PRODUCTION OF AMMONIA, NITRIC ACID, UREA AND N-FERTILIZER

1 GENERAL INFORMATION

Mineral fertilisers contain one or more of the primary nutrients (macronutrients) such as nitrogen, phosphorus or potassium as salts or in form of urea. The primary nutrients N, P, K are required by plants in large or moderate amounts. Depending on the formulation mineral fertilisers also contain other nutrients required by plants to a minor degree, such as Ca, Mg, and S. Trace elements required in small quantities (micronutrients) are B, Cu, Fe, Mn, Mo, Zn. Fertilisers can be classified as follows in terms of their major nutrient contents (IFA 2016):

- Single-nutrient or straight fertilisers generally contain only one mayor (primary) nutrient.
- Multi-nutrient fertilisers (MN-fertilisers) or compound fertilisers contain two or more major nutrients. The term complex fertiliser refers to a compound fertiliser formed by mixing ingredients that react chemically.

Table 1: Main mineral fertiliser types with regard to their primary nutrient composition. (IFA 2016)

Common names	**nutrient composition as % of product**				
	N	**P_2O_5**	**K_2O**	**S**	**MgO**
Nitrogen fertilizers					
Ammonia	82	0	0	0	0
Ammonium sulphate	21	0	0	23	0
Ammonium nitrate	33 – 34.5	0	0	0	0
Calcium ammonium nitrate (CAN)	20.4 – 27	0	0	0	0
Urea	45 – 46	0	0	0	0
Phosphate fertilizers					
Single superphosphate	0	16 – 20	0	12	0
Triple superphosphate	0	46	0	0	0
Diammonium phosphate	18	46	0	0	0
Monoammonium phosphate	11	52	0	0	0
Ground rock phosphate	0	20 – 40	0	0	0
Potash fertilizers					
Muriate of potash (potassium chloride)	0	0	60	0	0
Sulphate of potash	0	0	50	18	0
Sulphate of potash magnesia	0	0	22 – 30	17 – 22	10 – 11
Magnesium fertilizers					
Kieserite	0	0	0	20 – 22	25 – 27
Epsom salt	0	0	0	12 – 13	15 – 16
Complex fertilizers					
NPK fertilizers	5 – 25	5 – 25	5 – 25	*	*
NP fertilizers	15 – 25	15 – 25	0	*	0
NK fertilizers	13 – 25	0	15 – 46	*	0
PK fertilizers	0	7 – 30	10 – 30	*	*

