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für Mensch und Umwelt

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German Notes on BAT for the production of

Large Volume Solid Inorganic Chemicals

NPK - Fertilizer

Final report

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1 General Informations

Multi-nutrient fertilizers have increasingly gained importance in the last decades mainly for economic reasons, but also due to technical and physiological aspects. According to the type of manufacture, they are divided into mixed fertilizers and complex fertilizers. The manufacture of mixed fertilizers is generally effected by simply mixing dry single fertilizers, so that there are not caused any essential emissions or residues. For this reason the present project only concentrates on complex fertilizers. In this case the compound of nutrients takes place already during the manufacture process. Among multi-nutrient fertilizers the most important group consists of NPK fertilizers, which contain all three macro-nutrients (nitrogen, phosphorus and potassium) and therefore they are also called triple-nutrient fertilizers. Even without a phosphorus or potassium share, these fertilizers belong to the group of multi-nutrient fertilizers, but then they are called NP or NK fertilizer. Normally these fertilizers can also be produced in the NPK plants and their emissions are comparable with those from the NPK fertilizer production. If a NPK fertilizer additionally contains trace elements, it is colloquially called complete fertilizer.

Numerous multi-nutrient fertilizers have been developed in the passed for the variety of different soil conditions. Actually more than 200 different NPK fertilizers exist only on the European market. They are characterized by their content of N, P_2O_5 and K_2O (in weight percentage), e.g. 20 – 10 – 10 indicates that this particular grade contains 20 % N (nitrogen compounds), 10 % P_2O_5 (phosphorus compounds) and 10 % K_2O (potassium compounds). Most well-known NPK fertilizers in Europe contain nitrate and/or ammonium salts.

There are diverse techniques for the manufacture of NPK fertilizers, which are generally divided into the Mixed Acid Process and the Nitric Acid Process or the Nitrophosphate Process (Odda Technique).

The selection of the used production process and the applied technology is based on different factors, like e.g.:

- NPK nutrient relation
- Raw materials
- Quality characteristics

- Flexibility of the process
- Production capacity of the plant
- Integration of further processes
- Economic factors

In Germany, NPK fertilizers are produced by BASF in Ludwigshafen and Compo in Krefeld. Both companies exclusively apply the mixed acid process and can vary the input shares of materials like nitric, phosphorus or sulfuric acids (not at BASF Ludwigshafen), in order to obtain a wide range of NPK fertilizer products with different nutrient contents. The production capacities of BASF and Compo figure in **table 1**.

Table 1: Manufacturers and Production Capacities of NPK Fertilizers

Company	Location	Capacity
BASF AG	Ludwigshafen	NPK: 1,1 mio t/a
Compo GmbH & Co. KG	Krefeld	Ammonium sulfate fertilizer: 450.000 t/a

Amsterdam Fertilizers in Ludwigshafen produces mixed NPK fertilizers on demand by mixing dry single fertilizers. This production technique, however, does not cause any important emissions and consequently is not presented further in this project.

In the last decade, the fertilizer industry in Western Europe and Germany was confronted to a sharp competition. As a consequence, many companies had to be restructured or even closed-down their businesses. Following a publication of the EFMA, only in the last 3 years some 4.000 employees lost their jobs. The reason for the long lasting price decay were the important decrease of the fertilizer demand in Eastern Europe and the Soviet Union at the beginning of the 90s and the increasing offer of fertilizers from East European productions on the West European market. In addition, China stopped and India reduced its imports, which led to excess production capacities and to a further price reduction. According to a publication of the EFMA, all fertilizer manufacturers in West Europe had to realize high losses in 1998 and 1999. Although since the beginning of the year 2000 fertilizer prices have risen importantly, the economic situation of the fertilizer industry has improved due to higher energy cost. Consequently, further restructurations or even the close-down of some businesses must be expected. The ability for investments is generally low.

