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# PRODUCTION OF CALCIUM AMMONIUM NITRATE

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**PART A:**

**PRODUCTION OF CALCIUM-AMMONIUM-NITRATE: THE BASF PROCESS**

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## 1. INTRODUCTION

BASF is one of the largest chemical concerns in the world. From the beginning of the industrial fertilizer period, it was involved in improvement in fertilizers and its technology. In 1908, it achieved the decisive breakthrough in the fertilizer technology with the first technical process for the production of the ammonia synthesis by the Haber-Bosch process. In the following years, it expanded the production of straight nitrogen fertilizers: ammonium/sulfate nitrate (1919) and calcium nitrate (1925), which led in 1927 to the production of granulated multinutrient fertilizer, under the brand name "NITROPHOSKA". BASF developed and improved many other fertilizer processes and started in 1953 with its first Nitrophosphate plant with low W.S.$P_2O_5$ in order to be independent of the sulphur source and to avoid the deposit of gypsum. After further intensive research work, it improved this plant and built up, under licensing, the new BASF Nitrophosphate plant, with high W.S.$P_2O_5$ in BASF Antwerp (Belgium), Chemie Linz (Austria) and GNFC Bharuch (India).

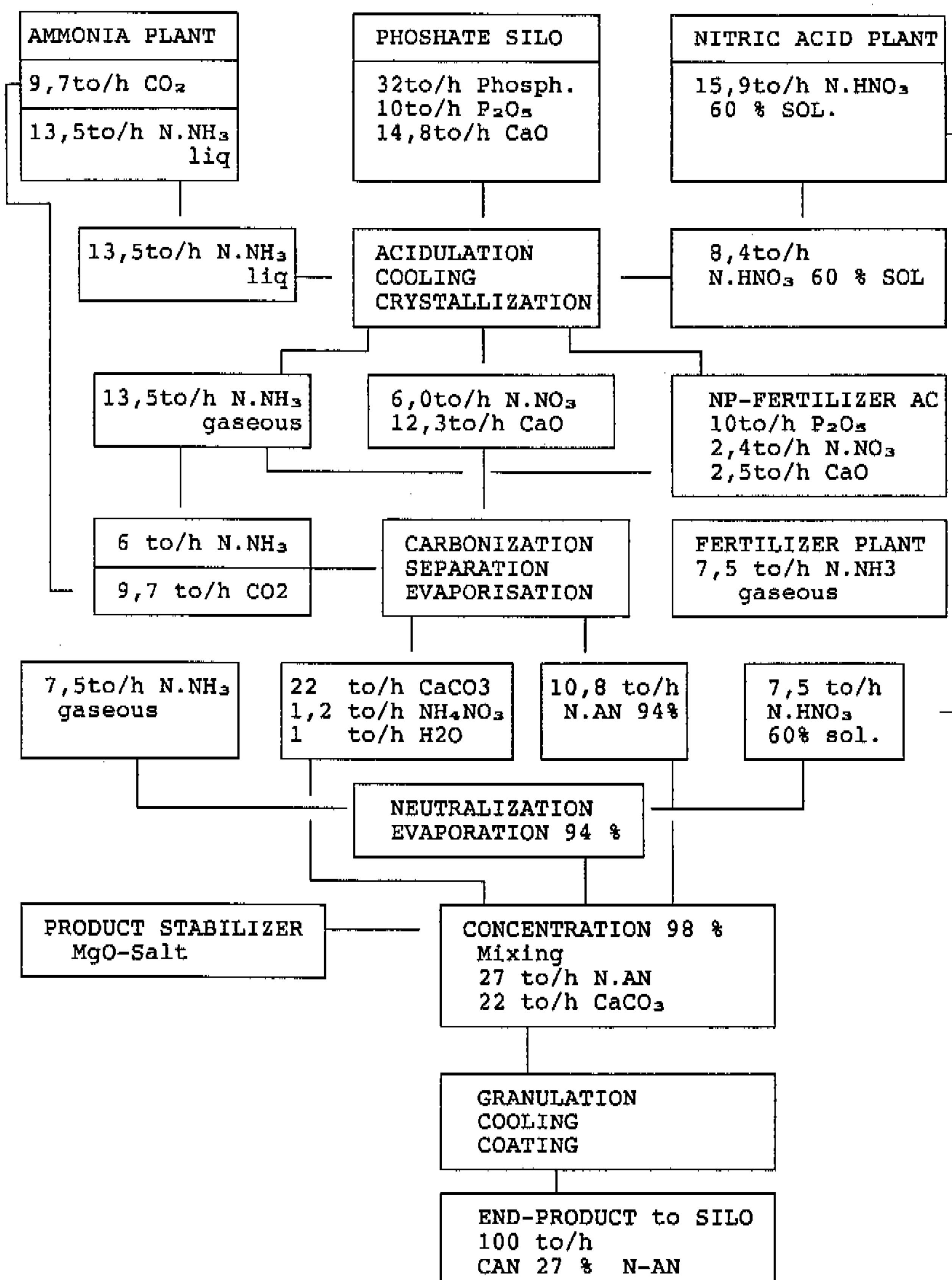
By integration of the products of the Nitrophosphate process and by many other technical improvements, another successful development is now be realized: the start up from the new integrated BASF granular CAN-Process, with low production costs, low environmental problems and high product quality, and that is the purpose of this presentation. This process is operated in BASF Ludwigshafen (Germany), CNO (Belgium), BASF Antwerp (Belgium) and Chemie Linz (Austria).