** some with S and/or Mg and/or micronutrients*

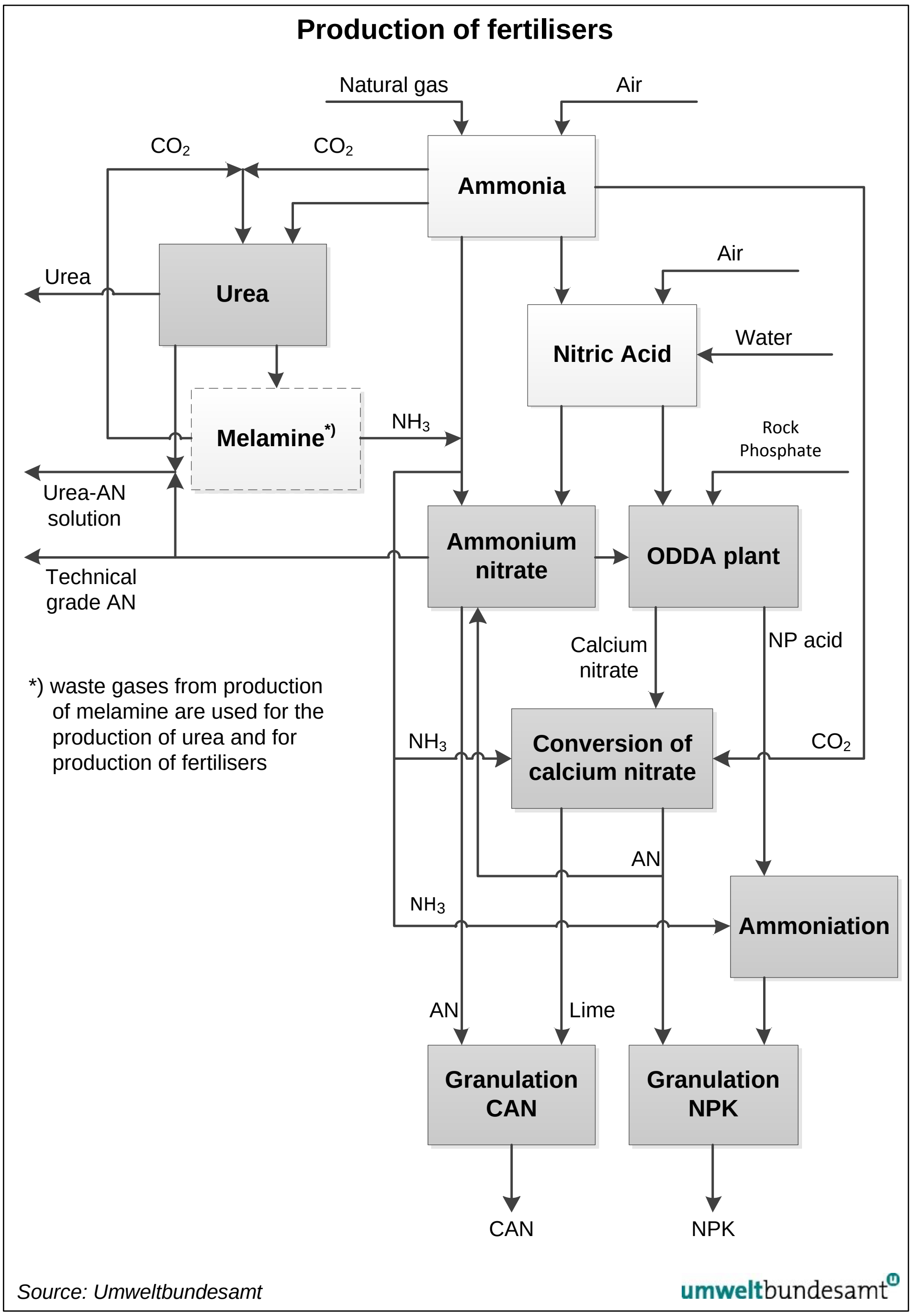
Solid fertilisers are the most important group of fertilisers in Europe. Solid fertilisers include granular, prilled, and compacted products. Granular fertiliser are composed of spheroid particles, usually 1.5–5 mm in diameter, and are formed by any of a number of granulation processes. Prilled fertilisers are of nearly spherical form and made by the solidification of freefalling droplets. (UMWELTBUNDESAMT 2002)

The installation is connected to the railway network. Phosphate rock is usually delivered by train, fertilizer products are also transported by ship.

At the highly integrated plant all reactors along the nitrogen value chain are interconnected. Starting from natural gas ammonia is produced ,and converted to nitric acid and urea and further processed to give final products like fertilisers (NPK and CAN), melamine or urea products (e.g. AdBlue®). Annually production capacities are approximately:

- 545,000 t ammonia
- 420,000 t urea
- 600,000 t nitric acid
- 1,100,000 t fertilizers (NPK and CAN)
- 54,000 t melamine

2 INDUSTRIAL PROCESSES USED



Source: Umweltbundesamt

Figure 1: Process scheme of the production of fertilisers (shaded) and of substances used for the production of fertilisers.

2.1 Ammonia production

Ammonia is required for the production of various fertiliser products such as urea, ammonium-nitrate, CAN, MN-fertiliser. At many fertiliser production sites ammonia is supplied by an associated ammonia plant.

Ammonia is mainly produced by steam reforming of hydrocarbons, with natural gas being the most common feedstock. By way of these processes the feedstock is reformed with steam in a heated primary reformer and subsequently with air in a secondary reformer, in order to produce synthesis gas (N_2, H_2), which also contains CO, CO_2 and H_2O. After removal of H_2O (condensation), CO (methanation) and CO_2 (chemical or physical absorption), the synthesis gas is compressed and synthesis of ammonia takes place on an iron catalyst.

