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**Nitrophosphate and Fertilizer Plants:
the Recycling Concept for Minimizing Pollution
of Air and Water**

**1. BASF scheme for fertilizer production by means of
the nitrophosphate process**

BASF prefers to link the productions of its multinutrient and nitrogen fertilizers by means of a common source of starting materials: both phosphates for multinutrient fertilizer and ammonium nitrate and calcium carbonate for the nitrogen fertilizer are provided by the nitrophosphate process.

In the first part of this process, also known as the Odda process (Fig. 1) rock phosphate is digested with nitric acid. The solution is separated from the inert residue of sand, then cooled, which brings down crystals of calcium nitrate tetrahydrate (CNTH). The CNTH is filtered off and the filtrate, called NP solution, is used as the starting material providing the phosphate for production of multinutrient fertilizer. The CNTH is treated with carbon dioxide and ammonia, converting it into calcium carbonate, which is filtered off, and a solution containing about 60% of ammonium nitrate, which is neutralized and concentrated. Calcium carbonate and ammonium nitrate are the two ingredients of nitrogen fertilizer, and some ammonium nitrate is required to adjust the ratio of nitrogen to phosphorus in multinutrient fertilizers.

For production of multinutrient fertilizer the NP solution is treated with ammonia in two stages, then the potassium component and any other nutrients required are worked in. For granulation we use spherodizers and drums, and in each drum-granulation

unit a granulating drum is paired with a drying drum. The screened product is finally coated and cooled.

Our aim in the production of nitrogen fertilizer is to make enough chalk and ammonium nitrate mixture (CAN) to use up all the calcium carbonate formed in the Odde process. For this mode of production, usual in BASF, an additional plant is needed for synthesis of extra ammonium nitrate, since the Odde process meets only about half the requirement.

In the autothermic CAN process as carried out by BASF the mass fraction of ammonium nitrate in the melt is brought to about 98%, then the unwashed, moist calcium carbonate formed from calcium nitrate is incorporated. The final processing stages are granulation, drying, cooling, and coating, in that order.

We have been making fertilizers at Ludwigshafen in the way described for more than thirty years, and in 1985 the linking process, the Odde process, was set up at the Antwerp works. The experience that BASF has gained is the basis of licences under which two fertilizer complexes are being constructed in conjunction with Uhde GmbH. The complexes will start producing in 1989.

2. Environmental protection: tasks, problems, and aims

The circumstances just described and improved standards of environmental protection led us to think again about our arrangements for avoiding pollution in the course of fertilizer production.

2.1 The waste products formed

Knowledge of the by-products of fertilizer production provides the simplest approach to the measures necessary for protection of the environment. Apart from

few exceptions there are no uses for these by-products, which are therefore true waste products and have to be disposed of or discharged in as pure a form as possible.

The waste products are carbon dioxide, sand, water, and air, as shown in Fig. 2. They are either substances set free from the starting materials for fertilizer production, such as carbon dioxide and sand from the rock phosphate and water from the nitric acid, or they are working materials used in various stages of production, which are discarded once they have done their job, such as water used for washing and air used for drying.

The quantities of substances set free from the starting materials cannot be reduced. For instance, all the water introduced in the nitric acid used for digesting the rock phosphate has to be got rid of by the end of the process, since the granulated fertilizers are dry products. It is apparent from Fig. 2 that this water leaves the process as condensate after the ammonium nitrate solution has been evaporated down or as vapour after the various granulation or drying stages.

The quantities of water and air made use of in the process for washing and drying are essentially reducible. For instance, the air used for drying in our NPK production can be recirculated until it is more highly saturated, to reduce the rate of discharge to waste.

2.2 Contaminants in the waste products

The waste products carbon dioxide, sand, water, and air are natural substances, and as such they can be disposed of or discharged at any time if they are uncontaminated. However, in the course of the process they pick up substances that would pollute the environment, as shown in Fig. 3.

The sand separated from the rock phosphate is contaminated with digestion liquor, whose essential components are phosphoric and nitric acids. The condensate from ammonium nitrate concentration is contaminated with entrained ammonium nitrate. The contaminants in the air vary according to the part of the process.

The air from the acid stages of the Odda process is contaminated mainly with nitrogen oxides. The alkaline stages and the alkaline to neutral stages of the CAN and NPK processes emit ammonia. Air from the granulation and drying stages carries dust as well. As shown in Fig. 3, air from different stages of the processes can be combined before treatment when the known contaminants are the same.

2.3 Aims

Given knowledge of waste products formed in the course of the processes, and bearing in mind what is technically and economically feasible, we must devise a scheme for environmental protection in fertilizer production that achieves the following aims.

1. The reducible quantities of the waste products air and water are to be minimized.
2. Contaminants in those waste products whose quantities cannot be reduced are to be eliminated as far as possible within the process.
3. The cleaning-up that remains to be done is to make use of processes by which contaminants are recovered and recycled.

In what follows we shall be concerned mainly with solutions of problems connected with the achievement of Aim 3, assuming that measures to achieve Aims 1 and 2 are carried out in accordance with good practice.

3. Solutions in the context of the scheme for environmental protection in fertilizer production

3.1 Production of NP solution, ammonium nitrate, calcium carbonate

An earlier version of the scheme for environmental protection applying to the acid and neutral parts of the Odda process is shown in Fig. 4. Here all contaminants are collected in water and discharged with it.

The sand is freed from 90% of the digestion liquor adhering to it by means of a prewash, the solution being recovered, then it is given a thorough afterwash. The product is sand with a neutral reaction, which can be used in the building-materials industry. The digestion liquor removed by the afterwash is discharged with the washing water.

The traces of ammonium nitrate entrained during concentration of the solution by evaporation are also discharged in water, in the condensate.

In this version the stream of waste water is swollen considerably by the fresh water introduced for thorough two-stage scrubbing of the waste air, although the two packed towers are connected to the supply in a 'water-saving' way, in series.

The way the waste air is connected to the towers is determined by the quantities and degree of contamination of air to be scrubbed. Less air comes from the digestion and sand-separation stages, but the concentration of nitrogen oxides is about fifty times as much as in the air from the cooling stage. In spite of very good scrubbing efficiency the mass concentration of nitrogen oxides in the air emerging from the first packed tower can be as much as 2000 mg/m³, expressed as nitrogen dioxide but actually due almost entirely to nitric oxide, which is difficult to absorb. The air from the cooling stage contains

nitrogen oxides with a high proportion of nitrogen dioxide, and is also difficult to scrub. However, mixing the two air streams before they enter the second tower produces a mixture of nitrogen oxides with the optimum degree of oxidation, between 40% and 60%.

The mass concentration of nitrogen oxides in the air leaving the second tower can be brought below the maximum allowed by German regulations, 500 mg/m³ at standard temperature and pressure, expressed as nitrogen dioxide, if the tower packing is high enough.

The quantities of nitrogen transferred from the waste air to the scrubbing water are greater than the total quantities washed out of the sand and carried over into the condensate from concentration of ammonium nitrate, and more than 90% comes from the digestion stage of the Odda process. A second version of the scheme for environmental protection makes use of these facts in reducing nitrogen pollution in an economic manner. It is illustrated by Fig. 5.