## 2. GENERAL DESCRIPTION OF THE INTEGRATED BASF GRANULAR CAN-PROCESS

BASF has produced calcium ammonium nitrate granules for more than 50 years. In order to minimize production and investment costs and to get granules of high quality, it centered its applied research on the optimization of the nitrophosphate acid- and granular CAN-process. This has led to the construction from new the BASF Nitrophosphate plants under licence the new BASF granular CAN-processes in optimum integration with the outlet products of the BASF Nitrophosphate route.

The CAN-process starts logically in the Nitrophosphate plant (See Figure 1), where gaseous ammonia, ammonium nitrate solution of 94% and wet calcium carbonate are generated. The gaseous ammonia is mixed with 60% $HNO_3$ in a natural circulated neutralizer at low pressure. This ammonium nitrate solution is flashed out to 94%, mixed with the ammonium nitrate solution of the Nitrophosphate plant and concentrated in evaporators to about 98%. An optimum energy recovery is ensured by integration of several heat exchangers. The concentrate solution flows into a small vessel and is mixed with cyclone dust, and the wet calcium carbonate and stabilizers like ammonium sulphate solution, coming from the production of caprolactam and magnesium salts like magnesium sulphate or magnesium nitrate. The AN solution from 145-150° C is then pumped into the granulator drum. After passing through this granulator at temperatures between 100 and 110° C, the wet granules are discharged into a drying drum in order to obtain the low final moisture content. By means of screens, the mass flow is separated into under- and oversize and onsize granules. The oversize granules after crushing and the undersize granules are recycled and form the bed of the granulator. The onsize product with uniform granule size between 2 and 4 mm is then supplied first to a cooler drum in order to cool the granules to 75° C and led subsequently in a fluidized bed to get a product temperature under 40° C. This product is finally supplied to a coating drum and transported to the silo.

## 3. Material Balance for a CAN 27%-Production of 100 to/h



## 4. DETAILS OF PROCESS AND RESULTS

### A. The BASF - NITROPHOSPHATE PROCESS

Since 1953, BASF has been operating a nitroposphate plant at Ludwigshafen producing low water soluble $P_2O_5$. After fundamental improvements they installed in 1985 in Antwerp a new plant with high solubility-$P_2O_5$ of 85 percent and in 1989 in Austria and India. In this new process, rock phosphate is decomposed with 60% nitric acid in stirred vessels (see Fig. 2). The acid-insoluble components (mainly sand) are removed virtually without any loss of phosphate and nitrogen. The resultant solution is cooled with liquid ammonia, in order to crystallize calcium nitrate tetrahydrate.

$$Ca_3(PO_4)_2 + 6\ HNO_3 \text{ ------> } 3\ Ca(NO_3)_2 + 2H_3PO_4$$

The calcium nitrate crystals are separated on a belt filter. The mother liquor which contained a high water soluble $P_2O_5$ of 80 to 85% is processed in the BASF NITROPHOSKA-plant. The calcium nitrate crystals are dissolved in a $NH_4NO_3$-solution and stored in a tank. A part of the gaseous ammonia is reacted with carbon dioxide from the ammonia plant to an ammonium carbonate solution. The $Ca(NO_3)_2$ 4 aq crystals are converted with this ammonium carbonate to ammonium nitrate and calcium carbonate. After separating on an other belt filter, the wet calcium carbonate is transported to the CAN-plant. This wet calcium carbonate contains about 4% water and 5% $NH_4NO_3$. The ammonium nitrate solution is concentrated from 65% to 94% in a multistep evaporating devicer and used either for the production of straight ammonium nitrate fertilizers or for NPK fertilizers. The process has low maintenance costs, high yield (99% of $P_2O_5$ and N) and a high on stream factor of 96%.