Relevant environmental parameters for the production of ammonia are the amount of feedstock required, the consumption of energy for heating the primary reformer, and the existence of an efficient heat recovery system. Relevant waste gas emissions from the primary reformer are CO_2, NO_x and NH_3 (in case of an NO_X abatement technology), SO_2 and dust (depending on the fuel). Waste gas emissions result from the desorption of carbon dioxide (CH_4, CO and CO_2) and from the removal of purge gases from the synthesis loop (NH_3 and CH_4). At the primary reformer, NO_x emission reduction processes can be used. (UMWELTBUNDESAMT 2002)

At the reference plant purge gas is removed from the synthesis loop between the first and second cooling step. For emission reduction, purge gas is supplied to an old modified ammonia plant, comprising of an NH_3 converter and a refrigerating plant. This ammonia plant operates as a normal NH_3 synthesis with the purge gases being the feedstock.

Process water is removed from the synthesis gas by condensation and discharged; here, an efficient wastewater treatment, such as recovery of ammonia by stripping processes, can be considered state-of-the-art technology. Wastes arise from used catalysts and hydraulic fluids.

2.2 Nitric acid production

Processes for the production of nitric acid are based on the Ostwald process, in which ammonia is oxidised with air to form nitric monoxide (NO). NO is further oxidised to form nitrogen dioxide (NO_2) which finally is absorbed in water to produce HNO_3.

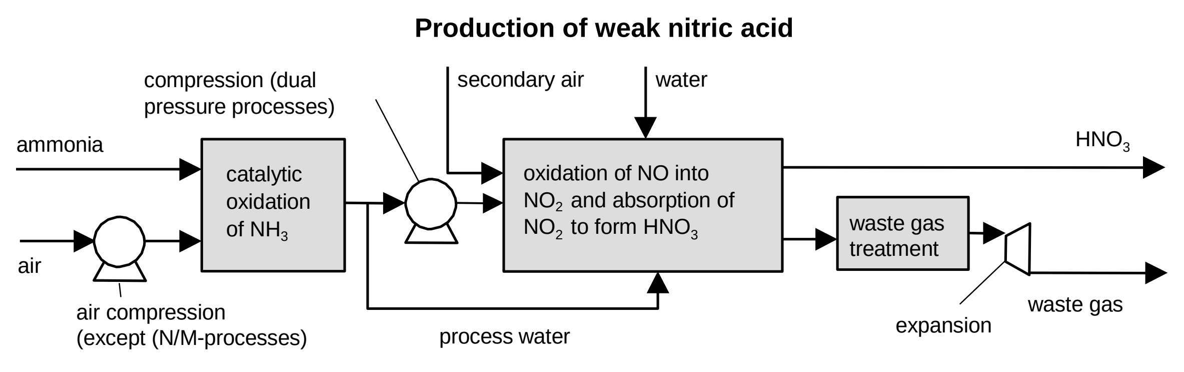
The main part of the nitric acid is produced as weak nitric acid, which has concentrations of up to 69.2% and is used for the production of fertilisers. Due to different thermodynamic conditions for ammonia combustion and absorption, process technologies differ with regard to working pressure levels. Pressures are classified in:

- N: normal pressure; only applied for ammonia oxidation
- M: medium pressure (3 – 6 bar) and
- H: high pressure (> 8 bar).

Generally, two types of plants can be distinguished: single pressure plants and dual pressure plants:

With **single pressure** plants, oxidation of ammonia takes place at the same pressure as oxidation and absorption. M/M processes (medium pressure for NH_3 oxidation and for ab-sorption) and H/H processes (high pressure for NH_3 oxidation and for absorption) are in operation.

With **dual pressure** plants, oxidation of ammonia takes place at a lower pressure than absorption. M/H processes (medium pressure for NH_3 oxidation and high pressure for absorption) and some N/M processes (normal pressure for NH_3 oxidation and medium pressure for absorption) are in operation.



Source: Umweltbundesamt

Figure 2: Simplified schematic illustration of the production of weak nitric acid.