2 Production of NPK Fertilizers in Germany

2.1 Chemical Bases of the Raw Phosphate Decomposition

At both production plants in Germany raw phosphates, which at first have to be decomposed by the help of nitric acid, are used for the manufacture of NPK fertilizers. This exothermic reaction proceeds according to the following idealized equation :

(1) $Ca_5[(PO_4)_3(F)] + 10\ HNO_3 \longrightarrow 5\ Ca(NO_3)_2 + 3\ H_3PO_4 + HF$

$\Delta H = -\ 290$ kJ/mol

The raw phosphates contain approximately 4 % fluorides. During the decomposition of nitric acid, a small share of these fluorides forms hydrofluoric acid (see reaction equation 1), which is generated together with the SiO_2 always existing in the raw phosphate to gaseous silicon tetrafluoride SiF_4 and to hexafluoro silicic acid H_2SiF_6 according to equations (2) and (3).

(2) $4\ HF + SiO_2 \longleftrightarrow SiF_4 + 2\ H_2O$

(3) $2\ HF + SiF_4 \longleftrightarrow H_2SiF_6$

The main fluoride share in the raw phosphate goes through the entire production process and finally remains in the fertilizer.

2.2 Manufacture of NPK Fertilizers by the Mixed Acid Process

Until 1994 BASF in Ludwigshafen applied the nitric acid process respectively the nitrophosphate process (Odda Technique) for the manufacture of NPK fertilizers. For economic reasons this production method has been given up and replaced by the mixed acid process, using parts of the previous installations. So the mixed acid process is the only technique presently applied in Germany for the manufacture of NPK fertilizers. At first the NPK production procedure is described at the example of Compo, Krefeld. In the following chapter the differences in the NPK production technique of BASF Ludwigshafen are explained.

2.3 Compo, Krefeld

Figure 1 shows the production technique of NPK fertilizers of Compo in Krefeld in a block scheme. The production is generally divided into a wet process part and and a dry process part. Whereas the wet part includes the decomposition and neutralization, all further treatment steps (like the granulation, the drying etc.) belong to the dry part.

In the decomposition reactor the raw phosphate with a P_2O_5-share of 30 - 40 % is intensively mixed with the 60 % nitric acid. The exothermic reaction of the nitric acid with the raw phosphate causes off-gas loaded with NO_x and fluorides. The fluorides are often connected to silicon (see reaction equations 2 and 3). At the same time different volumes of volatile compounds, like e.g. CO_2, are emitted, which depend, however, on the used raw phosphate. Before being discharged into the atmosphere, the off-gas is led into a scrubber. The heat generated by the decomposition reaction increases the temperature of the solution. So the reactor is driven at a temperature of approximately 70 °C.

In the further process, phosphoric acid, H_2SO_4, monoammon phosphate (MAP), diammon phosphate (DAP) and other components are added to the decomposition mixture. According to the product, ammonium nitrate solution can also be added. The acidity mixture is neutralized with gaseous NH_3. The neutralization reaction is exothermic and the generated heat is used for the concentration of the solution. Sometimes, low volumes of steam are added, e.g. during the start process. Further materials, like e.g. potassium chlorid, potassium sulphate, magnesium salts and trace nutrients are added to the neutralized solution The mixing of the materials as well as the neutralization reaction is carried out in several tanks.