### B. THE INTEGRATED BASF GRANULAR CAN-PROCESS

Neutralization and concentration

**a) PROCESS**

Ammonium nitrate solution is produced from the two feedstocks nitric acid 60% and gaseous ammonia: it is formed by the following reaction:

$$NH_3(\text{gas}) + HNO_3\ (\text{aqueous}) \text{ ------> } NH_4NO_3\ \text{sol}$$

The reaction is exothermic and the heat is about 100 to 115 joule pro mole gram $NH_4NO_3$. In order to maximize the evaporation of water the two products are preheated: Ammonium to 50-60 centigrades and nitric acid to 90-95 centigrades. The reaction takes place (see Fig. 3) under a light pressure from 1 to 1.6 bar and a temperature of 168 centigrades and it gives enough heat to generate a natural circulation in the reactor loop. During the neutralization, this circulation is very important in order to avoid local overheating, nitrogen losses and product decomposition. It is therefore necessary to control the quality of the raw materials: organic materials or oil concentration lower than 70 ppm, chlorine or catalyst max 1 ppm and $HNO_2$ max 100 ppm. The concentrated AN-solution (89-92%) in the neutralizer is flashed out (93-94%) and mixed with the 94% AN-solution, coming from the nitrophosphate plant. This mixture is stored in a tank with a large storage capacity in order to bridge short production stops (half a day) in the concentration or granulation part of the process.

The 94% AN-solution from the storage tank is pumped through the evaporator from the falling film type, by 0.3-0.4 bar and 155-160 centigrades and so concentrated to 97-98%. An optimum energy recovery is ensured by integration of heat exchangers.

**b) pH - NEUTRALIZER**

The most important parameter of the neutralization unit is the proper ratio between ammonia gas and nitric acid supply into the reactor.

This is done automatically by measuring and controlling of the flow of the preheated $NH_3$, the flow of $HNO_3$ and the pH-value of the produced AN-solution. This pH-value is connected as cascade to the ratio controller, and thus controlling the $NH_3$ : $HNO_3$ ratio. The value is after measuring, linearized in a characterizer computer module and given as cascade to the $HNO_3$ - valve.

In this way, the neutralization can be operated at a stable pH-value. Nevertheless, it is important to operate at a distinctly acidic range around a pH-value of 2-4 in the neutralizer in order to avoid high nitrogen-losses.

**c) SAFETY**

The process is so designed that perfect safety of operation is guaranteed by quality control of the inlet products, by many special safety precautions like e.g. a safety watertank above the neutralizer to empty when temperature reaches above 180 centigrades and by optimum operating conditions of temperatures, pressures, flows, AN-concentration and pH-values.

The heat needed for the AN-concentration is supplied by saturated heating steam with a pressure of approx. 8-9 bar. The temperature should always be under 180 centigrades.

**d) PROCESS VAPOURS**

The process vapours of the neutralizer are cleaned in a first step in a packing tower, passed through a demister and washed with an AN-solution. Part of the cleaned vapours are used to preheat the $HNO_3$ to 90-95 centigrades. The rest is conveyed to a condenser. The process condensates are partly recycled in the process, partly pumped to the nitric acid and to the granulation plant.