The reference installation produces weak nitric acid in two plants (N/M process and M/H process). The entire capacity of nitric acid is about 565,000 t/a (based on 100% HNO_3). About 95% of the nitric acid is used as raw material to produce NPK and ammonium nitrate based fertilizers. The production of technical ammonium nitrate is also of relevance.

Table 2: Summary of the reference installations HNO_3 plants. (Source: Operator information 2016)

Data for 2015	**Line E (M/H process)**	**Line F (N/M process)**
Capacity [1)]	345,000 t/a	220,000 t/a
NH_3 input	100,020 t	60,100 t
HNO_3 production [1)]	344,730 t	207,130 t
Pressure for catalytic NH_3 oxidation [1)]	3.9 bar	-0.01bar
Oxidation temperature	895 °C	875 °C
Pressure for absorption [2)]	8.5 bar	4.5 bar
Absorption temperature	25 °C	25 °C
Absorption efficiency	99.6%	98.6%

[1)] *related to 100% HNO_3*

[2)] *Pressure above atmospheric*

2.3 Urea production

Urea is produced by reacting ammonia and carbon dioxide at elevated temperature and pressure. NH_3 and CO_2 react under the formation of an intermediate stage of ammonium carbamate:

$$2\,NH_3 + CO_2 \rightarrow NH_2COONH_4 \quad \Delta Hr = -117\ kJ/mol$$

$$NH_2COONH_4 \rightarrow (NH_2)_2CO + H_2O \quad \Delta Hr = +15.5\ kJ/mol$$

The formation of ammonium carbamate is fast and exothermic, whereas the dehydration of carbamate is slow and endothermic. Since more heat is produced in the first reaction than consumed in the second, the overall reaction is exothermic. The following side reactions have to be taken into considerations for the process design:

- Formation of biuret:
  $2\ CO(NH_2) \rightarrow NH_2CONHCONH_2 + NH_3$
- Formation of isocyanic acid:
  $2\ CO(NH_2) \rightarrow NH_4NCO \rightarrow NH_3 + HNCO$
- Hydrolysis of urea:
  $CO(NH_2) + H_2O \rightarrow NH_2COONH_4 \rightarrow 2\ NH_3 + CO_2$

Urea synthesis takes place at temperatures of about 185 °C, pressures of about 154 bar and a molar NH_3/CO_2 ratio of about 3.5. The yield of urea is approximately 62%. The solution of urea and unconverted carbamate leaving the reactor is supplied to a thermal stripper, in which carbamate is decomposed. Since stripping is achieved thermally, relatively high temperatures of 200 – 210 °C are required.

For the decomposition step, three strippers are used, which work at different pressure levels. The high pressure stripper works at 150 bar. Residual NH_3 and CO_2 are recovered in two following stages: The second stage works with medium pressure (~15 bar) and the third stage works with low pressure (~5 bar). The condensation energy of the high pressure section is recovered for steam production and of the medium pressure section for heat integration.

Gases leaving the decomposition sections are condensed and supplied to the recovery section which comprises an ammonia-carbamate separation step. Separated ammonia is condensed and recycled into the reactor. Carbamate solution is also recycled into the urea reactor. Non-condensable purge gases of the ammonia condensers are treated by conventional absorption techniques.

For production of AdBlue (32.5% aqueous urea solution) or Urea-ammonium nitrate (UAN) solution, a concentrated urea solution taken out from an intermediate process step is used. UAN solution with 13.5% AN-N and 13.5% urea-N is produced by mixing the appropriate amounts of urea and AN.

The remaining urea solution is concentrated by two staged evaporation. Two vacuum evaporators, one with 0.4 bar and the other with 0.04 bar, are used to remove water from the urea solution. After concentration of the urea solution, there are two options for further processing, depending on the form of urea required.

A prilling tower is used for the production of solid urea. Molten urea coming from the vacuum evaporators is fed to rotating buckets at the top of the tower. The formed liquid droplets solidify and cool on free fall through the tower. Forced up-draft of air is used for cooling and drying of the liquid droplets forming prills.

For the production of melamine, the urea melt is used directly as feedstock.

About 300 kg of process water are produced per metric ton urea. The process water is partly reused after stripping of ammonia.