The waste air from the digestion stage is prescrubbed with dilute nitric acid flowing in a closed circuit. Absorption of nitrogen oxides tends to increase the acid concentration, but by returning acid to the process and admitting fresh water the mass fraction of nitric acid is kept at a constant value between 30% and 40%. The acid returned to the process contains nitrite and fluoride in low concentrations. The air leaving the prescrubbing tower still contains about 40% of the oxides originally present and from 10% to 40% of the fluorine, thus it needs to be scrubbed with water in the usual way. For this purpose it is led to the first of the two scrubbing towers connected in series, as before.

The materials balance for an Odda plant with a daily throughput equivalent to 200 metric tons of phosphorus pentoxide shows that the rate of discharge of nitrogen in the waste water produced by scrubbing

the air from the digestion and sand-separation stages is reduced from 80 kg/h to 32 kg/h.

A third version of the scheme for environmental protection eliminates the waste water (and waste nitrogen) produced by scrubbing the air from the digestion and sand-separation stages. It is illustrated by Fig. 6.

Such a process needs a scrubbing liquor in a closed circuit that absorbs nitrogen oxides as well as fresh water does. This is possible only if the nitric acid that is formed is neutralized by ammonia and most of the nitrous acid is decomposed.

Decomposition of nitrous acid can be carried out thermally, by steam stripping at 100 °C, or by treatment with urea. Before urea solution is added, in a closed cascade, the ratio of the amount of urea to the amount of nitrite being 1:2, the scrubbing liquor is heated to a temperature of 70 °C; subsequently it is cooled again.

The mass fraction of ammonium nitrate in the scrubbing liquor is kept between 15% and 20% by returning solution to the process and replacing it with fresh water.

In the version just described it is possible to avoid producing waste water from scrubbing air because ammonium nitrate solution absorbs nitrogen oxides about as well as water does. However, to wash the sand it is necessary to start with clean water and produce contaminated water. The contaminated condensate from the concentration of ammonium nitrate must also be discharged as waste unless it can be purified sufficiently to allow its employment elsewhere.

The version that produces no waste water arising from operation of the acid and neutral stages of the Odda process is presented in Fig. 7. It has just been indicated that it inevitably entails the conversion of waste water into a clean product that can be used. This

can be done, but at not inconsiderable expense, by means of an ion-exchange process that we have developed from an idea on paper to the industrial stage in conjunction with Christ AG.

The waste water produced by washing the sand is freed from suspended matter and combined with the condensate from evaporation of ammonium nitrate solution. This water is freed from calcium and ammonium ions by means of a cation-exchange unit, then passes to an anion-exchange unit together with the water that leaves the air-scrubbing tower. Another ion-exchange unit provides a final clean-up, delivering water whose conductivity is about 1 microsiemens. This water is of such quality that it can be used as boiler feed; some of it is drawn off to allow for the excess input of contaminated condensate.

The ion-exchangers are regenerated with nitric acid and ammonia solution. The eluate from the cation-exchanger is returned direct to the process. The eluate from the anion-exchanger contains about 2.5% nitrite, which must first be decomposed thermally, and it also needs to be concentrated by evaporation before it is returned to the process.

The conversion of CNTH to ammonium nitrate and calcium carbonate, the alkaline part of the Odda process, involves neither evaporation nor drying, so there is no waste process water to discharge. In the BASF process the calcium carbonate is not washed, so there is no contaminated washing water either. The exhaust air contains carbon dioxide and ammonia, so it has to be scrubbed, but the scrubbing liquor is circulated in a closed circuit (Fig. 8). This part of the process thus produces no waste water at all.

The exhaust air is scrubbed in such a way that it carries much less ammonia than the official limit. Given the quantity of air to be treated, the temperature, and the ammonia concentration, there is a

minimum pH-value for optimum scrubbing. Introduction of nitric acid is controlled in such a way that the pH-value does not fall below the set limit. If it did, ammonium nitrate aerosol would be carried out with the air. To ensure complete neutralization of peak quantities of ammonia at the chosen pH-value the liquor must be circulated at a sufficiently high rate (300 m³/h in the example); in this way both aerosol formation and carry-through of ammonia are avoided. The mass fraction of ammonium nitrate is kept at about 50% by density-controlled introduction of water and level-controlled return of solution to the process.

3.2 NPK process

The part of the environmental protection scheme concerned with the various stages of the NPK process has to deal with waste air carrying different quantities of water vapour and contaminated variously with ammonia, fluorine compounds, and dust. It is shown in Fig. 9.

The exhaust air from the two neutralization stages and the incorporation of potassium salts is combined in one stream. Its temperature is 95 °C, and it is nearly saturated with water vapour. An NPK plant producing about 1 200 metric tons of 16 + 16 + 16 NPK daily would be expected to put out air from this part of the process at the rate of 20 000 m³/h, and this would carry 9.2 metric tons/h of water as vapour. The hot, nearly saturated air is scrubbed with nitric acid solution to remove ammonia, which is returned to the process as ammonium nitrate.

The scrubbing tower is operated in the way described above in connection with exhaust air from CNTH conversion. Because the temperature of the air is 95 °C initially the ammonia is not removed quite so effectively, but its concentration in the air discharged is still well below the official limit. The

risk of formation of ammonium nitrate aerosol is greater, therefore the pH-value is set higher and the liquor is circulated at a correspondingly higher rate. It has been found that the appropriate rate for the peak concentrations of ammonia that are encountered is 800 m³/h.

The second combined air stream comes from the granulation and drying stages. It is much larger than the stream from neutralization and incorporation of potassium salts -- 90 000 m³/h compared with 20 000 m³/h -- , in spite of recirculation, but it carries only 5.4 metric tons/h of water vapour. The gas is freed from dust by a battery of cyclone separators, which it leaves carrying 50--75 mg/m³ of dust at s.t.p. The ammonia content depends on the type of NPK involved, but for the commonest types it is about 100 mg/m³ at s.t.p. on average, so scrubbing is not required.

The third and largest air stream -- 240 000 m³/h -- combines the exhaust from cooling and coating. The use of fluidized-bed coolers and well-designed flow paths keeps the level of contamination down to a level that allows the air to be discharged without treatment.

3.3 CAN process

That part of the environmental protection scheme concerned with the CAN process is shown in Fig. 10. It is designed for plant producing 2 000 metric tons/d of CAN containing 27% nitrogen, which uses all the calcium carbonate and more than the ammonium nitrate produced by the Odda plant described previously. The additional ammonium nitrate is supplied by a synthesis plant, as mentioned before.

The stages in which moist calcium carbonate and ammonium nitrate are mixed, granulated, and dried produce half the water that leaves the plant, which is

carried by about 110 000 m³/h of air. The temperature of the air stream, which is not saturated with water vapour, is 85 °C. The hot air is first passed through cyclone separators to remove much of the dust, then it is scrubbed with nitric acid and ammonium nitrate solution in a closed circuit to remove ammonia in the way that has been described already. The quantities involved are such that it suffices to circulate the liquor at the rate of 700 m³/h.

Scrubbing the waste air and returning ammonium nitrate solution to the process have some additional advantages. First, the dust content is reduced to below 10 mg/m³; the dust content of the air leaving the cyclone separators is about 75 mg/m³ at s.t.p. Second, all the contaminated condensate from the concentration of ammonium nitrate can be fed into the scrubbing liquor, to make up for evaporation losses caused by the hot, not nearly saturated waste air; thus the entrained ammonium nitrate can be recovered.