| BASF | BLOCK DIAGRAM OF THE INTEGRATED BASF GRANULAR CAN-PROCESS |
|---|---|

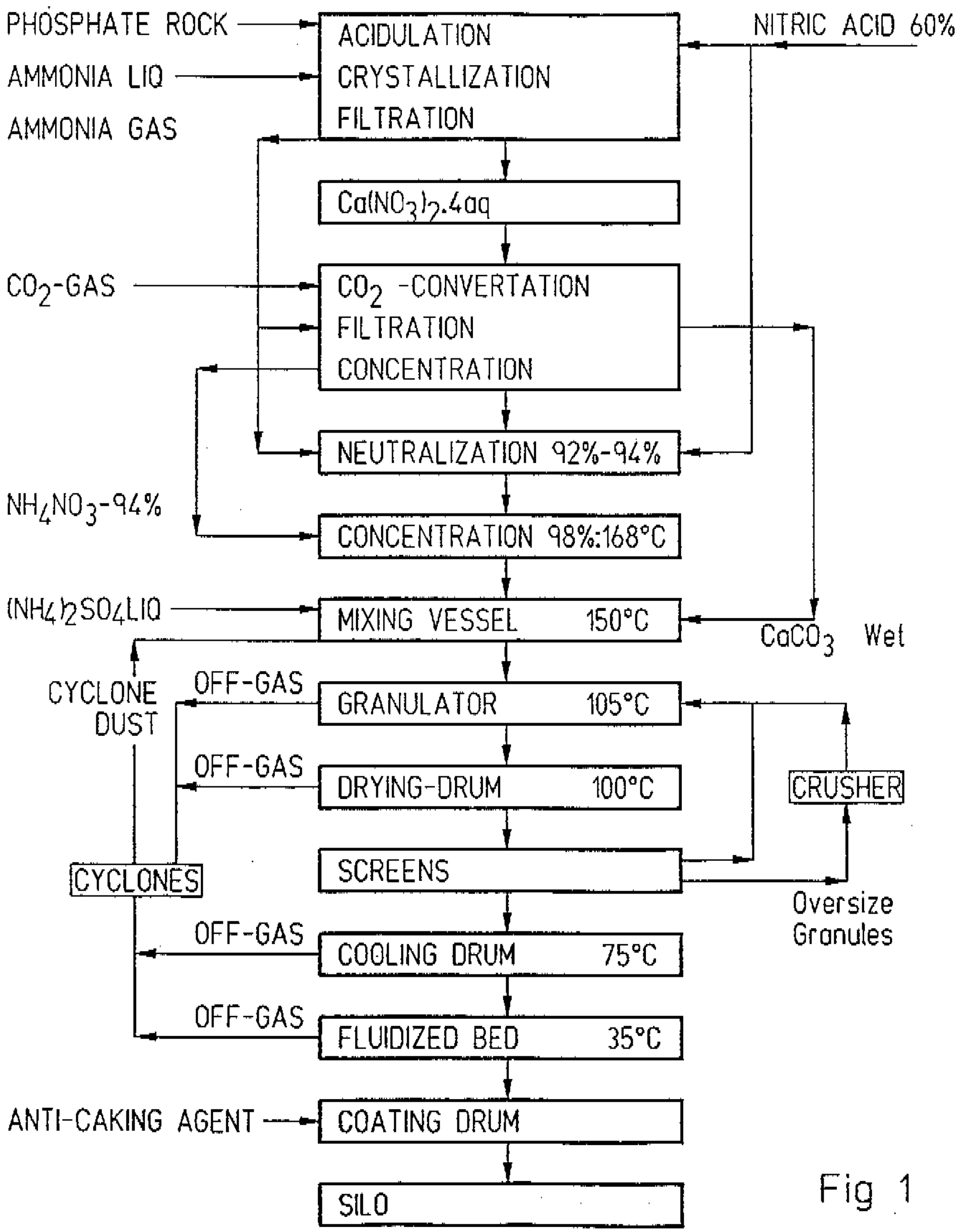
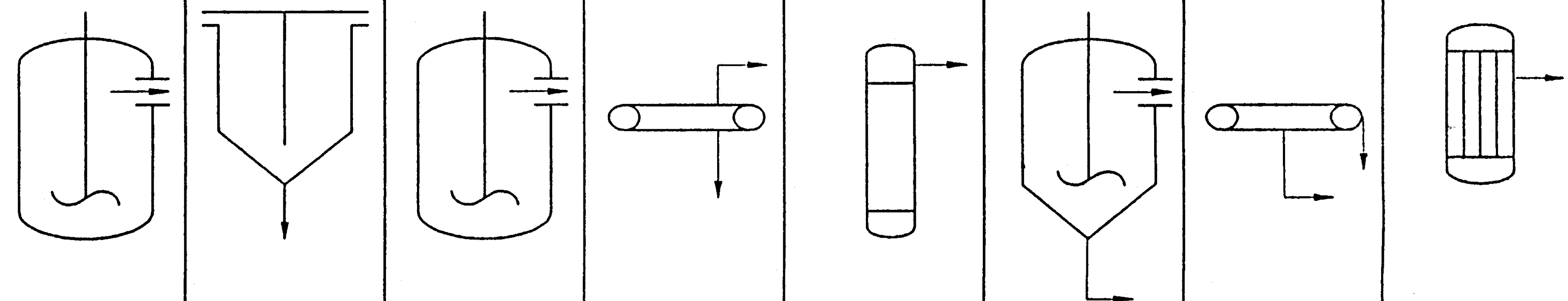



