

IFA Technical Conference

**Johannesburg, South Africa
30 September-4 October 1996**

ECOLOGICAL AND ECONOMICAL ASPECTS OF THE BASF NITROPHOSPHATE PROCESS

T. Meyer and R. Nitzschmann
BASF AG, Germany

RESUME

Les exigences au point de vue économie et écologie imposent de plus en plus une conception et une opération souples des procédés. A cet égard, plusieurs aspects du procédé BASF de production de nitrophosphate seront présentés.

Un résumé comparatif à propos du procédé nitrophosphate par attaque nitrique et production de nitrophosphate par un mélange d'acides montre la rentabilité de la voie nitrique. Les coûts des matières premières et des investissements basés sur notre propre expérience ont été pris en considération.

La souplesse est également recherchée dans le traitement de l'environnement selon le site et l'environnement. Des développements récents conduisent à des solutions pour la maîtrise des gaz et liquides résiduels. Les aspects présentés peuvent servir de solutions pour des problèmes partiels et sont disponibles comme système combiné pour une intégration globale de l'environnement.



Ladies and Gentlemen,

For more than 40 years BASF is running the nitrophosphate process based on the Odda-concept. During this time the demands on the process flexibility and ecology changed and they will change in the future. So every plant is adapted taking into account the types of rock phosphates, the NPK-grades to be produced and of course the local environmental regulations. BASF has continued its research and development efforts to keep up with the requirements.

In this presentation I want to show you, that the nitrophosphate process is economically attractive compared to alternative routes for the NPK production. And I want to show you a comprehensive summary about the environmental possibilities, which we have experience in.

(Slide 1, left side)

The rock phosphate is digested in nitric acid and insolubles, mostly sand, are separated. Calcium nitrate-tetrahydrate (CNTH) is then crystallized by cooling the solution down to approximately 0°C with optimized energy efficiency. Calcium nitrate is separated with a filter.

The resulting solution is the nitro-phosphoric acid or NP-solution. This is neutralized with ammonia and excess water is evaporated to obtain the so called NP-melt. After the addition of potassium the melt is ready for granulation, drying and finishing.

The above mentioned CNTH is further processed with ammonium-carbonate synthesized from carbon dioxide, available from different sources, and ammonia. The conversion reaction with calcium nitrate leads to calcium carbonate, lime, which precipitates, and to ammonium nitrate. The lime is then separated and the ammonium nitrate solution is concentrated. Both can either be sold as products or can be combined in a further granulation route to calcium-ammonium nitrate fertilizer, CAN. The lime does not need to be dried for this procedure.

Raw materials needed are rock phosphate, nitric acid, ammonia and carbon dioxide.

(Slide 1, right side)

Another route for the production of NPK-fertilizers is using phosphoric acid. This is obtained from rock phosphate and sulfuric acid. For a comparable production of CAN and NPK an additional sulfuric acid plant and instead of the conversion an ammonium nitrate synthesis is required. Raw materials are rock phosphate, nitric acid, ammonia and sulfur and lime. Also, the phosphoric acid production leads to the costly discharge of gypsum.

In the following slides I would like to discuss the investment and raw material costs of different alternatives. I want to compare the nitrophosphate process with the phosphoric acid route.

First, you can go the long way and start your production with sulfur and rock phosphate. Or, second, you can buy sulfuric acid from the market. Or, third, you want to get rid of the gypsum problem and buy phosphoric acid from the market.

(Slide 2)

The calculation basis and the alternatives are summarized in this table. The raw materials are calculated based on a production of 1000 t/d NP 20+20 and 1000 t/d CAN. The rock phosphate has a phosphate content of 35% and a CaO: P₂O₅ ratio of 1,45. The price basis is West Europe, April 1996 (date of manuscript).

The investment costs are based on large capacity plants (1995, price basis Europe). For the comparison of the routes only the partial investment according to the required amount of product is calculated.

The comparison includes the four already mentioned alternatives:

1. The BASF nitrophosphate consisting of the Odda process, the conversion, the NPK and CAN process
2. The production of NPK and CAN, starting from rock phosphate and sulfur.
3. The production of NPK and CAN, starting from sulfuric acid.
4. The production of NPK and CAN using phosphoric acid from the market. This requires only a NPK-plant.

The last three alternatives have to use lime as raw material and require an ammonium nitrate synthesis. Since for one capacity and grade of NPK and CAN the amount of ammonia, nitric acid and potassium is the same in both routes, I omitted these costs.

(Slide 3)

This slide shows investment costs and raw material costs of the described alternatives.

The nitrophosphate process is splitted into the NPK and the CAN parts. That is around 55 Mio \$ for the Odda and NPK plant and another 35 Mio \$ for the conversion and CAN-plant.