The larger stream of waste air that comes from the cooling and coating stages does not need to be scrubbed, but it must be passed through cyclone separators to remove dust.

4. Summary

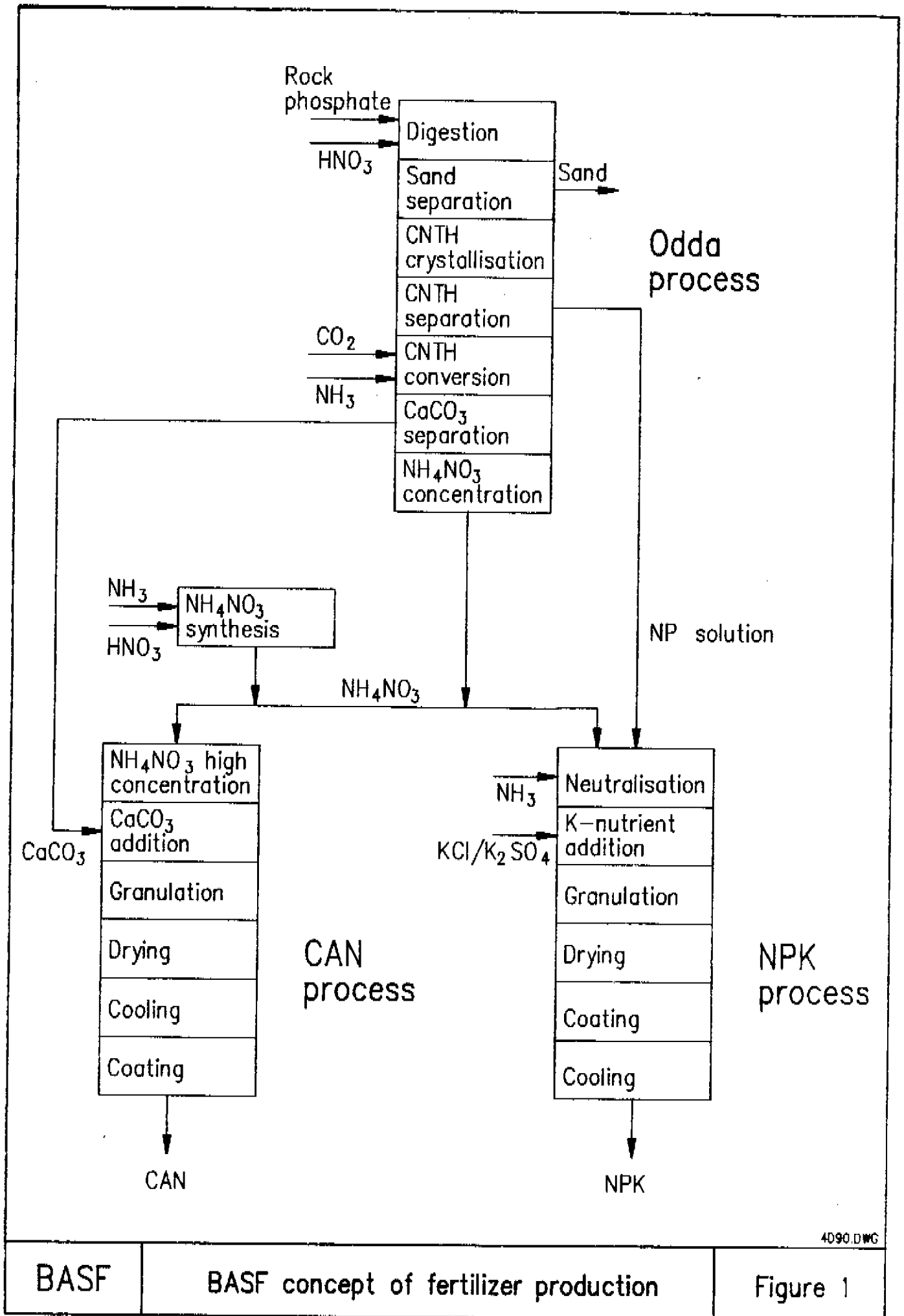
This paper has presented BASF's scheme for environmental protection in fertilizer production, whose aim is to recover as much as possible of the contaminants borne by the inevitable waste products sand, water, and air and return them to the process.

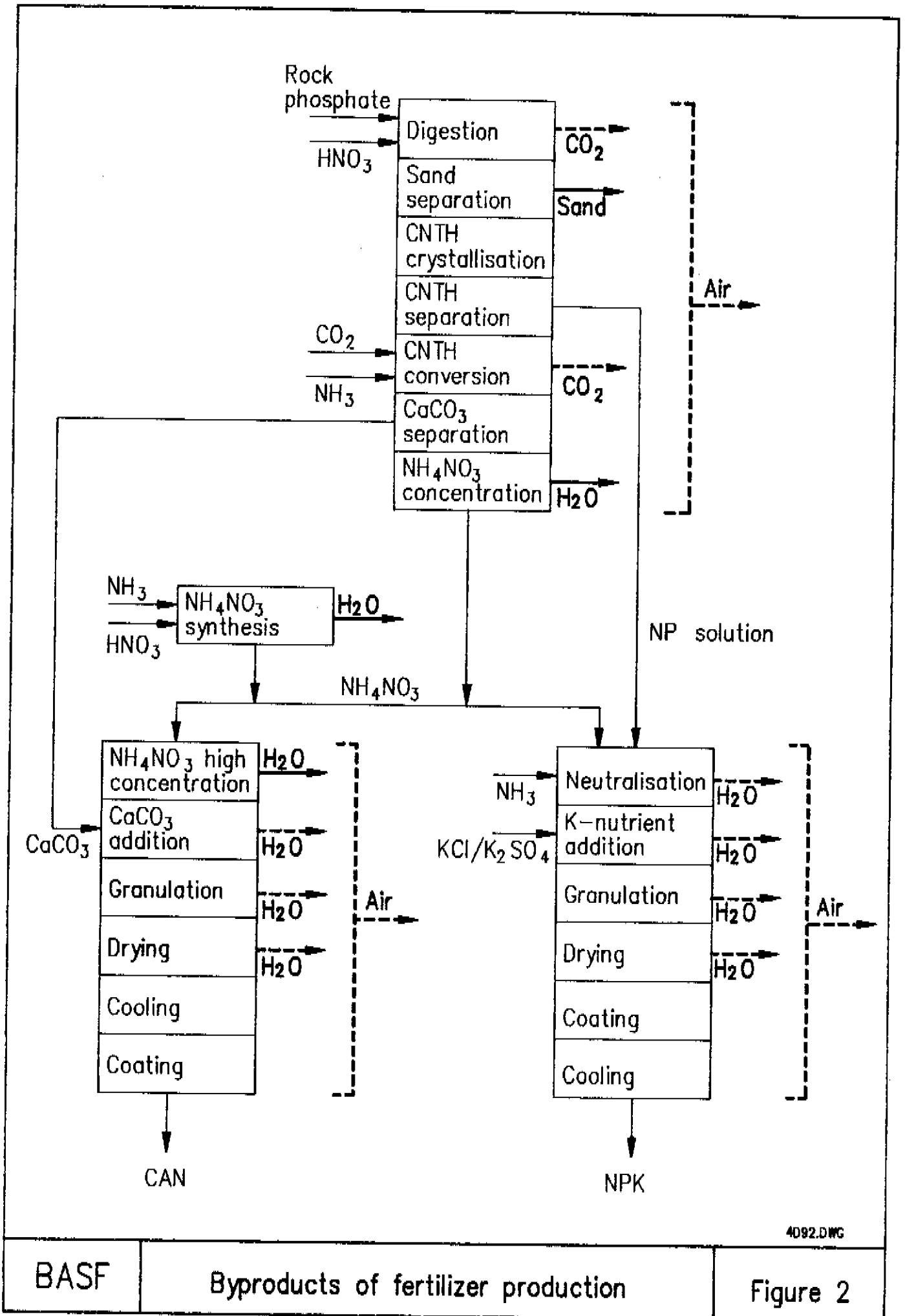
As far as the conversion of CNTH into ammonium nitrate and calcium carbonate, the NPK process, and the CAN process are concerned, this aim can be realized where necessary by scrubbing the waste air with nitric acid in a closed circuit and returning ammonium nitrate solution and by dust removal in cyclone separators.