Table 3 presents the amount of the used feedstock (ammonia and carbon dioxide), energy used in form of steam and electricity and used cooling water. Therefrom a produced amount of urea is presented in Table 4.

NH_3	
Total usage	**245,878 t**
Specific NH_3 usage	0.566 t/t
CO_2	
Total usage	221,442 t
Specific CO_2 usage	0.743 t/t
Steam	
Import	377,617 t
Export	63,361 t
Net import	314,256 t
Specific net steam usage	0.723 t/t
Electricity	
Total usage	172,873 GJ
Specific usage	0.398 GJ/t
Prill tower scrubber	8,461 GJ
Specific usage	0.038 GJ/t
Cooling water	
Total usage	17,653,378 m³
Specific usage	40.6 m³/t

Table 3: Input used in 2015. (Source: Operator information 2016)

Melt (feedstock for melamine)	169,871 t
Solution (AdBlue. UAN)	43,274 t
Prill	221,442 t
Total urea	**434,587 t**

Table 4: Urea production volume 2015. (Source: Operator information 2016)

2.4 N-Fertilizer production

2.4.1 Nitrophosphate route (Odda process)

Fehler! Verweisquelle konnte nicht gefunden werden. schematically presents the MN-fertiliser production process (ODDA process) according to the nitrophosphate route, which is used in the reference plant. Main steps of the ODDA process are:

- Digestion of phosphate rock with nitric acid;
- Crystallisation and separation of calcium nitrate tetrahydrate (CNTH) from nitrophosphoric acid (NP-acid);
- Ammonisation i.e. neutralisation of nitrophosphoric acid (adjustment of N/P ratio);
- Granulation of the slurry and coating of the product;
- Conversion of calcium nitrate tetrahydrate into ammonium nitrate and lime and production of CAN fertilisers.