Starting from sulfur the investment consists of the NPK, the sulfuric acid and the phosphoric acid plants adding up to 65 Mio \$. For the CAN production the ammonium nitrate synthesis and CAN process add up to 39 Mio \$, which is the same for all Phosacid-alternatives.

Buying sulfuric acid from the market, the investment includes the NPK and phosphoric acid plant. The investment is around 40 Mio \$.

Starting from phosphoric acid, the investment is 18 Mio \$.

The comparison demonstrates, where the nitrophosphate process rates. Regarding only the investment costs, it ranges between the alternatives, which include a phosphoric acid plant.

The lower diagram shows the raw material costs in thousand \$ per day. Since I omitted nitric acid and ammonia there is only the rock phosphate for the NPK production. It makes 32 T\$/d. The lime for the CAN production comes with the process, so no costs arise for it.

Starting from rock phosphate and sulfur, the raw materials add up to 45T\$/d. Also lime has to be bought. We did not evaluate the costs for the gypsum deposition here, since they strongly depend on local prices. But they increase the costs in any case significantly.

The second phosphoric acid route needs rock phosphate and sulfuric acid. It makes close to 60 T\$/d, again not including the deposition costs.

The low investment route needs only phosphoric acid, which is quite expensive and causes respectable costs of 80 T\$/d.

The nitrophosphate process is a high investment comparable to the alternatives. But the raw material costs are significantly lower and there are no deposition problems and costs. These savings justify a higher investment, giving a high profitability, and makes the nitrophosphate route attractive. This economic advantage is indeed very large especially in a situation of expensive sulfuric and phosphoric acid, as we face it this year.

(Slide 4)

The advantages of the nitrophosphate process are summarized in this slide:

- The investment costs are comparable to the phosphoric acid route and rate between the two phosphoric acid routes starting from sulfur or sulfuric acid.
- Only few and low price raw materials are necessary.
- The process is independent from the sulfur market.
- There are no solid wastes, which have to be deposited.

Concerning the flexibility, in which I did not go much into detail, a few points maybe mentioned:

- Instead of solid wastes there are high quality byproducts as AN and lime, which can easily be further processed to CAN.
- The lime from the conversion does not have to be dry and can be used directly from filter.
- Due to the waste gas and water management, I will describe later, there is a close to 100% yield of nutrients from rock phosphate.
- A wide variety of available rock phosphates and rock phosphate mixtures is suitable.
- A wide variety of NPK-grades can be produced. In the NPK plant other phosphate sources as phosphoric acid, MAP, DAP can be used in special situations.

Beside these basic economic evaluation, other constraints, especially environmental requirements, become more and more significant when choosing the right process for the production of NPK.

I would like to go through the technical possibilities for the waste gas and water treatment and show the available options, which are included in the above mentioned investment costs.

(Slide 5)

The slide shows a more detailed view of the BASF nitrophosphate process. In the following, the possibilities for a tailor-made environmental design will be discussed.

(Slide 6)

For the NP-acid/conversion section the slide shows different possibilities for the waste gas and water treatment.

The sand treatment:

The sand is separated by centrifuges (moving device, high efficiency separation) or with lamella separators (static device, only for crude sand) depending on the type of sand, i.e. rock phosphate, and the custom requirements:

- The sand slurry can be recycled to the granulation.
- The sand can be cleaned to discharge it to the building industry. This can be done with belt filters or so called paddle washers. The paddle washer is a type of equipment, in which the sand is moved slightly upward from one tub to another by rotating paddles, while the water is flowing countercurrent to this movement. Due to this true countercurrent mechanism, the amount of water needed is minimized.

The NP-acid section:

The NO_x gases from the digestion and CNTH-crystallization can be treated differently:

- A water scrubbing results in a dilute nitric acid solution, which can be discharged for example to a biological purification, if available.
- With the addition of ammonia, the scrubber can be designed to produce an AN-solution, which can be recycled to the process. This reduces significantly the amount of fresh water needed and avoids waste waters.

The conversion section:

For the NH₃ containing offgases from the conversion and AN concentration there are also several possibilities:

- The offgases from the conversion can be scrubbed with nitric acid to produce an AN-solution, which is recycled to the process.
- Vapors from the AN concentration can be condensed and treated with ion exchange techniques, so only clean water (boiler feed water quality) is discharged. Alternatively, the vapors can be supplied directly to the scrubber for the conversion gases.

All these devices can be combined and optimized to meet the local requirements. If required, we are able to supply a combination of scrubbers, so that all liquids from the scrubbers can be recycled to the process and no process liquids are discharged.

(Slide 7)

For the NPK section this slide also shows different possibilities for the gas treatment.

The neutralization:

- The NH₃-vapors from the neutralization and evaporation are treated in a similar way as shown before in the conversion section. The scrubber discharges an AN-solution to be recycled to the process. Due to the vapors the scrubbing is performed at elevated temperatures, which allows an AN concentration in the discharged scrubbing solution of at least 40 %.

