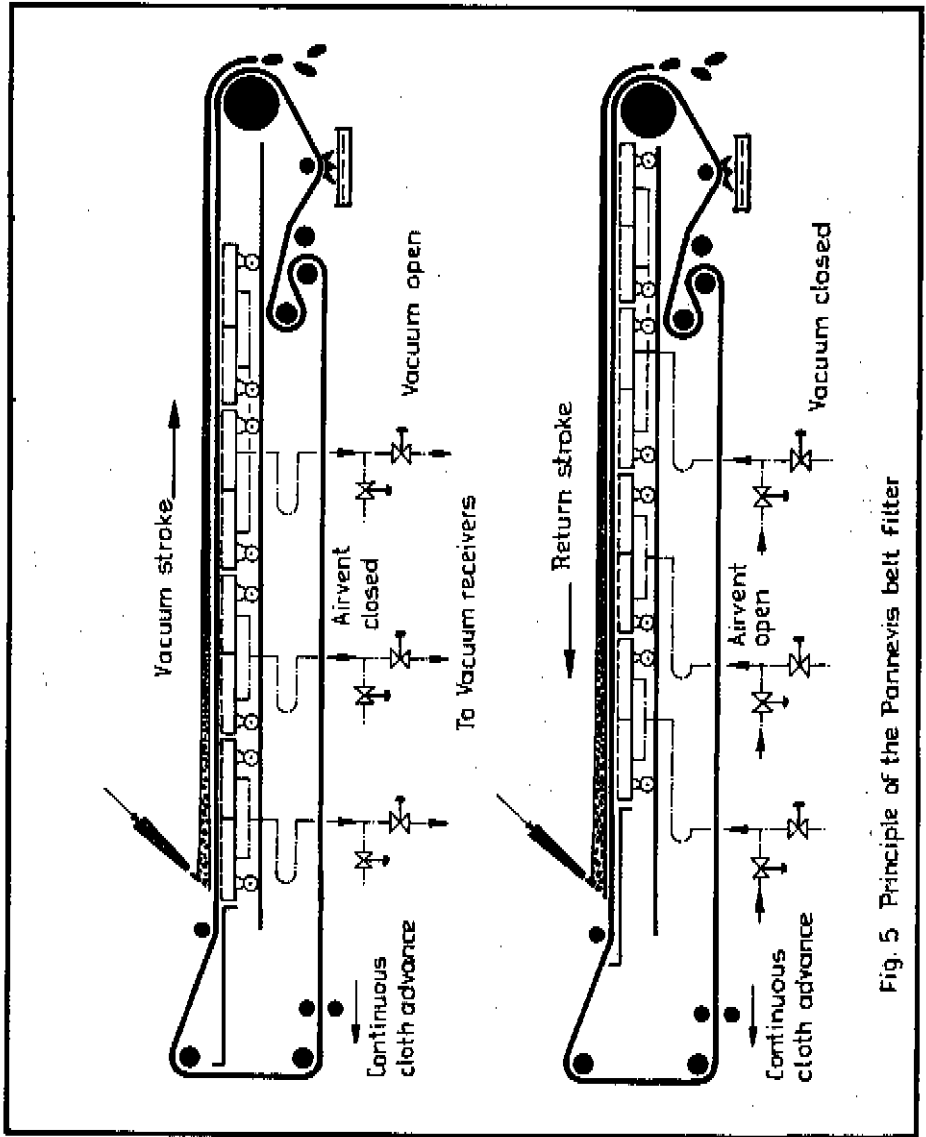


Fig. 5 Principle of the Pannevis belt filter

By employing the four-stage counter-current wash system, the amount of washing water required can be kept so low that, as in the Hoechst plant, the suspension after conversion consists of 24 %  $\text{CaCO}_3$  and 76 % ammonium nitrate solution with 65 % ammonium nitrate. This development provides the possibility of feeding the apatite back into the NP solution upstream of the neutralization section together with the advantage of saving refrigeration energy in the Odda section of the NP plant.

#### 2.1.2 Influence of the apatite mud filtration on the $\text{P}_2\text{O}_5$ yield

The  $\text{P}_2\text{O}_5$  losses are kept at a low level due to the fact that the apatite mud is fed back into the NP fertilizer plant. Apart from the losses in the NP fertilizer plants of Stamicarbon, which are between 1.5 % and 2.5 %, depending on the combination of feedstocks, additional low losses occur during filtration.