In relation to the acid stage of the Odda process and the stage in which ammonium nitrate solution is concentrated by evaporation various alternative ways of scrubbing the waste air have been discussed. The several versions of the scheme for environmental protection provide a stepwise approach to full realization of the principal aim. The first version involves scrubbing waste air with fresh water; there is no recovery. In the second version part of the nitrogen oxides is recovered from waste air, as nitric acid. In the third version much of the nitrogen oxides is recovered from waste air, as ammonium nitrate.

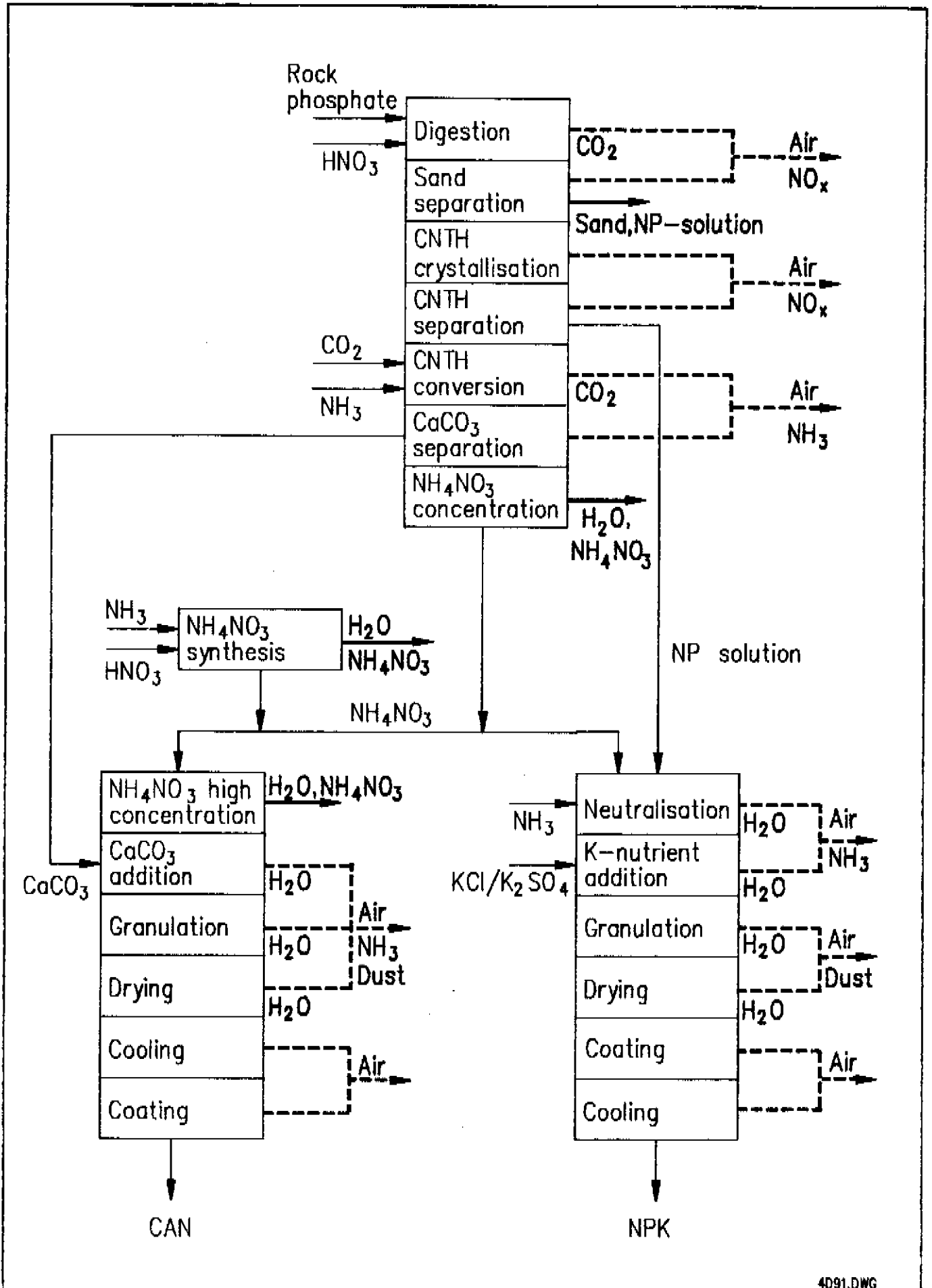
A fourth version of the scheme shows that full realization of the declared aim is feasible, though expensive. With the aid of ion exchangers contaminants are recovered from waste sand, waste air, and all sources of waste water.

Regulations, planning restrictions, and local circumstances will determine what is essential, but it is possible to devise a scheme for every level of environmental protection.