The granulation and drying:

- The dust containing offgases from granulation/drying and are treated by cyclones and the collected dust is recycled directly to the granulator.
- In case of very severe environmental regulations, the dust gases can be processed together with the NH₃ gases in one scrubber, from which an AN/dust-slurry is discharged back to the process.

The CAN section (not shown as slide):

The NH₃ vapors from the AN high concentration and the dust containing gases from the CAN granulation are treated with a similar scrubber as described before. Due to their low relative humidity the gases simultaneously take up a large amount of water from the scrubbing solution. The high concentrated scrubbing solution is directly recycled in the CAN section. This results in any case in no liquids discharged from this section.

(Slide 8)

This slide summarizes the ecological features:

Custom design of waste gas and water treatment:

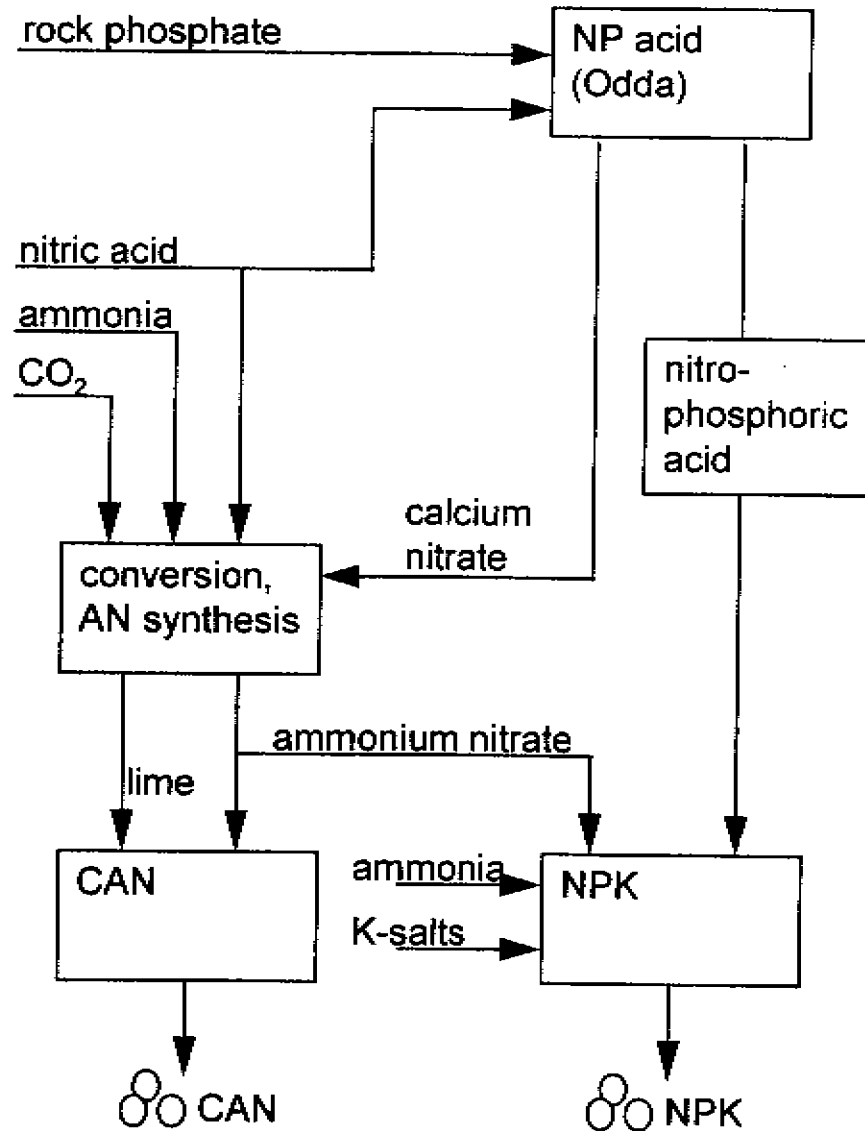
- Technical solutions for single water treatments to minimize or clean process liquids
- Overall waste water minimization; also a design is possible with no process liquids leaving the nitrophosphate process
- Consequent use of the evaporation capacity of the gas scrubbers
- Full recycling of process liquids to the process

- **Recuperation of nutrients close to 100%**
- **No solid wastes to be deposited**