The filtered CN solution contains 0.03 %  $\text{P}_2\text{O}_5$  that was not retained by the filter. Referred to the total  $\text{P}_2\text{O}_5$  used, this represents an additional loss of 0.15 %  $\text{P}_2\text{O}_5$ .

#### 2.1.3 Improved lime filtration

Another improvement compared with the Hoechst plant is that a belt filter was installed for filtering the calcium carbonate instead of two rotary drum filters connected in series with intermediate slurring.

Tests have shown that, with three-stage counter-current washing and an extended drying zone, the residual moisture is below 13 % and the residual adherent ammonium nitrate is below 0.15 %. The amount of washing water saved in comparison with the intermediate slurring method is 5-6 %.

As a result of this, the concentration of ammonium nitrate increased to 65 % in the Trombay plant. Compared with the suspension downstream of the conversion section, the first filtrate is not diluted because the second filtrate is removed separately and used for diluting the acid CN solution prior to apatite precipitation.

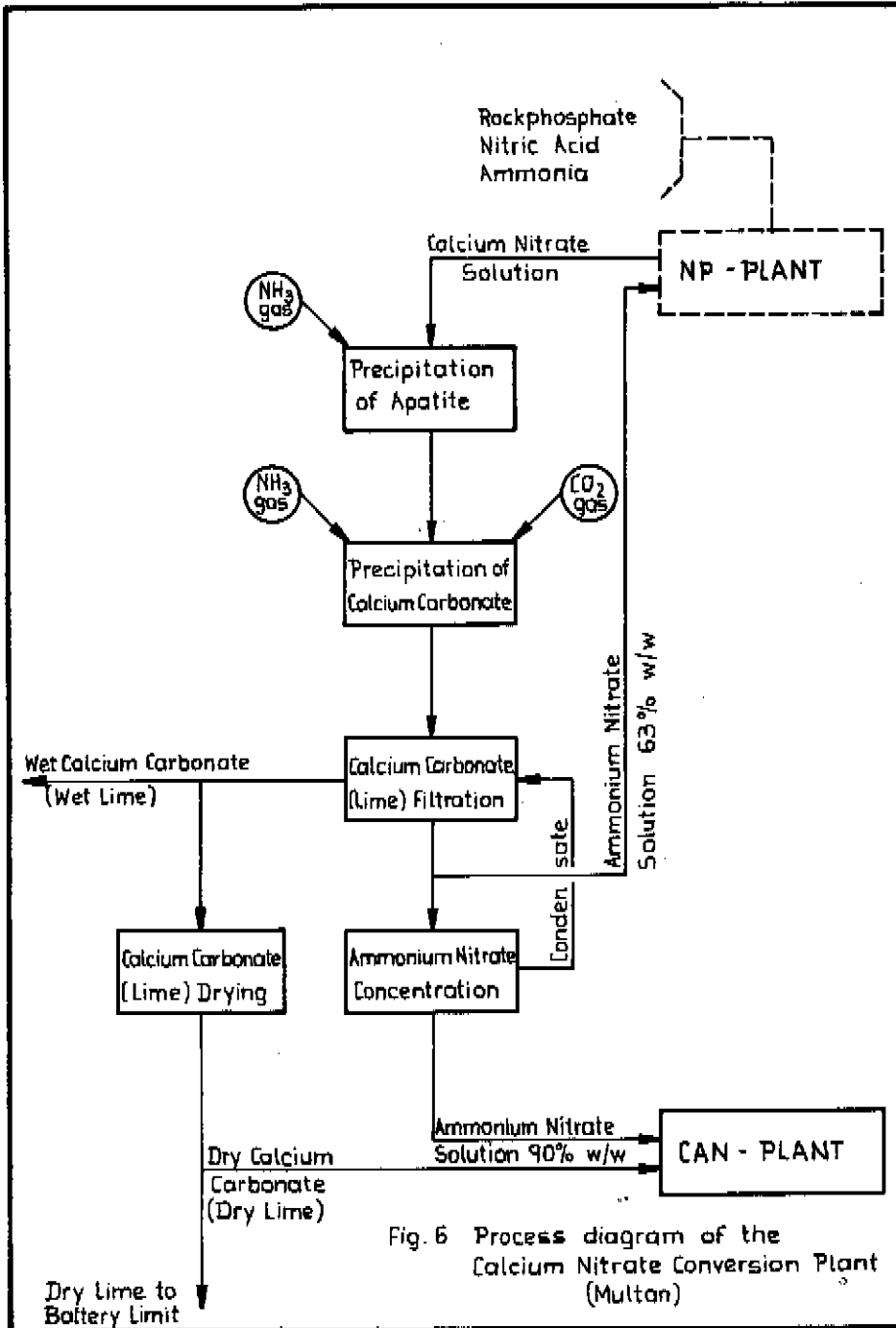


#### 2.1.4 Nitrogen yield of a conversion unit

If one considers the nitrogen content of the lime and of the apatite mud as a loss, the calculated nitrogen yield of the conversion unit, including the ammonium nitrate concentration unit, is 96.9 %. However, as the apatite mud is fed back into the NP unit, the nitrogen yield is increased to 97.8 %. The loss also includes the occluded nitrogen in the calcium carbonate. If the total lime production were to be used for the production of calcium ammonium nitrate, the nitrogen content of the lime thus not being a loss, the nitrogen yield would then be 98.7 %.

#### 2.2 The fertilizer complex of PFL in Multan

The complex comprises a NP fertilizer unit with a capacity of 1015 tpd NP 22.6:22.6 with a  $F_2O_5$  water solubility of the fertilizer product of 80 %, a conversion unit, and a calcium ammonium nitrate (CAN) unit with an additional ammonium nitrate neutralization unit. The capacity of the CAN unit is 1500 tpd CAN with 26.5 % N. A mud filtration section in the conversion unit was dispensed with, as the filtered lime is mainly used for the production of calcium ammonium nitrate and, at present is not used for other purposes. The process diagram shows the individual process steps.



### 2.2.1 The $P_2O_5$ yield in a fertilizer plant complex with a conversion unit without mud filtration section

The process diagram shows that the calcium nitrate (CN) solution from the NP unit is neutralized. However, the precipitated apatite is not filtered, but remains in the CN solution, which is converted to ammonium nitrate solution and calcium carbonate in the conversion reactor. The apatite is filtered, together with the precipitated calcium carbonate. The  $P_2O_5$  content in the lime is 0.65 %. In order to attain this