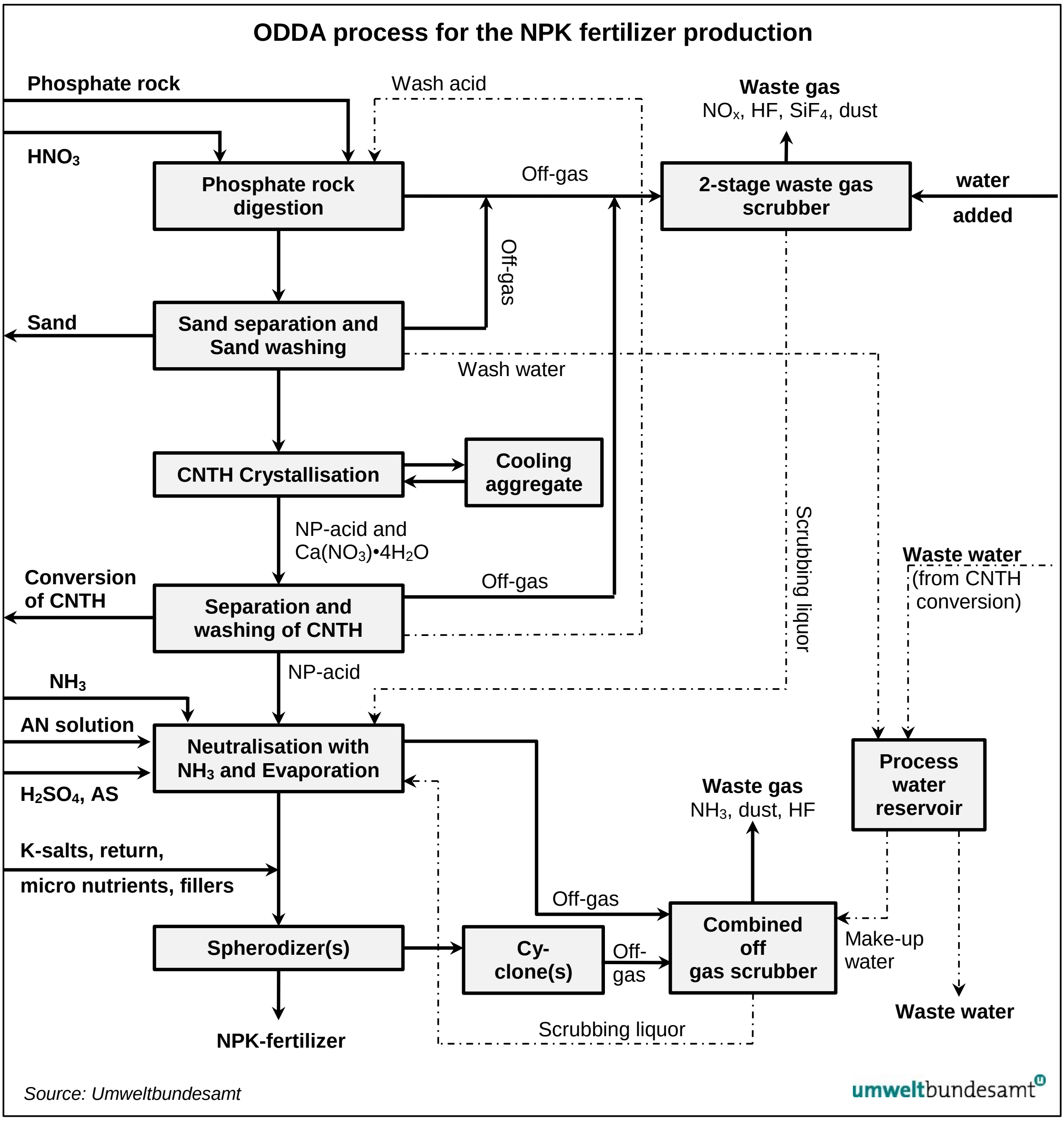


Figure 3: ODDA process for the NPK fertilizer production.

2.4.1.1 Digestion of Phosphate Rock

Phosphate rock is dissolved in an excess of weak nitric acid (< 60% HNO_3) using a cascade reactor. The reaction takes place at a temperature of about 70 °C and is maintained by the reaction heat. The overall reaction can be represented by the following chemical equation:

$$Ca_5(PO_4)_3F + 10\ HNO_3 \rightarrow 5\ Ca(NO_3)_2 + 3\ H_3PO_4 + HF$$

Dissolution of phosphate rock in HNO_3 causes the formation of HF and SiF_4. Nitrogen oxides are formed by the reduction of HNO_3. The NO_x formation is in particular favoured by a high content of organic substances and ferrous salts. The digestion reaction is governed by three interrelated factors: temperature, particle size, and residence time in the reactor. If the temperature is too low and the particles are too large, a longer residence time will be necessary. If the temperature is too high, excessive formation of NO_x will take place. Antifoaming agents are added in order to prevent foaming. Acid-insoluble material mostly consists of quartz sand and is separated with lamella separators and belt filters. The filtered sand is washed and dried. It either can be used in the construction industry or is disposed. Waste gas is collected, combined and treated together from the following operations: digestion of phosphate rock, separation and washing of sand and filtration and washing of calcium nitrate.

2.4.1.2 Crystallisation and Filtration of Calcium Nitrate Tetrahydrate (CNTH)

$Ca(NO_3)_2$ formed by the digestion of phosphate rock is removed from the solution, in order to guarantee the production of plant-available P_2O_5 and in order to increase the nutrient content of the MN-fertilizer. $Ca(NO_3)_2$ precipitated as calcium nitrate tetrahydrate (CNTH) is obtained by cooling to temperatures of about 0 °C. CNTH crystals are separated with belt filters, washed with cold nitric acid and a solution of ammonium nitrate in order to recover the adherent dissolving solution on the crystals and to minimize the residual P_2O_5 content. The washing acid can be totally recycled to the rock phosphate digestors. The remaining nitrophosphoric acid (NP-acid) is further processed into MN-fertilizer.

2.4.1.3 Conversion of Calcium Nitrate Tetrahydrate (CNTH)

The production of nitrophosphate fertilisers by digestion of phosphate rock with nitric acid in the ODDA process produces as a by-product calcium nitrate tetra hydrate (CNTH). The conversion of CNTH with NH_3 and CO_2 results in the production of AN and lime, which can be used for the production of CAN.