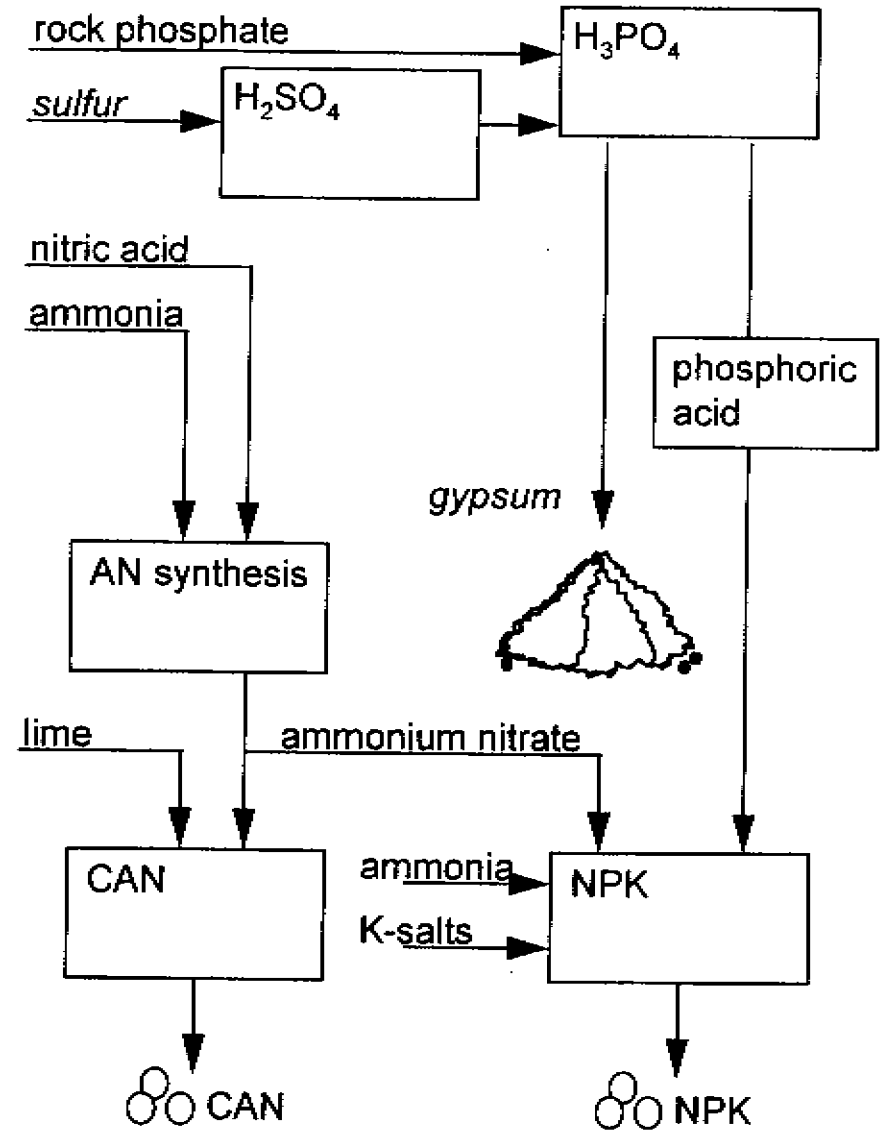
References

- **Diehl, Nitrophosphate and Fertilizer Plants: the Recycling Concept for Minimizing Pollution of Air and Water, IFA Technical Conference, Edmonton, Alberta, Sep. 1988**
- **Reuvers, W. Wichmann, Agronomical and Technological Advantages of Modern Nitrophosphates, Seminar « Fertilizer and Food Security », Fertilizer Association of India, New Delhi, Dec. 1992.**