low  $P_2O_5$  content, the tetrahydrate is separated from the NP solution in a two-stage centrifuge with one washing zone and an extended drying zone. The NP solution is washed out with cooled nitric acid to a  $P_2O_5$  content of maximum 0.25 %, in order to keep the  $P_2O_5$  loss at a low level as this quantity is notified back into the NP unit as apatite mud. This process is also applied in other UHDE plants. In the Multan plant, this  $P_2O_5$  is equivalent to 1.5 % of the total  $P_2O_5$  used. The total  $P_2O_5$  yield is 97.0 %.

### 2.2.2 Influence of the $P_2O_5$ adhering to the calcium nitrate on lime filtration

As no mud filtration section has been provided here, the precipitated mud must be filtered together with the calcium carbonate.

In comparison with lime filtration without apatite, the result of the filter test with a belt filter was, that the filter capacity decreased to 50 %. The reason for this is, that the apatite is present in very fine-grained form and this causes the calcium carbonate to be a little more fine-grained. Three-stage counter-current washing has proved to be satisfactory for washing out the adherent ammonium nitrate to 0.15 %. However, the consumption of washing water rose by 50 %. As a result the concentration of the ammonium nitrate solution drops to 63 %, compared with 65 % for lime filtration with prior apatite filtration. Altogether the conversion unit with mud filtration has an approximately 50 % higher water consumption which however, is only partly reflected in a reduction of the ammonium nitrate concentration because one part of the washing water is fed to the NP unit, together with the recycled apatite mud.

### 2.2.3 Possible applications of calcium carbonate which contains some apatite

Calcium carbonate which contains some apatite is suitable for processing to calcium ammonium nitrate. Some of the uses for pure calcium carbonate are no longer open to calcium carbonate which contains some apatite. This calcium carbonate can be used for cement production, if natural calcium is added to reduce the  $P_2O_5$  content. This lime can also be used in agriculture as lime fertilizer. Another use is the deacidification of waste water for pollution abatement.

### CONCLUSION

In order to achieve an optimum design for a fertilizer complex with an Odda section and a conversion unit, it must be decided whether a mud filtration section should be installed in the conversion unit.

The price of phosphate rock will influence the decision, as the  $P_2O_5$  yield is then increased by 1.35 %. On the other hand this improvement of the  $P_2O_5$  yield involves considerable costs for the installation and operation of the mud filtration section.

However, the possibility of utilizing the whole quantity of the calcium carbonate produced, is the most important criterion, as the value of the lime is determined by its various applications.