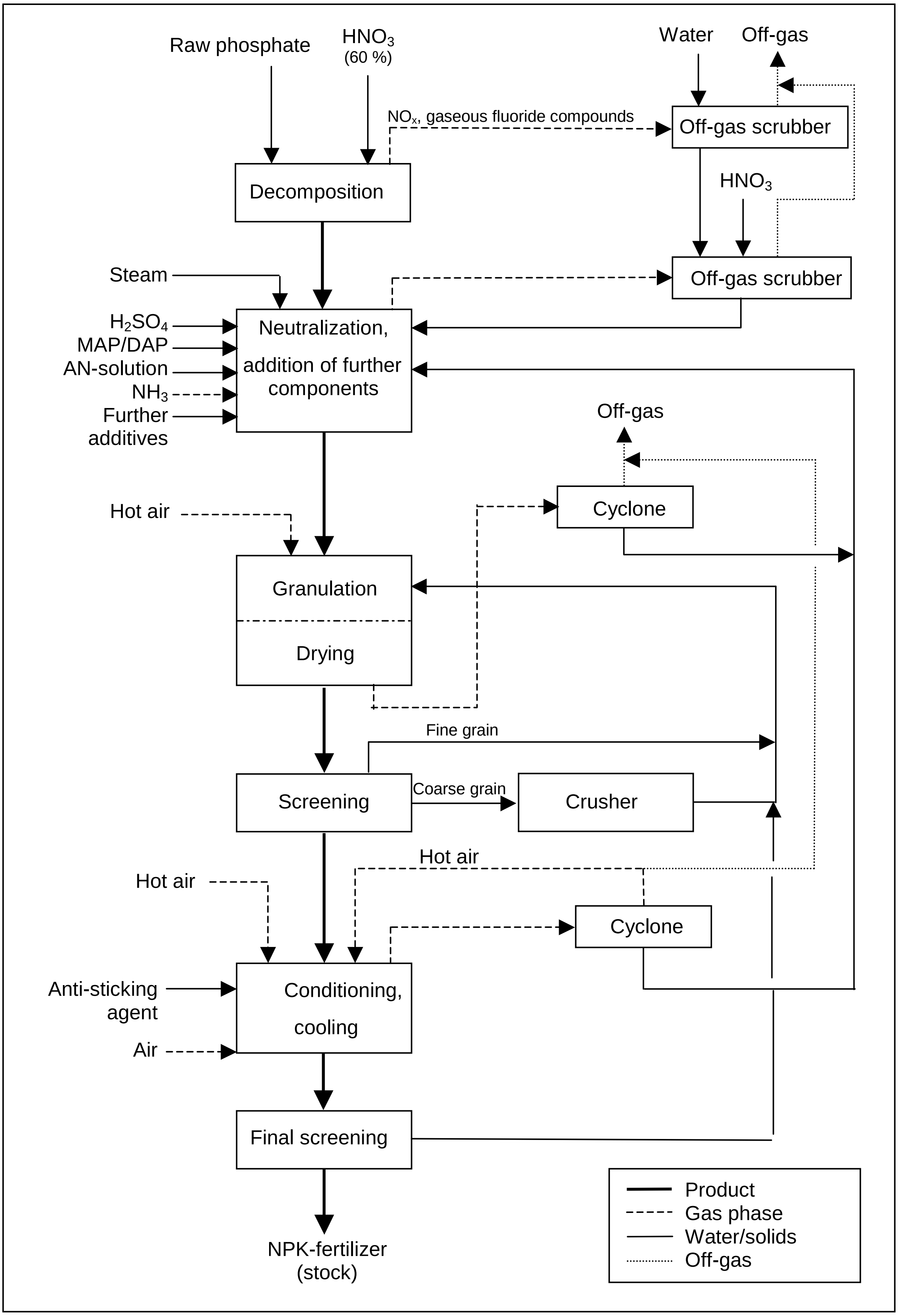

Figure 1: Manufacture of NPK fertilizers at Compo, Krefeld

The off-gas streams from the decomposition and from the generation of ammonia are collected separately and are led over washers. The wash water from the decomposition washer is led to the neutralization washer. Here it must be changed to an acid pH-value by the addition of HNO_3 because the off-gases to be treated are alkaline. The off-gas streams of both scrubbers are discharged together into the atmosphere.
After the neutralization and the addition of further components the fertilizers have to be formed to the desired size. Therefore, the mash is firstly fed into the granulation. Compo in Krefeld uses a spherodizer (rotation granulator) with an integrated drying step. Under simultaneous inblow of hot air the mash, with a water content between 10 and 30 % (according to the produced kind of fertilizer), is fed into the rotation drum of the spherodizer. In order to separate the dust as far as possible, the off-gas streams of the spherodizer (granulation and drying) are led over a multicyclone before being discharged into the atmosphere.
Then the dried grains are sieved and divided into three different fractions. The coarse grain is crushed and is led back into the spherodizer together with the fine grain.
After the screening the product is conditioned by the addition of an anti-sticking agent and cooled by the inblow of air in a drum or a fluidized bed cooler. The resulting off-gas is first led over a cyclone battery and then discharged into the atmosphere together with the off-gas from the spherodizer. If required, the off-gas can also be supplied as additional air to the drying process. The dust separated in the cyclones is led back into the wet process part of the production. Finally the product is sieved again and is transported to the fertilizer stock.