BASF Nitrophosphate Process



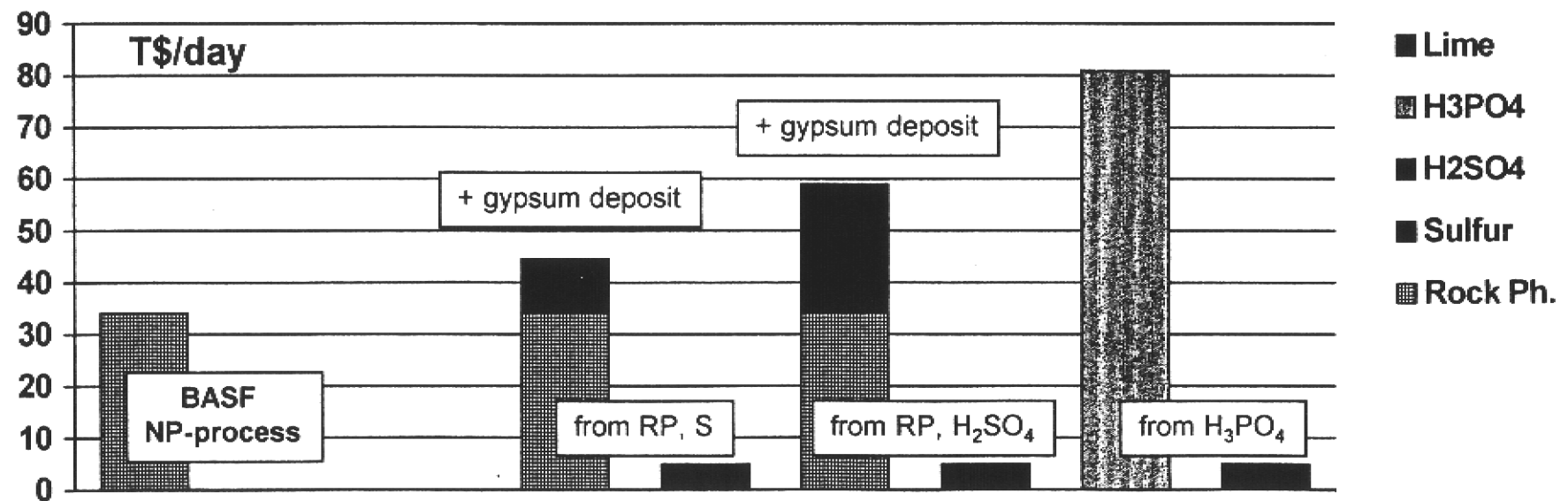
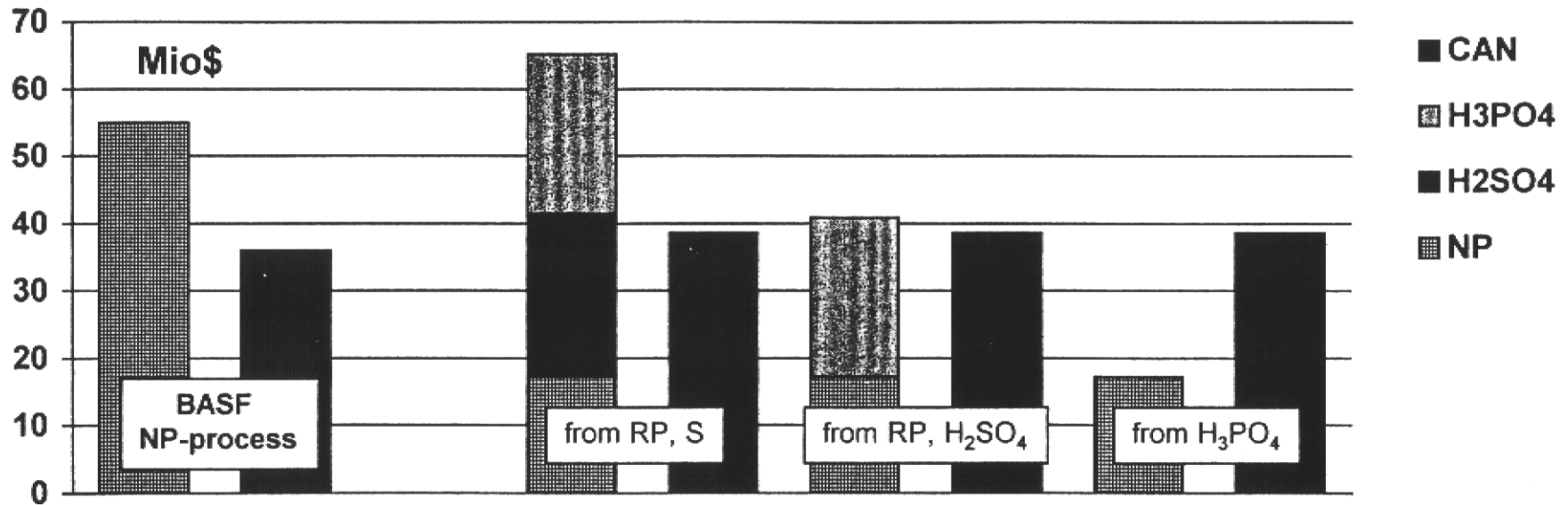
Phosphoric Acid Route



Calculation Basis

- 1000 t/d NP 20 + 20
- 1000 t/d CAN
- Rock phosphate 35% P₂O₅, CaO: P₂O₅ =1,45
- Investment prices based on large capacity plants (European basis, 1995)
- Raw material costs January 1996

Process Routes	Raw Materials	Plants
BASF NP Process	RP	Odda, conversion, NPK, CAN
from RP, S	RP, S, CaCO ₃	H ₂ SO ₄ , H ₃ PO ₄ , NPK, AN, CAN
from RP, H ₂ SO ₄	RP, H ₂ SO ₄ , CaCO ₃	H ₃ PO ₄ , NPK, AN, CAN
from H ₃ PO ₄	H ₃ PO ₄ , CaCO ₃	NPK, AN, CAN