Fig 1

# THE BASF NITROPHOSPHATE PLANT

SCHEMATIC PROCESS DESCRIPTION

| | ACIDULATION | SEPARATION | COOLING | FILTRATION | SYNTHESIS | CONVERTATION | FILTRATION | CONCENTRATION |
|---|---|---|---|---|---|---|---|---|
| INLET PRODUCTS | Ca3(PO4)2<br>HNO3 CO2 | SAND<br>NP-ACID<br>Ca(NO3)2 | NP-ACID<br>Ca(NO3)2 | NP-ACID<br>Ca(NO3)2 4aq | NH3 Gas<br>CO2 | Ca(NO3)2<br>(NH4)2CO3 | NH4NO3 Sol<br>Ca CO3D | NH4NO3<br>65% Sol |
| |  | | | | | | | |
| OUTLET PRODUCTS FOR: | | | | | | | | |
| NP-ACID-PLANT | NP-ACID<br>SAND<br>Ca(NO3)2 | NP-ACID<br>Ca(NO3)2 | NP-ACID<br>Ca(NO3)2 4aq | —<br>Ca(NO3)2 4aq | (NH4)2CO3 | NH4NO3 Sol<br>Ca CO3 | NH4NO3 65%<br>Sol | —<br>— |
| STONE-PLANT | — | SAND | — | — | — | — | — | — |
| CAN-PLANT | — | | — | — | — | — | WET CACO3 | NH4NO3 94% Sol |
| NPK-PLANT | — | | — | NP-ACID | — | — | — | NH4NO3 94% Sol |