2.3.2 Emission Data and Energy Consumption

The emissions essentially depend on the specifications of the product as well as on the quality of the input materials. The emissions stated in this research project are average values.

2.3.2.1 Off-gas Emissions

There are two main sources of off-gas emissions at Compo in Krefeld: the off-gas volume of the wet process (approximately 8.000 – 12.000 m³/h) and the off-gas volume of the dry process (approximately 90.000 m³/h). Before being discharged into the atmosphere, the off-gas streams of the wet process are led over off-gas scrubbers and those of the dry process over cyclones. **Figure 2** shows the emission sources as well as the off-gas concentrations. The concentrations are average values of four separate measurements (half hour values). Altogether it must be taken into account that the stated concentrations depend to a high extent on the product qualities and therefore fluctuations of up to 25 percent can be expected. Specific concentrations per ton of the product cannot be indicated due to possible product changes.

The essential parameters of the off-gas emissions at the manufacture of NPK fertilizers are NO_x, gaseous fluoride compounds, NH_3 as well as dust.

NO_x, mainly NO and NO_2, are emitted by the decomposition of the raw phosphate with HNO_3. The emission values depend on the quality of the used raw phosphates (e.g. the share of organic compounds and ferric salts) as well as on the process temperatures. A small share of the fluoride contained in the raw phosphate goes into the gas phase. In the off-gas treatment, NO_x and fluorides are washed out and are recycled into the process. The NH_3-emissions mainly result from the neutralisation with ammonia and to low extent from the forming of the product (granulation).

Dust emission sources are the granulation and the conditioning drums. Minor emissions are caused by the product cooling.

2.3.2.2 Waste Water

All wash waters are recycled completely, so that no process waste water is caused by the production of NPK fertilizers at the location Krefeld.

2.3.2.3 Residues

At the location Krefeld, no residues are caused by the manufacture of NPK fertilizers. The dust separated in the cyclones is completely recycled back into the process.