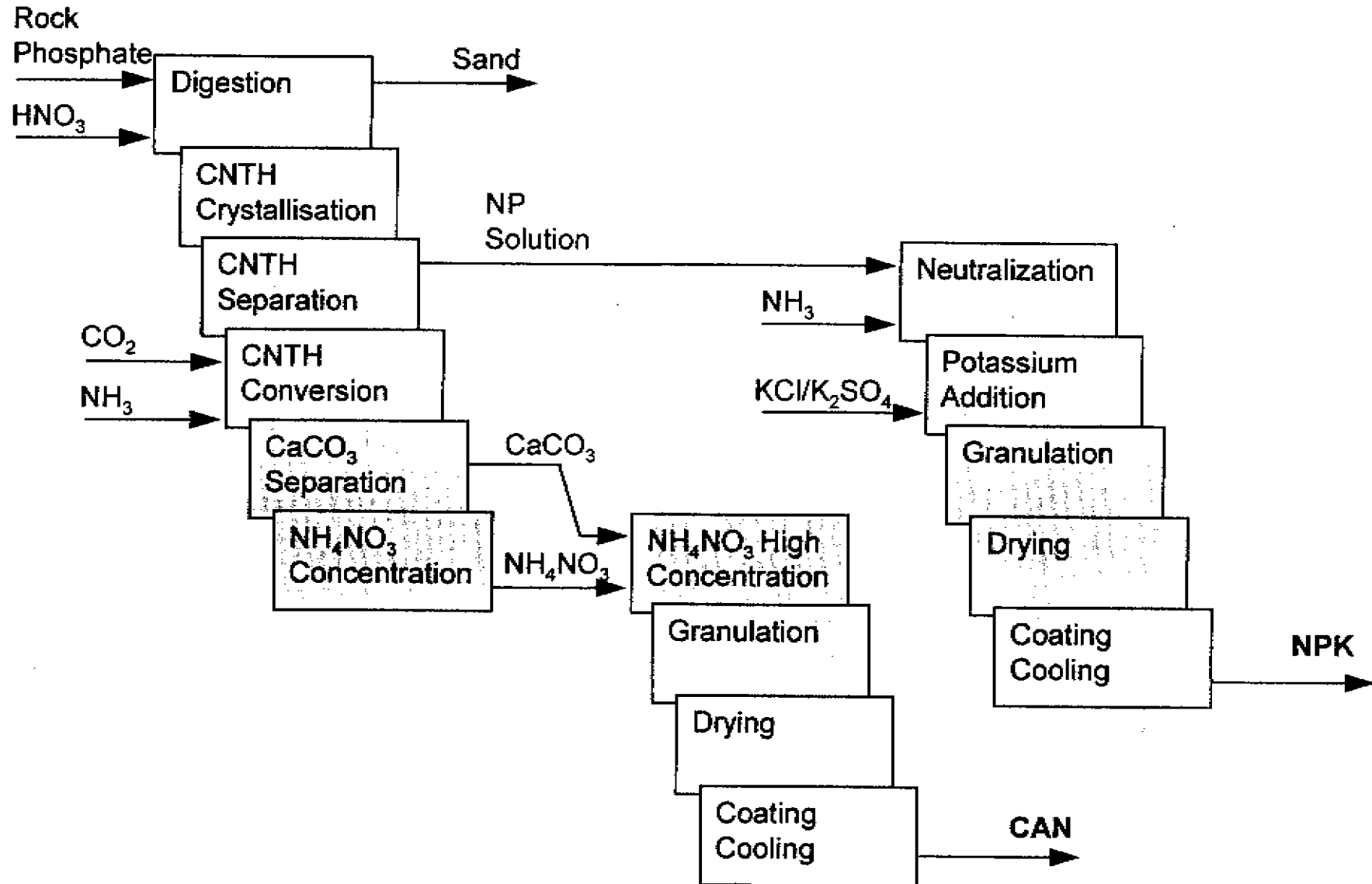
- Investment between mixed acid route alternatives
- Only few and low price raw material (Rock phosphate, CO₂)
- Independence from sulfur or sulfuric acid and the fluctuation of its prices
- No gypsum production and deposition costs, no other solid wastes