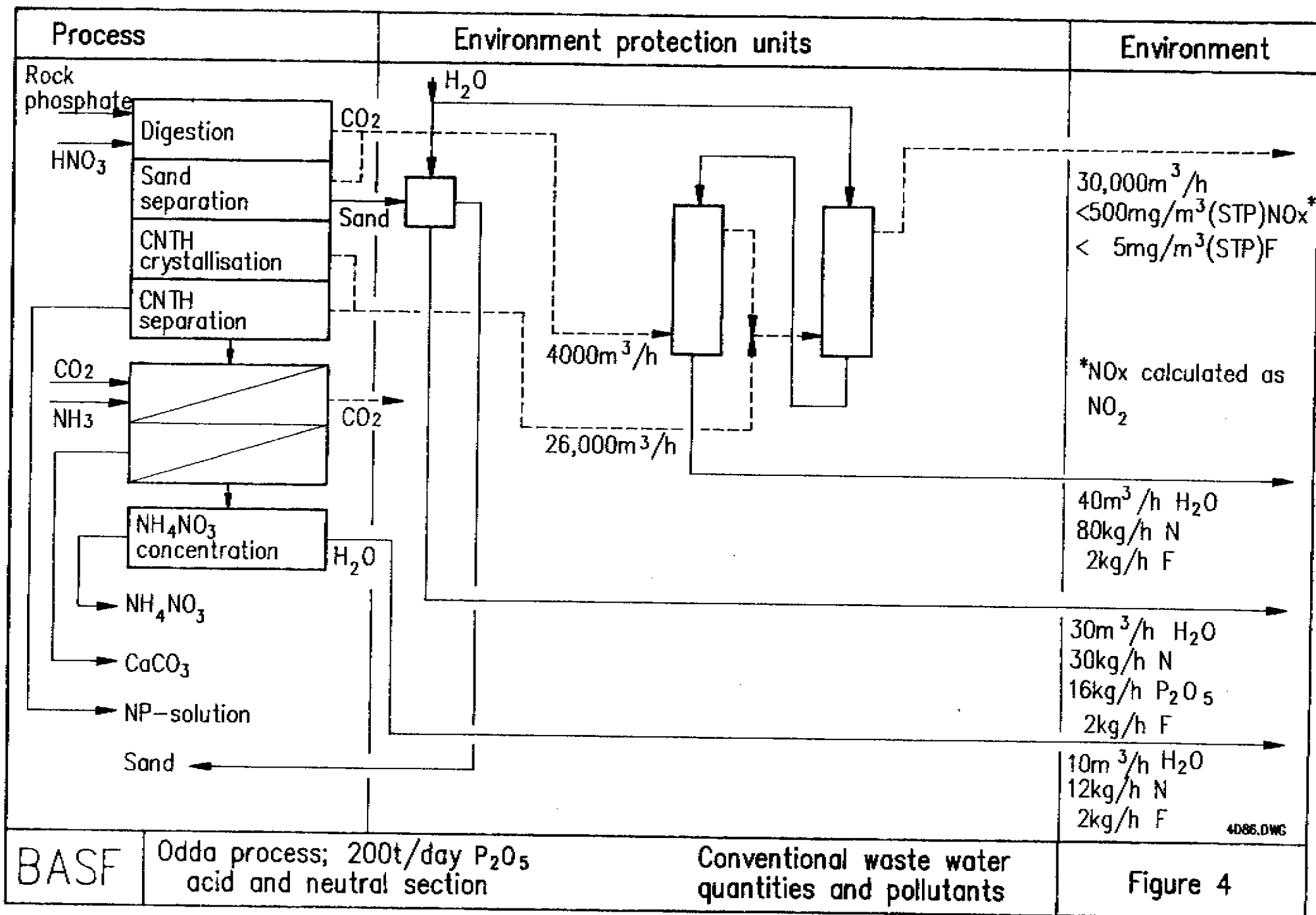


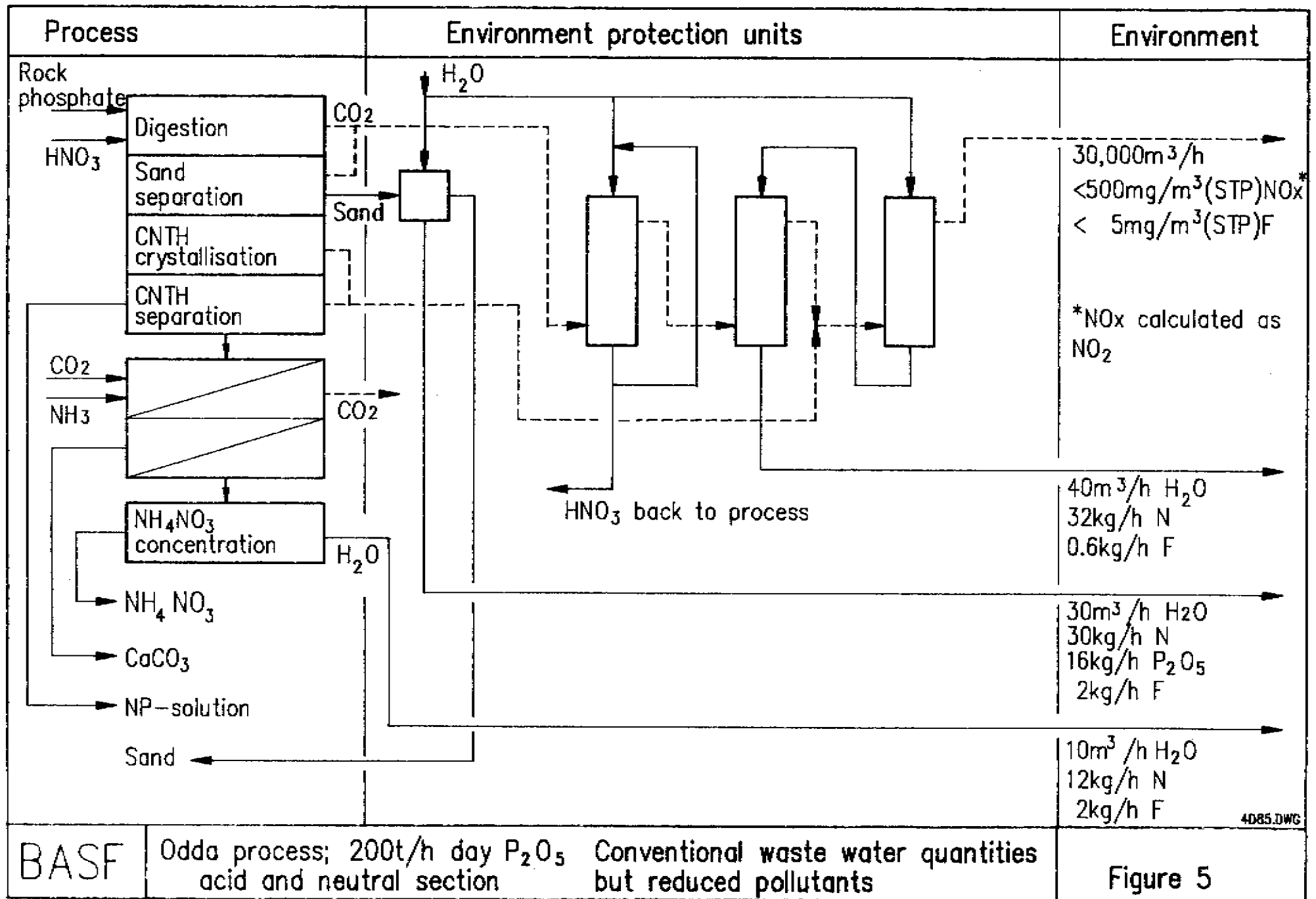
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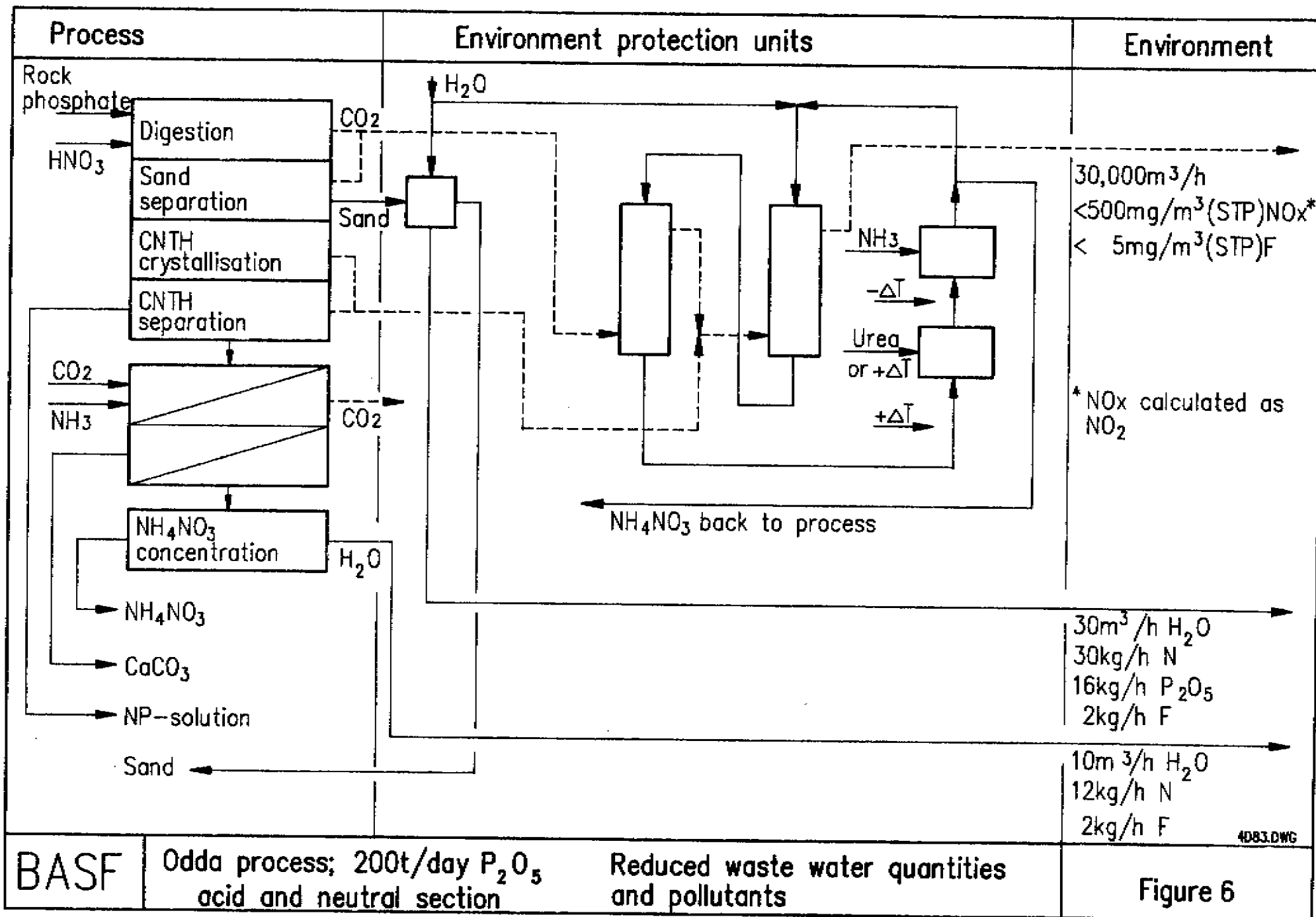