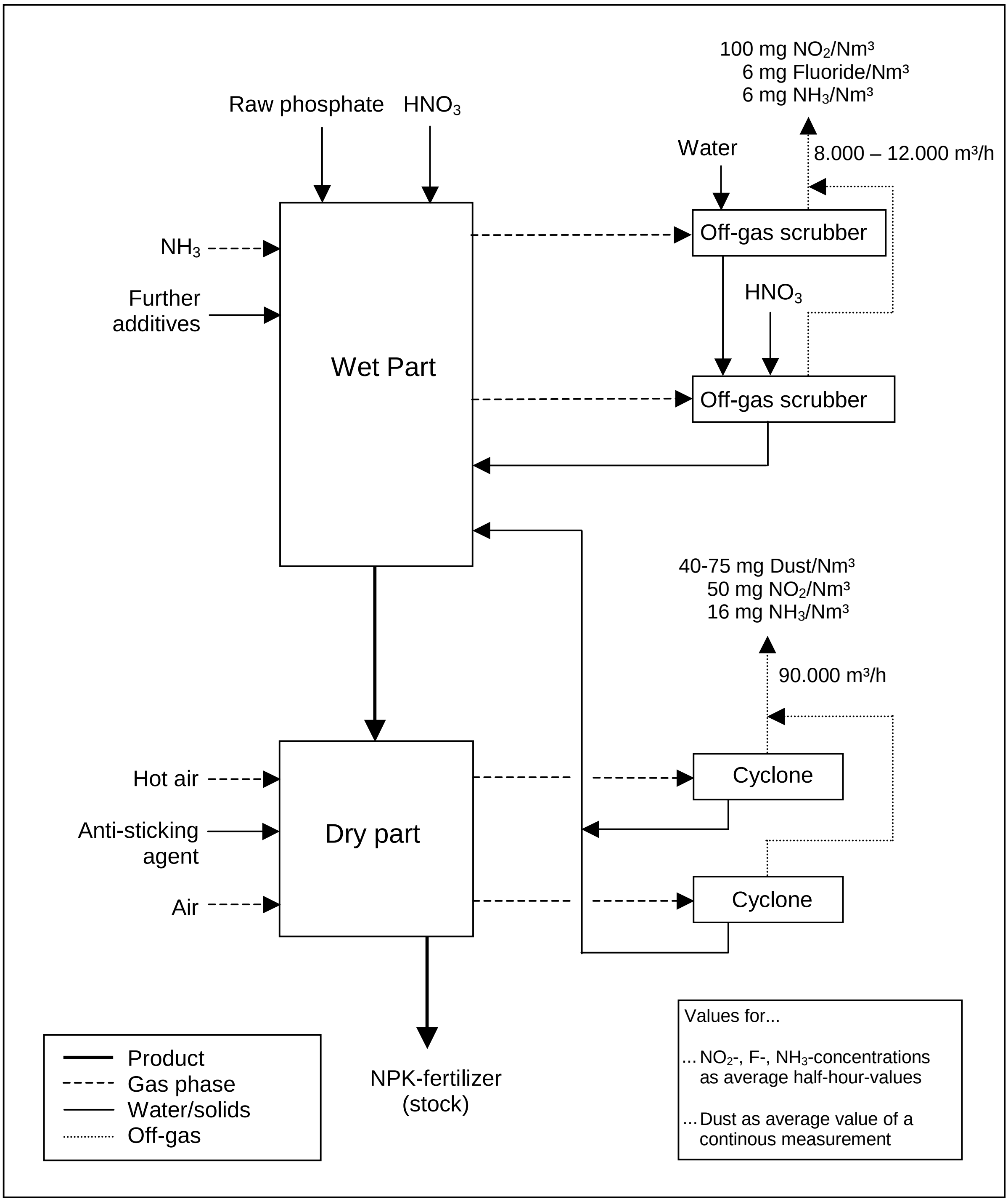

Figure 2: Emission Sources and Off-gas Concentrations

2.3.2.4 Energy

Heavy fuel oil is required for obtaining hot air for the spherodiser (between 10 and 35 kg of oil per t product). The sulphur share in the fuel oil amounts to approximately 1,8 %, about half of it goes into the product. The residual sulphur share is discharged with the off-gas into the atmosphere. The electric energy demand is 25 - 80 kWh_{el} per t product.

2.4 Fa. BASF, Ludwigshafen

2.4.1 Production Process

Since the production process of the BASF in Ludwigshafen is very similar to Compo in Krefeld, the following presentation concentrates on the differences and peculiarities at the location Ludwigshafen. The production technique of the BASF in Ludwigshafen is shown as a block-scheme in **figure 3**.

1. Separation of Inert Materials

The BASF in Ludwigshafen still uses the installation parts of the preceeding production for the separation of inert materials. Here are separated the solids contained in the decomposition solution, especially quartz sand, whose quantity depends on the quality of the used raw phosphates. The separated sand is cleaned and reused in the building industry or discharged on a waste disposal. The wash water contains P_2O_5 and NO_3 and is cleaned in the biological waste water treatment plant.

2. Off-gas Scrubbing as Treatment of the Off-gases from the Neutralization and the Granulation

Beginning of the 90s, BASF Ludwigshafen initiated a variety of projects with a total of 40 measures, in order to reduce the ammonium freight discharged at the outlet of the waste water treatment plant into the Rhine. The investment volume of these projects amounted to some 120 million DM, resulting on the other hand in a reduction of the waste water cost of approximately 18,5 million DM per year.