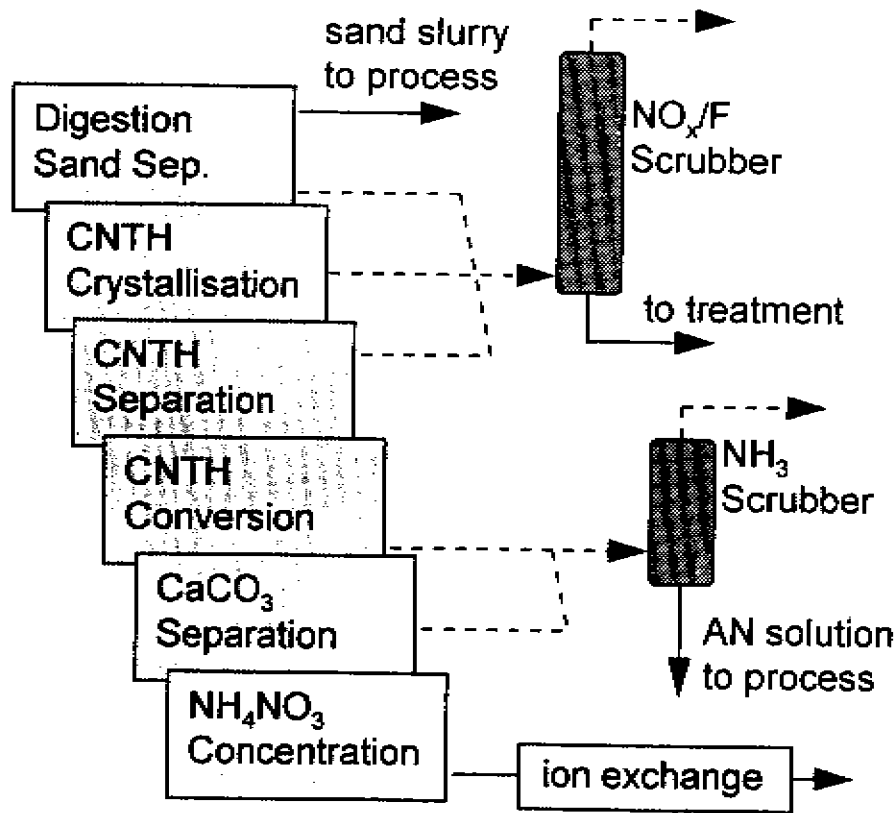
Flexibility:

- High quality, sellable byproducts as AN and lime, if not further processed to CAN
- Energy saving CAN process using wet lime from the conversion
- Close to 100 % yield for the nutrients from the rock phosphate
- High flexibility concerning the NPK formula to be produced to meet the local agronomical demands
- Use of a wide variety of commercially available rock phosphates
- Use of other phosphate sources in the NPK plant, if necessary