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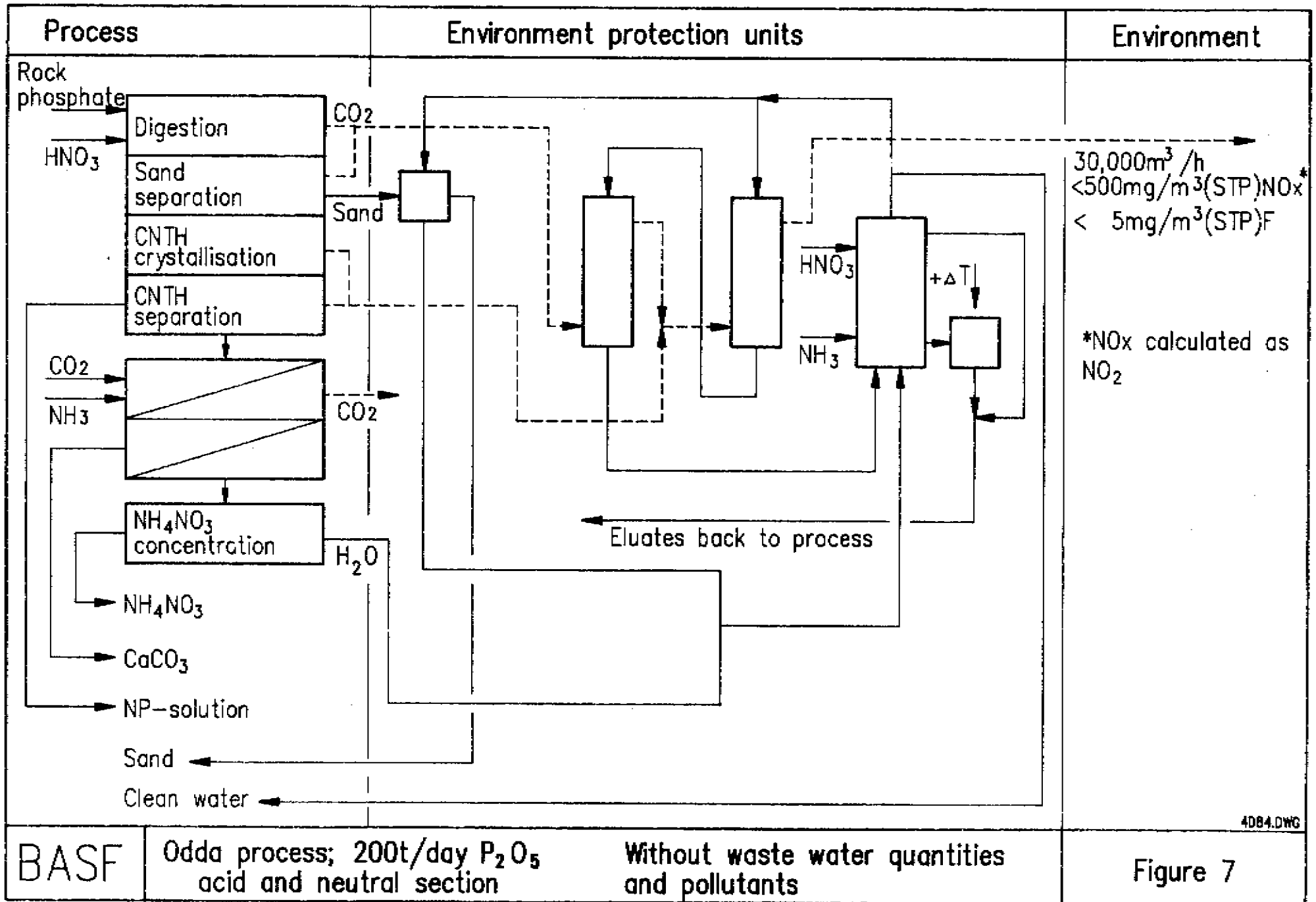
BASF Environment polluting substances in byproducts of fertilizer production Figure 3