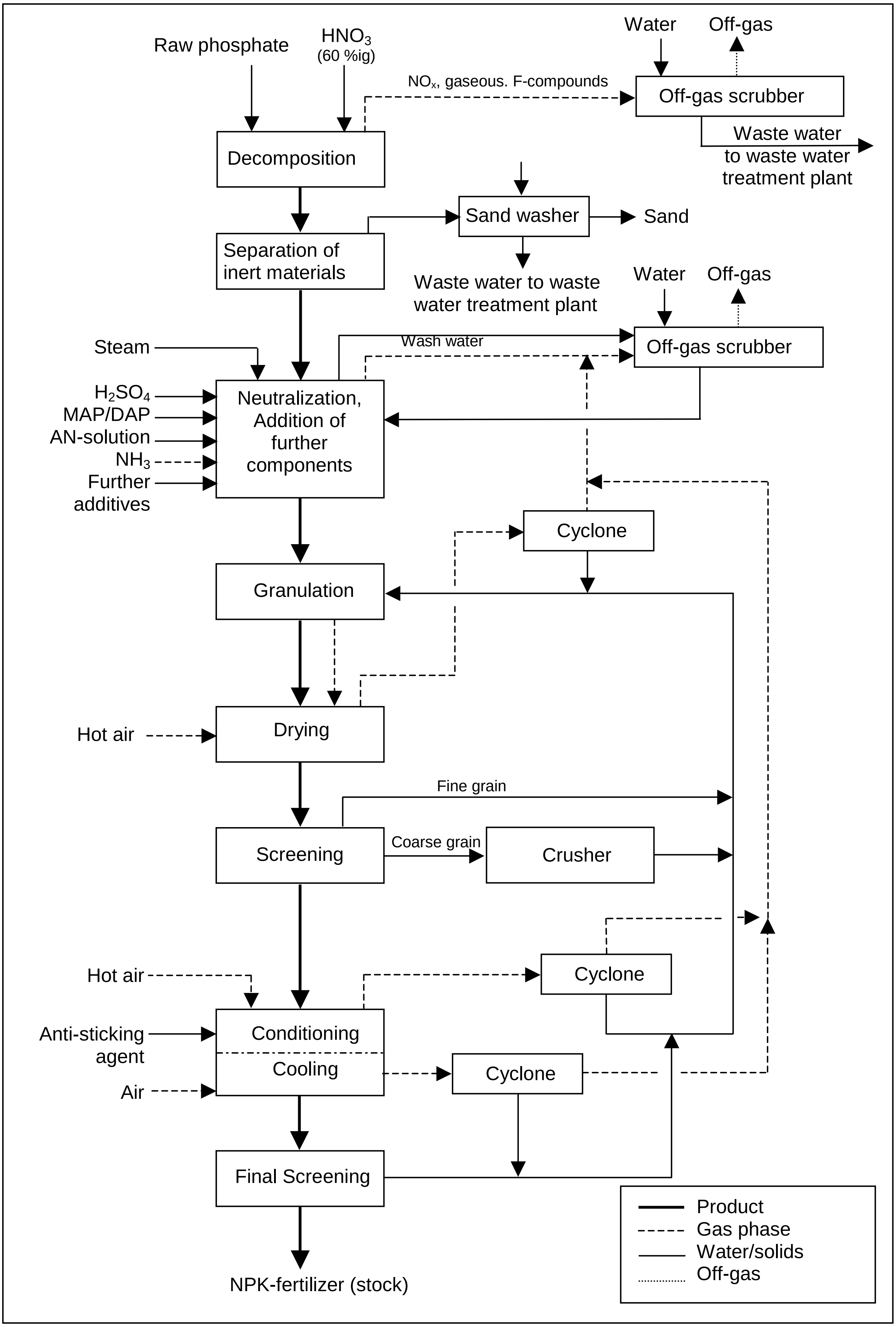

Figure 3: Manufacture of NPK-fertilizers (BASF, Ludwigshafen)

For the manufacture of NPK, the installations of the granulation were rinsed with water in case of product change-overs. The average ammonium freight in the waste water treatment caused by this procedure amounted to 2,3 tons per day. So the NPK manufacture was the biggest discharger of ammonium salts.

Therefore, a new technique was installed in 1994 and optimized until 1997, which avoids waste water and cleans off-gas streams. The main part of the installation is a colomn of 8,7 m of diameter and 25 m of height, where the rinsing waters are concentrated, reusing the heat of the hot off-gases from the neutralization and the drying. By means of a weak-acid pH-value, ammonia is separated from the off-gas at the same time. After a further concentration in the subsequent evaporation, the complete recycling back into the fertilizer production process is possible.