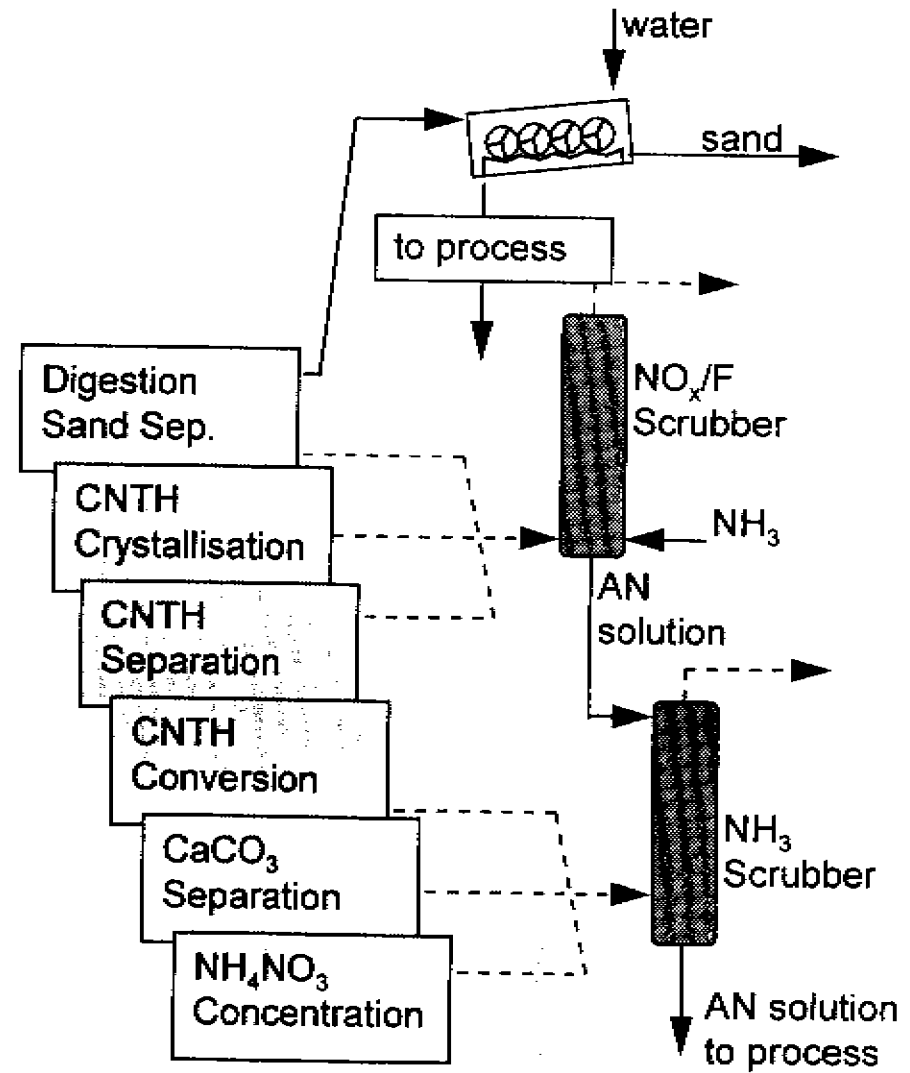
The BASF Nitrophosphate Process

BASF

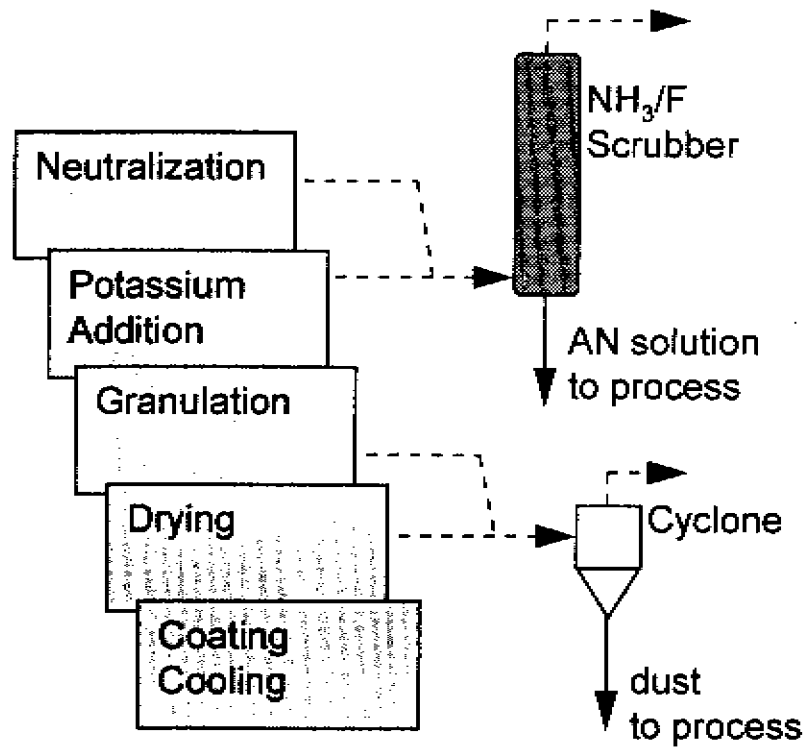




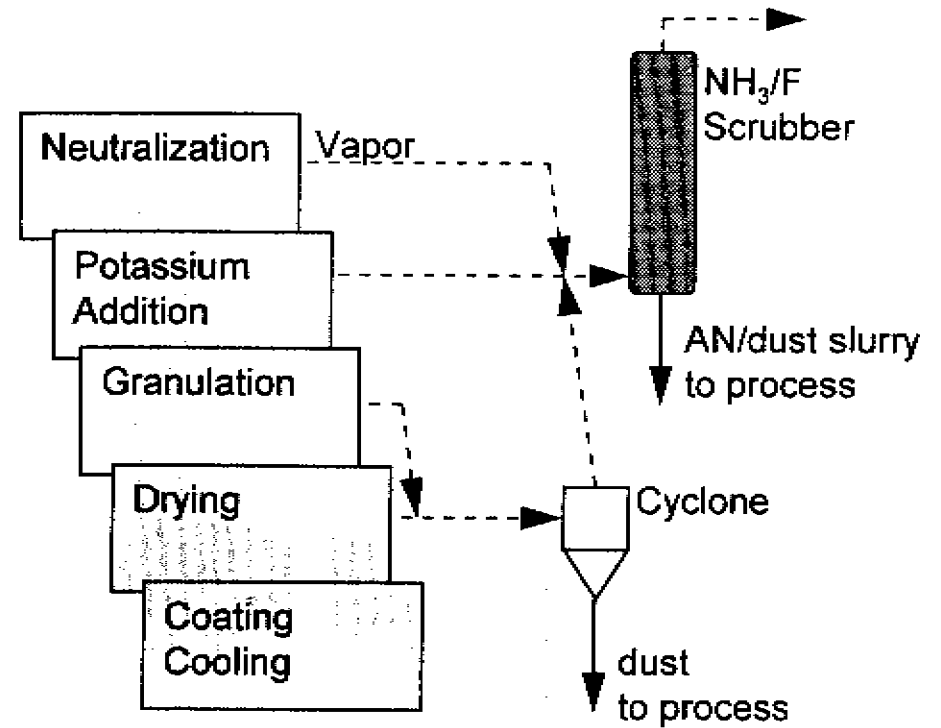
dilute nitric acid to biological purification and clean water from ion exchange



no waste water



no waste water



no waste water

Custom design of waste gas and water treatment:

- Technical solutions for single water treatments to minimize or clean process liquids
- Overall waste water minimization; also design possible with no process liquids leaving the process
- Consequent use of the evaporation capacity of the gas scrubbers
- Full recycling of high concentration liquids to the process
- recuperation of nutrients close to 100%
- no solid wastes to be deposited