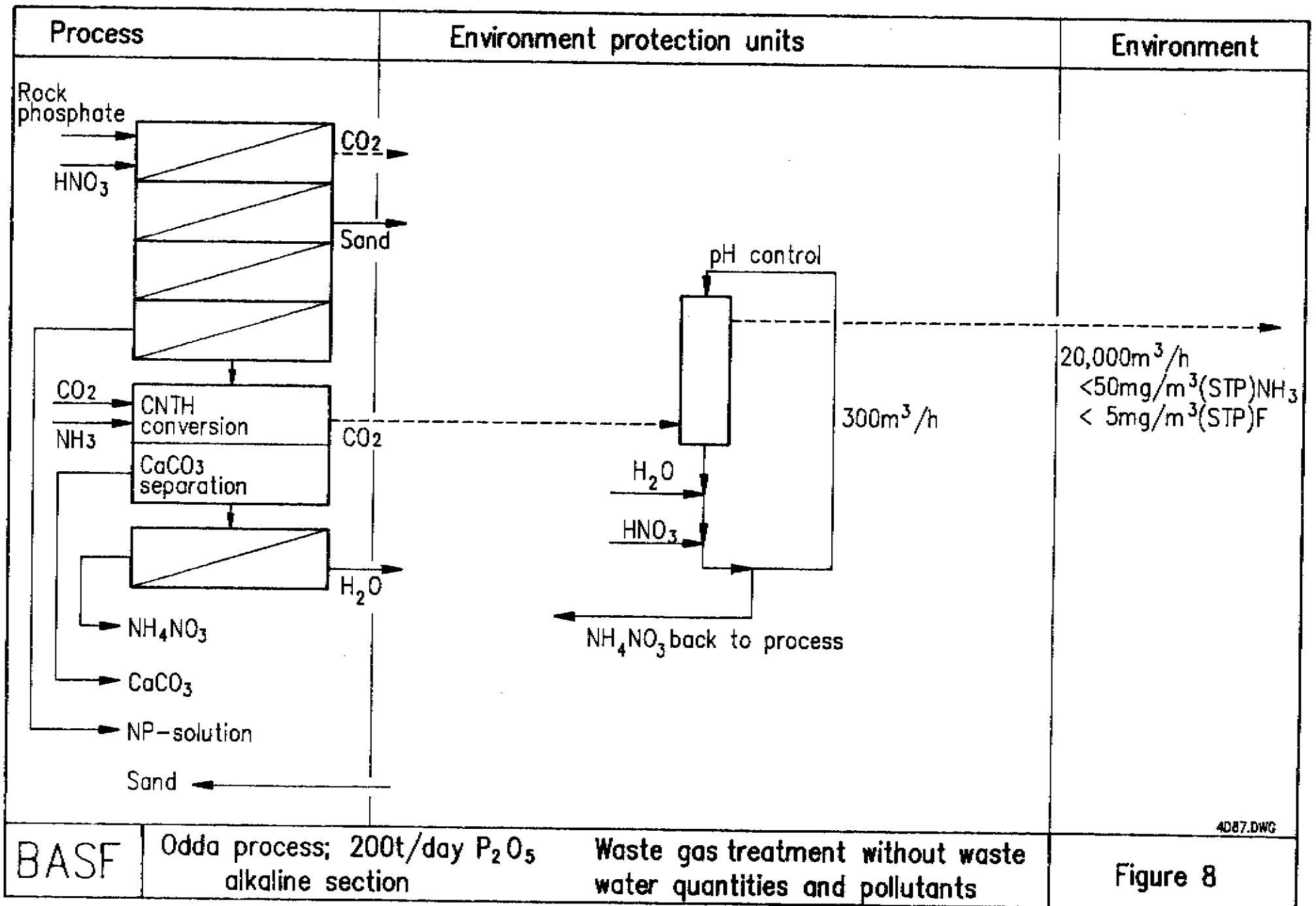


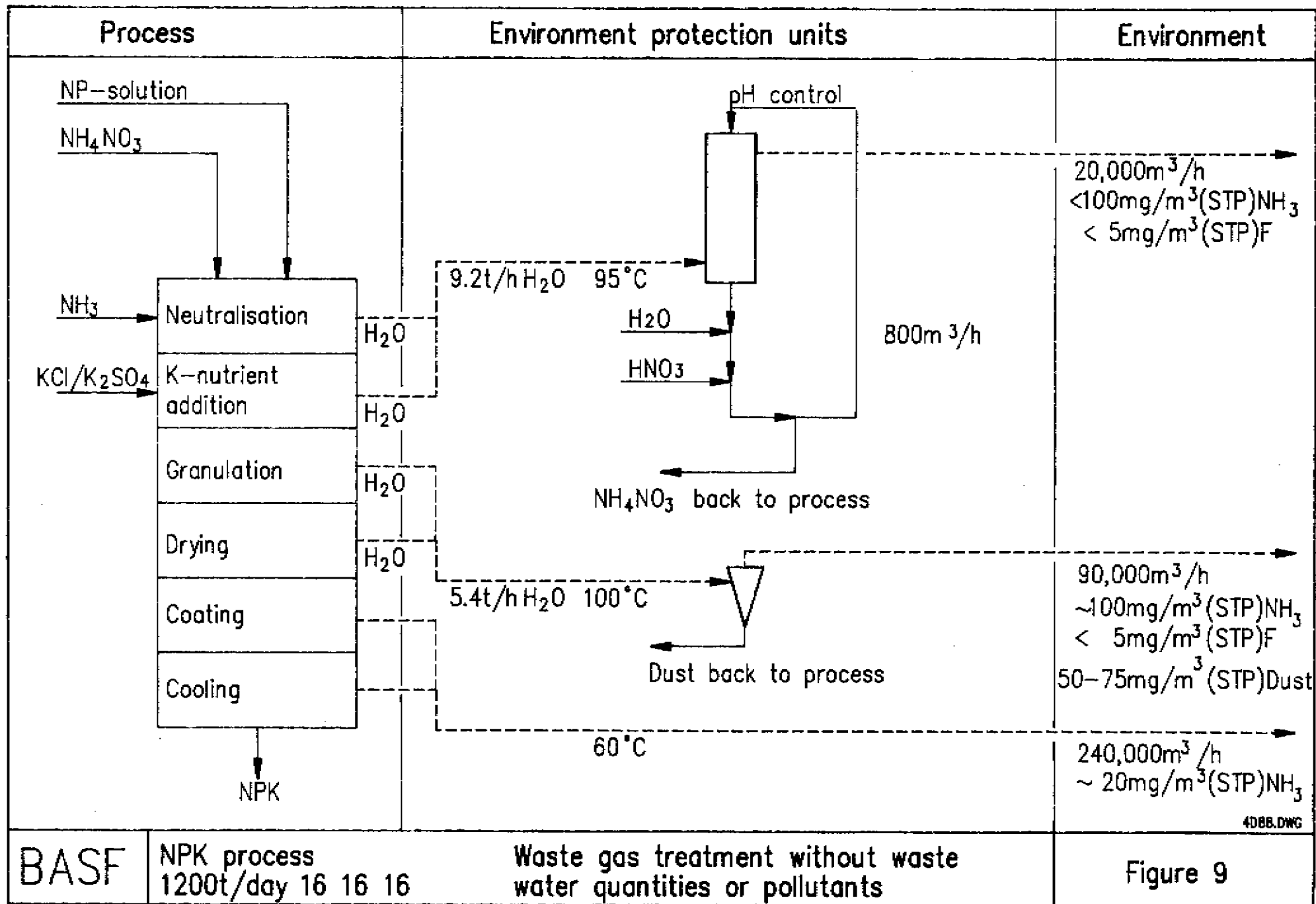
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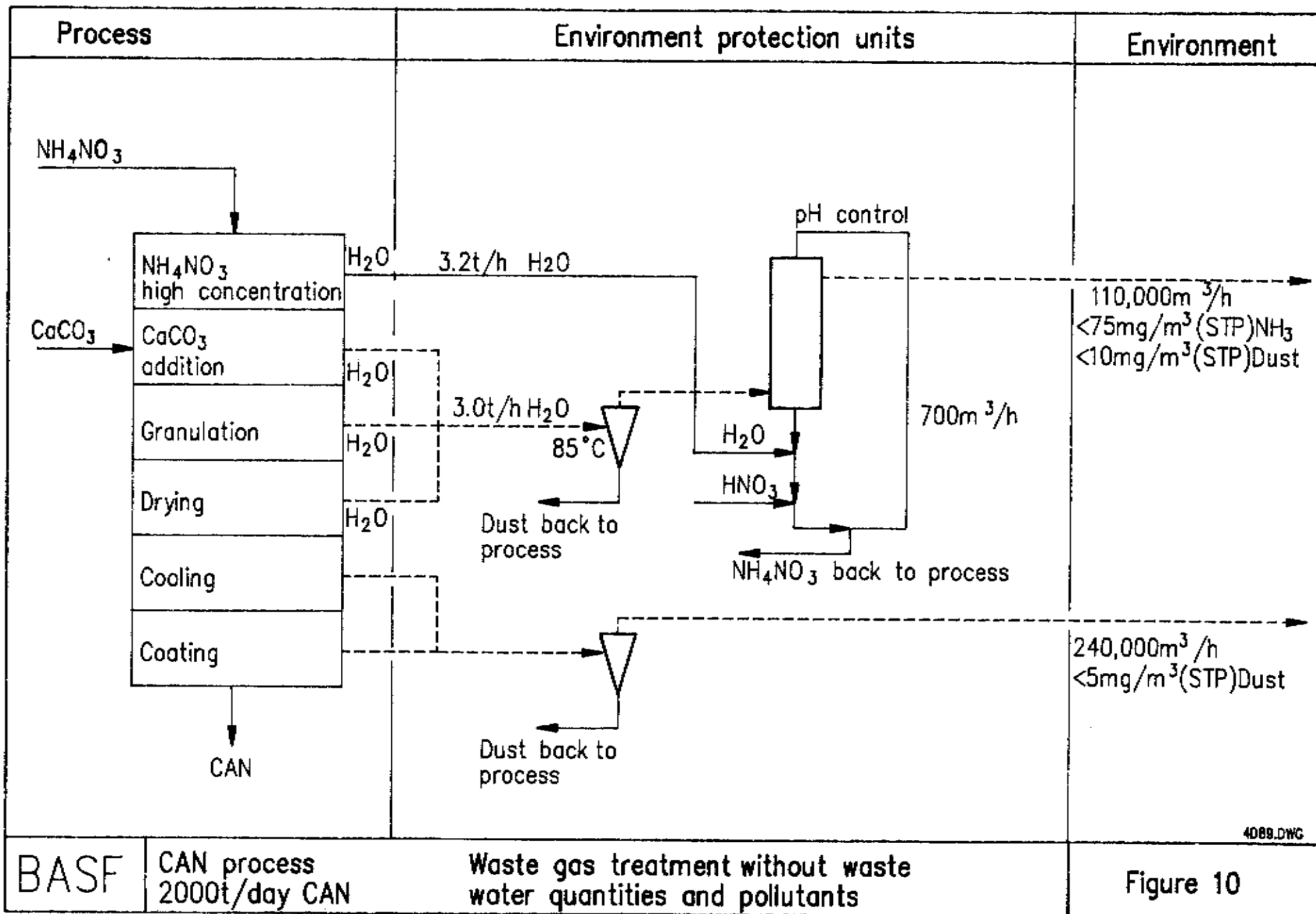