In order to reuse the waste heat economically, the installation also includes a system of sorters and receptacles, where the waters are collected separatly according to the concentration.

The investments for this project amounted to 41,5 million DM, including the receptacles, but excluding the subsequent evaporation. Some 340.000 m^3/h off-gas are treated. Due to the acid pH-value, the high temperatures and the aggressive chlorides, fluorides, phosphates and nitrate ions, an high-alloyed special material was required for the installations.

3. Wash Waters

In case of a product change-over, BASF has to rinse the granulation installations. These wash waters are reused in the off-gas scrubbing and recycled back into the process. Compo generally uses a dry cleaning of the installations and consequently does not cause any wash waters.

4. Granulation and Drying

The granulation at BASF Ludwigshafen is followed by a separate dry dum. In this system the mash has to be concentrated to a solid content of 85 to 90 % before being led into the granulation.

2.4.2 Emission Data and Energy Demand

2.4.2.1 Off-gas Emissions

At the BASF Ludwigshafen there are two emission sources of off-gas:

- the off-gas from the raw phosphate decomposition,
- the off-gas from the neutralization and the granulation.

The emission sources as well as the off-gas concentrations are shown in **figure 4**.

Off-gas from the Raw Phosphate Decomposition

The off-gas from the raw phosphate decomposition is treated in a scrubber. The emissions, mainly the No_x emission, importantly depends on the used phosphate quality (content of organic material). The air volume required amounts to some 19.000 Nm^3/h.

The measured values of No_x are approximately 425 mg NO_2/m^3 $_{i.N.\ dry}$ (in case of IMC phosphate) and < 100 mg NO_2/m^3 $_{i.N.\ dry}$ (in case of cola phosphate). The fluoride content lies between 1 and 3 mg F/m^3 $_{i.N.\ dry}$.

Off-gas from the Neutralization and the Granulation

The off-gas from the neutralization is treated by a scrubber together with all other off-gas streams of the dry process part (granulation, conditioning and cooling). The required air volume of the scrubber amounts to some 340.000 Nm^3/h.