3A - 7

Fig 2

# THE INTEGRATED BASF GRANULAR CAN-PROCESS

NEUTRALIZATION AND CONCENTRATION

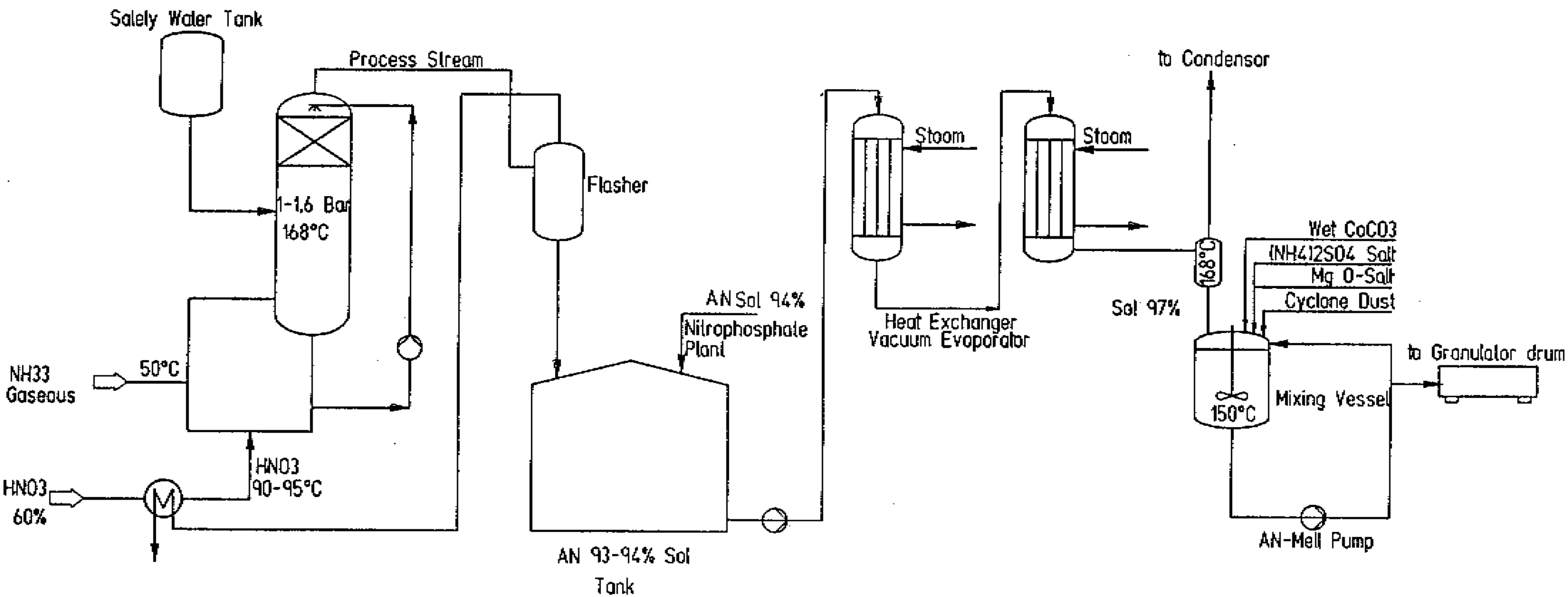



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Fig 3

**PART B:**

**BASF'S CAN PROCESS**

Robert E. NITZSCHMANN, BASF Ludwigshafen, Germany

## 1. RAW MATERIALS

The process is based on the use of 94 % (by weight) ammonium nitrate solution, which is a concentration at which ammonium nitrate can still be safely pumped and stored.
The following products can be granulated: dry lime and dolomite, and especially lime with up to 10 % adhering water or- which is particularly advantageous for the Odda process - with up to 12 % of adhering ammonium nitrate solution.

## 2. PROCESS

Figure 1 (process diagram)

The 94 % (by weight) ammonium nitrate solution is fed to a downward-flow evaporator in accordance with the requirements of granulation and overflows from the evaporator as a highly concentrated solution move directly into the lime-mixing vessel. A safety interlock ensures trouble-free operation of the downward-flow evaporator under all conditions.
The moist lime is also measured, metered and transported to the lime-mixing vessel by means of specially developed equipment. The ammonium nitrate solution is controlled with respect to temperature and density in accordance with the formulation. This results in a very accurate consistent finished product analysis.

In the lime-mixing vessel, inorganic additives for improving the product quality are added. They are distributed here very homogeneously. The mixture is sprayed in a granulation drum directly onto the recycled material. The crude granulated product is dried further in a drying drum and cooled down. The granulation and drying drums are unheated and are operated as cooling drums with only relatively low air rates. The crude granulated product is divided by means of twin-deck screens. The ground oversize and the undersize are recycled into the granulation drum. At 2 - 2.2 times the production, the necessary return flow is low. A yield of 70 % of on-size product is achieved, and this always allows to keep the granulation stable by adjusting the return flow rate. The heat losses associated with the recycled material are not harmful in BASF's CAN process but on the contrary are desired. The fraction of on-size product, which has been separated out, is cooled, observing defined residence times and finely screened.

To avoid a return flow with organic material into the process, the coating with anticaking agent is carried out only when the product leaves the factory. In the single stream plant described, outputs of more than 2000 tonnes/day are usually reached.

## 3. PRODUCT QUALITY

When lime from the Odda process and the inorganic additives developed by BASF are used, the CAN has a pure white color. It can be described by the following typical values:

| | |
|---|---|
| - water | 0,18 % |
| - calcium nitrate | 0,1 % |
| - grain hardness | 60 N |
| - grain hardness after 10 temperature cycles | 30 N |
| - attrition (after 1 hour) | 0,1 % |
| - grain spectrum (2 - 5 mm) | 98 % |
| - bulk density | 1,02 g/l |

## 4. UTILITIES

Steam is needed only for concentrating the ammonium nitrate solution from 94 to 98 % (by weight). The typical steam consumption figures including all heating are:

- 65 kg/tonne of CAN at 9 - 16 bar
- 25 kg/tonne of CAN at 4 bar.

The heat from solidification and transformation introduced into the process with the ammonium nitrate solution is suffice for heating up the lime and evaporating the water introduced with the lime and ammonium nitrate. Additional heating energy such as natural gas or fuel oil is required neither on start-up nor during operation. Under the conditions we have chosen, the process is autothermic.

The consumption of electric power is also low at 18 kWh/tonne of CAN, since no energy is required for generating fluidizing air or for spraying the paste.

## 5. ENVIRONMENTAL SAFETY

Figure 2, (column diagram)

The contaminated air streams from the granulation drum and drying drum are fed to a column for purification. Downstream of the column, typical contents of

- $NH_3$ < 30 $mg/m^3$ (s.t.p.)
- dust < 50 $mg/m^3$ (s.t.p.)

are maintained.