NH_3 and CO_2 are dissolved in a NH_4NO_3 solution, which is circulating in a carbonising column. CO_2 reacts with gaseous NH_3 forming ammonium carbonate $(NH_4)_2CO_3$. The heat of reaction is removed by cooling.

$$2\ NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$

CNTH is also dissolved in an NH_4NO_3 solution. The two solutions are then reacted.

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow 2\ NH_4NO_3 + CaCO_3$$

After the reaction, the approx. 65% NH_4NO_3 solution is separated from $CaCO_3$ and concentrated in a two stage evaporator. The AN solution can be used for the production of calcium ammonium nitrate fertiliser. The separated $CaCO_3$ still contains small amounts of ammonium compounds and phosphate and is only used for the CAN production.

2.4.1.4 Neutralisation of the Nitrophosphoric Acid

The NP-acid containing H_3PO_4, HNO_3, some HF, dissolved Ca- and Mg-nitrates, dissolved impurities (e.g., Fe, Al, Si), and suspended insoluble particles (e.g. quartz sand) is neutralised with ammonia under strict pH control. Due to the exothermic reaction the temperature increases to about 110 – 120 °C. Ammonium nitrate solution and sulphuric acid is added to ad-just the N/P_2O_5 ratio in the final product. Due to the heat of the reaction water, ammonia and HF are evolved during the neutralisation operations. Waste gases are treated by wet scrubbing. Process effluents might arise when the exhaust vapours are (partly) condensed before or during waste gas treatment. After addition of potassium, the slurry is ready for granulation, drying and finishing.

2.4.1.5 Spherodizer Granulation

Granulation of a slurry produced by the nitrophosphate route often proceeds in a Spherodizer, as this process is very efficient for slurry granulation. The Spherodizer process combines granulation and drying in a single process step. The Spherodizer is an inclined rotary drum consisting of two zones, the granulation zone and the drying zone. Recycled material consisting of undersize and crushed oversize particles (granulation loop) is fed into the granulation zone. The recycled particles generate a moving bed in the drum, into which the slurry containing 10 – 20% water is sprayed. Air is preheated with 3.5 bar steam to approx. 110 °C and with gas burners up to 400 °C depending on the formula. The heated air flows cocurrently in the spherodizer evaporating the water from the NP liquor and building up dry granules with a water content of <1.5%. A part of the granulation air can be taken from warm off-gas of the following cooling drum and the off-gas from de-dusting processes (conveyors and elevators). Waste gas from the Spherodizer drum is de-dusted with cyclones and treated by wet scrubbing. The product is cooled in drum coolers and/or bulk flow coolers and treated with anti-caking agents.

The combined waste water stream of the NPK fertilizer production is treated by neutralisation and directly discharged.

2.4.2 Ammonium Nitrate (AN) and calcium ammonium nitrate (CAN)

2.4.2.1 Production process

Ammonium nitrate is produced by pressure neutralisation. The neutraliser is a loop reactor and operates at a working pressure of about 4.5 bar and a working temperature of approx. 180 °C. Compressed gaseous ammonia and preheated nitric acid (59.7%) is supplied into the ammonium nitrate solution, which circulates through the loop reactor. In a separator installed at the top of the loop reactor superheated steam is separated from the AN solution. The ammonium nitrate solution drawn of the reactor has a concentration of approx. 74 – 76%.

Process water is injected into the superheated steam, which is cooled to 153 °C, i.e. the temperature of saturated steam. Condensate arising from the injection of process water contains NH_3 and AN and is recycled into the loop reactor. The saturated steam is used for concentrating the NH_4NO_3 solution in a first vacuum evaporator. An NH_4NO_3-solution with a concentration of approx. 96% is achieved without any additional heat input. Excess steam is used for other heating purposes.

In a second vacuum evaporator step, the concentration of the NH_4NO_3-solution is increased to about 98.5% using high-pressure steam. Two evaporation lines are operated. One line produces pure AN melt. The other evaporation line is used for the concentration of AN solution produced by CNTH conversion together with residual part of the AN produced by pressure neutralisation.