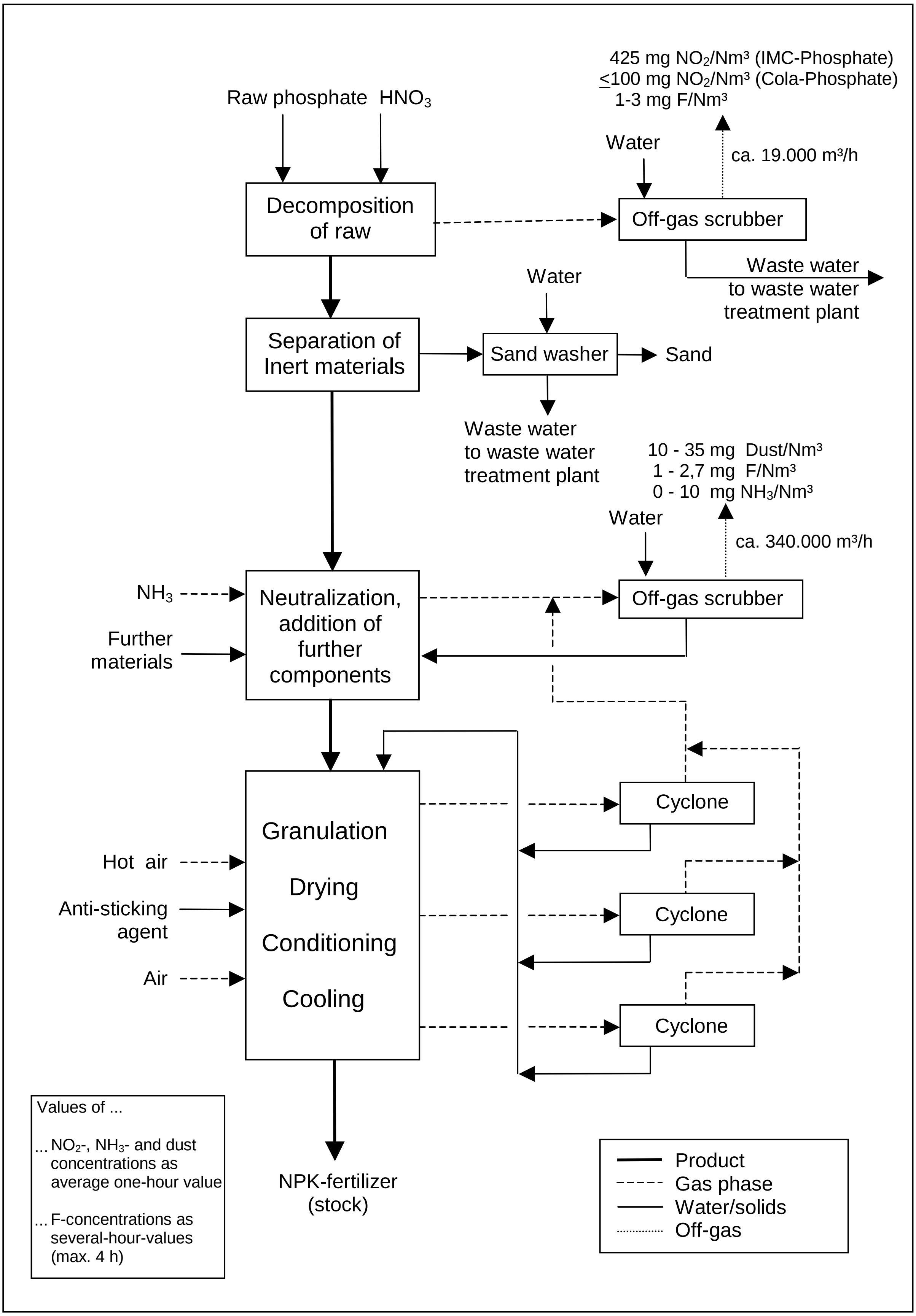

Figure 4: Emission Sources and Off-gas Concentrations of BASF, Ludwigshafen

The average dust concentration in the treated off-gas is around 20 mg/m^3 i.N., but the values can fluctuate between 10 and 35 mg/m^3 i.N. depending on the produced fertilizer quality and the operating state of the installations. The limit value of 50 mg/m^3 i.N. has never been reached or exceeded, even in case of short extreme values mainly due to aerosol problems. The average fluoride concentration is 1,4 mg/m^3 i.N. (< 1 – 2,7 mg/m^3 i.N.) and the NH3 concentration lies between 0 and 10 mg/m^3 i.N. .
The indicated off-gas concentrations are average one-hour-values, the fluoride values have been measured over 4 hours due to the low concentrations.

2.4.2.2 Waste Water

The raw phosphate decomposition causes waste water from the off-gas scrubbing, the sand washer and the washing and rinsing processes. The effluents from the sand washer and the off-gas scrubber are treated in the biological waste water plant. The principal waste water parameters are fluoride, nitrate and phosphate. The content of phosphate has a positive impact on the nutrient ratio in the waste water treatment.
The measurements of March 23 and April 06, 1998, revealed an average waste water volume of 3.026 m^3/d, the single measurements fluctuated between 2.400 and 4.000 m^3/d. **Table 2** shows the average freights of the waste water parameters as well as the specific freights in relation to the phosphate volume.

Table 2: Waste Water Parameters of the Raw Phosphate Decomposition

	Freight per day	Specific freight in relation to phosphate volume
P	237 kg/d	1,12 kg/t P_2O_5
F	282 kg/d	1,33 kg/t P_2O_5
NO_3-N = total N	901 kg/d	4,26 kg/t P_2O_5

The values stated in table 2 can fluctuate importantly depending on the phosphate quality.

All subsequent processes behind the neutralization are free of waste water. The rinse waters from the granulation are collected, concentrated and recycled back into the process.

2.4.2.3 Residues

A small quantity of sand of 1 - 2 t/d is caused by the inert material separation of the BASF in Ludwigshafen. It is partly discharged to a waste disposal, partly given to the building industrie.

2.4.2.4 Energy

In addition approximately 20.000 t of steam per year are required for the evaporation of the preconcentrated rinse waters to a final concentration of 85 – 90 % solids.