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TA/88/12 Nitrophosphate plants: the recycling concept to minimize pollution of air and water by L. Diehl, BASF, Western Germany.

DISCUSSION (Rapporteur Mr. P. Stokka, Norsk Hydro, Norway).

Q - Mr. R. PERANDER, Kemira Oy, Finland

Could you tell something about the fluorine balance in the process ?

A - You could say that 99% of the fluorine remains in the process and approximately only 1% of the fluorine goes in the air.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark

You state in your paper that the ammonia content in the off-gases from the alkaline part of the Odda process, and from the drying process is well below the official limits. What are the official limits in Germany and Belgium.

A - Dr. R. NITZSCHMANN, BASF, Germany

We have in Germany in our off-gases no limits for ammonia. But it was proposed that the fertilizer industry reduces the ammonia outlet in the off-gases. For new plants it was first spoken about a limit of 50 mg. At the moment there are discussions about values between 100 and 300 mg.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

Have you measured the content of ammonium nitrate aerosols coming directly from the NP neutralization stage ?

A - Dr. R. NITZSCHMANN, BASF, Western Germany.

We have made many investigations on this point. It turns out that if you choose a good pH of this washing fluid, and this pH depends on the temperature of the gases and the ammonia content of the gases, you can avoid absolutely all aerosols.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

How large a percentage of air from the drying or the spherodizer are you able to recirculate ?

A - Dr. R. NITZSCHMANN, BASF, Western Germany.

About 30 to 50%

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

My last comment is that I am greatly impressed that you are able to run a cyclone battery so that the dust content is reduced to less than 5 ppm.

A - Dr. NITZSCHMANN, BASF, Western Germany.

Low dust content coming from cooling and coating drums in the CAN process.

.../.../...

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway

To clean waste water containing nitrate, you are using ion-exchangers. What is your operational experience with this cleaning process, and have you experienced deposit problems since the waste water also contains P and F components ?

A - We worked together with a company named Christ AG, Switzerland, CH-4197 Aesch, and this company has great experience with this way of cleaning water. There are plants in Yugoslavia, Bulgaria and Romania where this process has been in operation for many years.

Q - Mr. B. CHRISTENSEN, Superfos Fertilizers, Denmark.

1/ Has BASF proved the use of by-product sand for building material, and to what extent has the pollutent to be washed out and what kind of filter is used.

A - To the last part of the question, we have belt filter from the companies Pannevis, Netherlands, 3542 Utrecht and BHS AG, Western Germany, D-8972 Sonthofen. The sand has indeed been used as building material for 15 years, and it is a good building material.

Q - Mr. B. CHRISTENSEN, Superfos Fertilizers, Denmark.

Does the possibility of this filtration of sand lead to use of low grade rocks ?

A - Yes, but you must use a big sandfilter.

Q - Mr. B. CHRISTENSEN, Superfos Fertilizers, Denmark.

I think you did not answer fully the first question. To what extent do you have to wash out the pollution from the sand ?

A - We have a pH neutral sand. It is washed very thoroughly. All these soluble things are acid. We have phosphoric and nitric acids in the sand, and if we come to a pH of 7, we have washed out all these things.

Q - Mr. G. BRUSASCO, Agrimont, Italy.

Have you realized all the reported environmental protection units in your plants ? If so, what were the investment and the increasing of the production cost of NPK ?

A - We have realized the environment protection units from figures 4, 8 and 10. We are constructing the protection unit from figure 5. We are planning the unit from figure 6 and the units from figure 7 and 9 exist as technical concepts. The investment costs depend on the plant volume and also regulations.

Q - Mr. S. ORMBERG, Norsk Hydro, Norway.

You stressed that you are trying to have a balance between chalk and ammonium nitrate to make calcium ammonium nitrate. Would you not be more flexible if you, for instance, sell some of the calcium carbonate to the farmers as liming aid ?

A - Oh yes, in Germany there are at the moment trials to do such things.