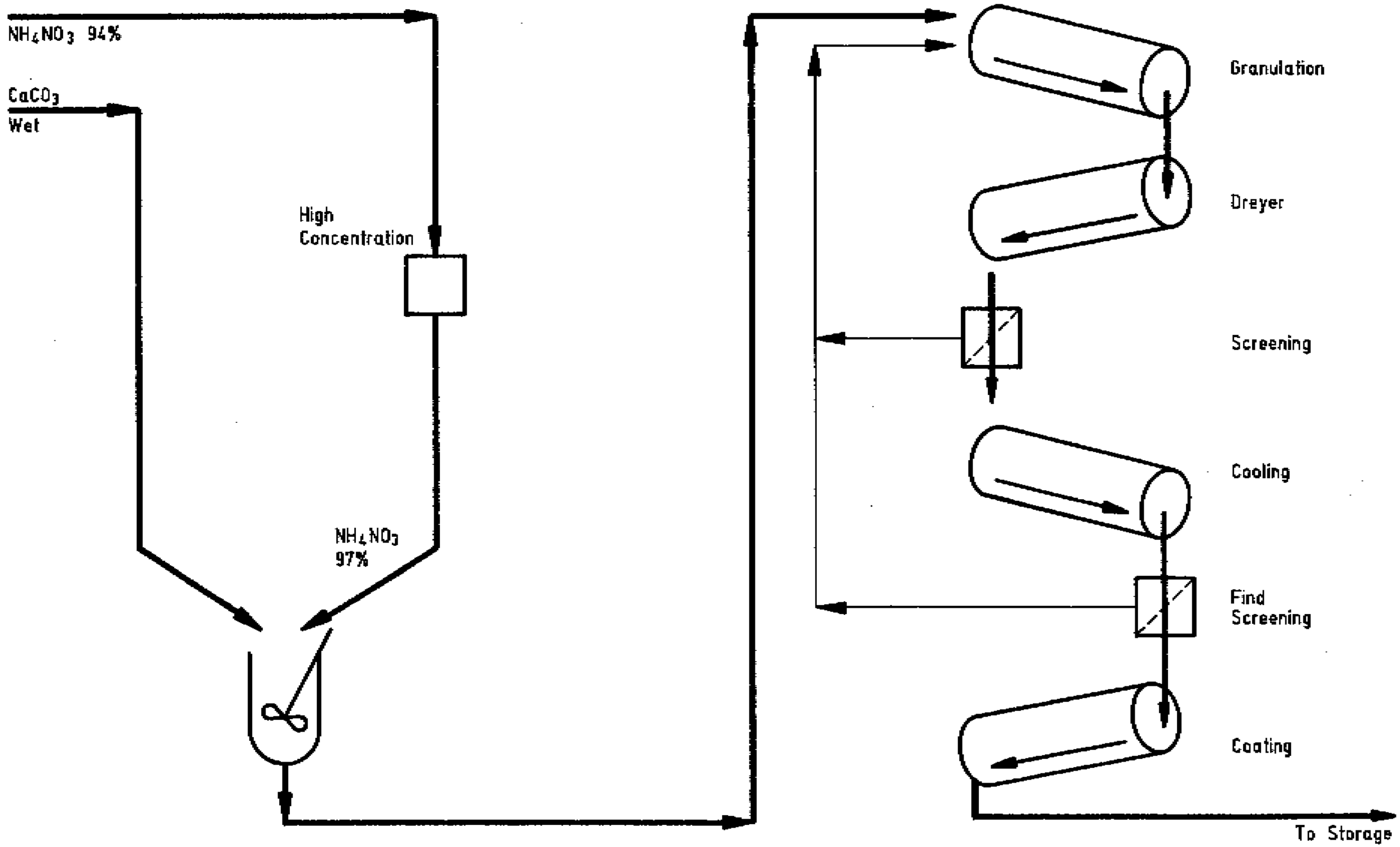
The hot gases introduced into the column evaporate the water. The column feed thus necessitated allows all the vapor condensates from the ammonium nitrate concentration step and any washing water to be accommodated in the column. The process is thus free of process effluent.

The outflow from the column is very small at about 0,5 % of production and, because of its high concentration, can be directly recycled into the process.

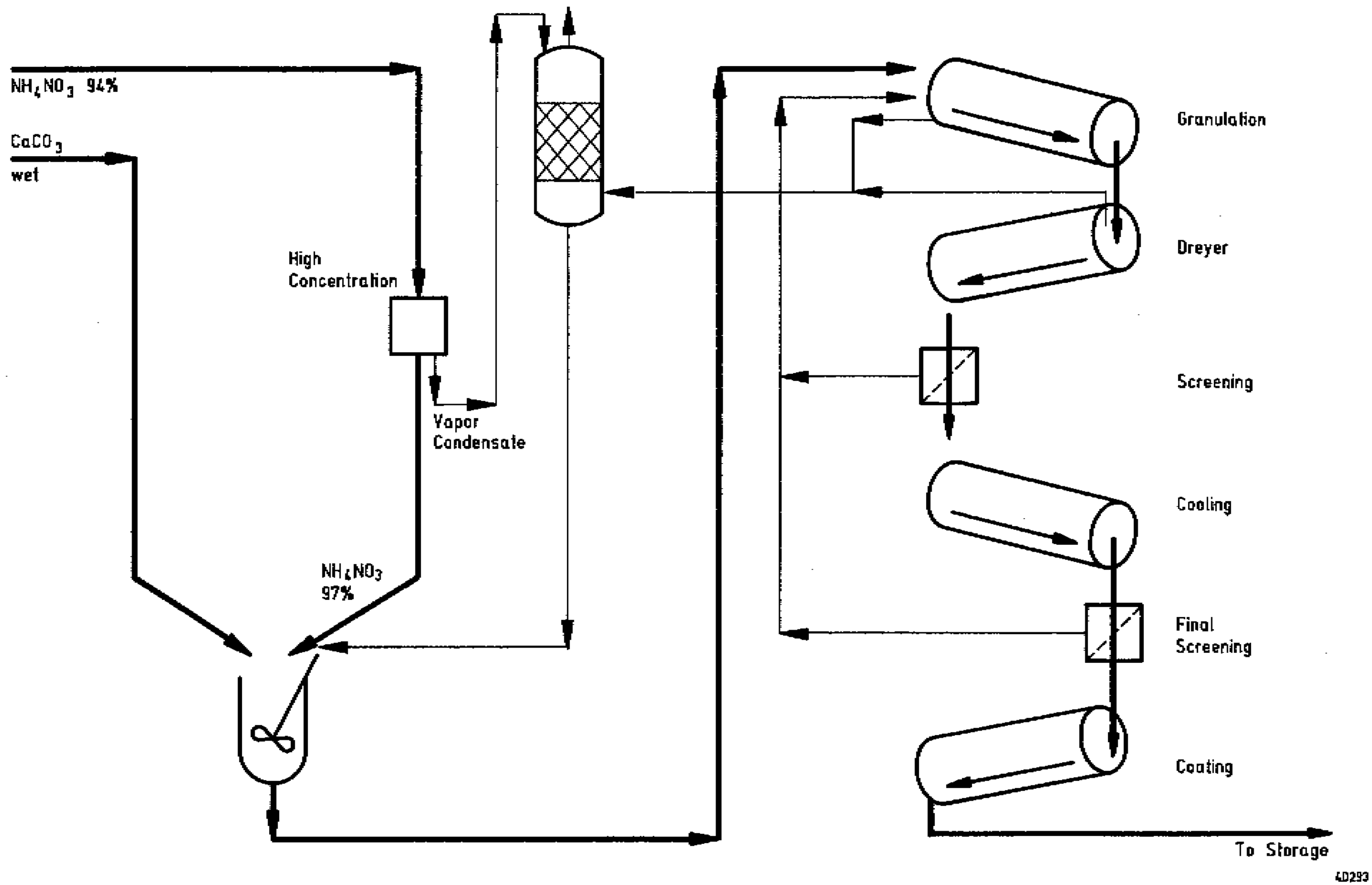
As a result of the use of 94 % by weight ammonium nitrate and of the immediate consumption of the 98 % ammonium nitrate, storage of highly concentrated ammonium nitrate is avoided. The plant inventory is usually only about 900 liters. Under German law, it was thus possible to avoid the classification of the CAN plant as a plant susceptible to major accidents.

## 6. CONCLUSION

The process was developed at Ludwigshafen in 1987. In the meantime, plants using the process have been established at Antwerp, Linz and Ostend by revamping or new construction. All the equipment is designed such that at worst a 5-hour cleaning period is necessary after 10 days. 345 days of on-stream time are usually achieved at Ludwigshafen.




| | | | |
|---|---|---|---|
| BASF | FIGURE 1 | CAN-PROZESS | NR.1 |




| BASF | FIGURE 2 | CAN-PROCESS | NR.2 |
|---|---|---|---|