A major part of the produced AN is processed into CAN fertiliser. Additionally, pure AN melt is used for the production of technical grade AN prills.

Calcium ammonium nitrate fertilisers are produced by mixing concentrated ammonium nitrate solution and lime both coming from the CNTH conversion. Ammonium nitrate solution coming from pressure neutralisation is also used for CAN production. Lime arising from the conversion of CNTH is directly used without washing and drying.

2.4.2.2 Granulation of CAN fertilizers

CAN-fertilisers are produced by rotary drum granulation. For feedstock, a slurry of 98.5% ammonium nitrate solution and lime is used. AN solution is obtained from both pressure neutralisation and CNTH conversion. Lime is directly taken from the conversion of CNTH without washing or drying. Steam is used for adjusting the slurry temperature of 140 – 147 °C. The addition of crushed limestone and/or Mg-salts might be necessary in order to obtain the specific product composition. The product is dried with a rotary dryer in an autothermal process. Dust is removed from the off-gas streams by cyclones and recycled into the production. Off-gases of the granulation and drying drums are treated in a wet scrubber together with other off-gases of the CAN production, such as non-condensable off-gases arising from the AN production.

2.4.2.3 Prilling of technical grade ammonium nitrate

About 14,600 t/a technical grade ammonium nitrate is produced by prilling. Starting material is 98.5% AN melt, which is derived after the second evaporation step of the pressure neutralisation process. The AN melt is concentrated in falling film evaporators, which are installed at the top of a prill tower and are operated in counter current with hot air. The falling film evaporators concentrate the AN melt to about 99.8%. The hot concentrated AN melt is sprayed via nozzles into the prill tower, where cooling air conducted in counter current causes solidification of the AN prills. The AN prills are finally cooled in a cooling drum.

Waste gases from the falling film evaporators and the prill tower are treated in a packed column. About 90% of the purified waste gas is recycled into the prill tower. The rest of the waste gas is used for cooling the product and is finally treated with an aerosol filter.

Cooling water from the CAN production is directly discharged.

Table 5 presents the input and output levels of the AN and CAN production in 2015 and Table 6 the specific energy consumption for the production of CAN fertilizers.

Table 5: Input/output levels of the ammonium nitrate and calcium ammonium nitrate production. (Source: Operator information 2016)

AN from pressure neutralisation	
Production 100% AN	372,00 t/a
Production capacity	1,800 t/d
NH_3 input	79,600 t/a
HNO_3 input	295,000 t/a
Cooling water ($\Delta T = 10$ °C)	28,000 m^3/d
AN from CNTH conversion	
Production 100% AN	151,000 t/a
Production capacity	890 t/d
CNTH input	
NH_3 input	32,100 t/a
CO_2 input	59,500 t/a
CAN (27%N)	
Production	696,000 t/a
Production capacity	2,200 t/d

Table 6: Specific energy consumption for the production of CAN. (Source: Operator information 2016)

Electric energy	47.5 MJ/t CAN
Steam	0.013 t/t CAN

3 CURRENT EMISSION AND CONSUMPTION LEVELS

3.1 Emissions to air and waste gas treatment

At the reference plants several processes cause emissions to air. The following list gives an overview of the main air pollutants and the production processes causing them.

- Ammonia
  - NO_x, CO, NH_3, CO_2, CH_4
- Nitric acid
  - NO_x, N_2O, NH_3
- Urea
  - Dust, NH_3
- Nitrophosphate route
  - Digestion of phosphate rock
    - NO_x, HF
  - CNTH conversion
    - NH_3, HF

  - Slurry granulation
  - Dust, NH_3, HF
- Ammonium nitrate and calcium ammonium nitrate
  - Dust, NH_3, HF
- Storage of raw material and product
  - Dust

Emissions caused in the ammonia production process are NO_x, CO, CO_2, NH_3 and CH_4 and are caused by following processes:

- Steam reforming,
- Methanation,
- Ammonia synthesis.

Pollutants arising from the nitric acid production are NO_x, N_2O and NH_3 from NO_x/N_2O reduction.

Pollutants arising from MN-fertiliser production by the nitrophosphate route are dust, NO_x, NH_3 and fluorine compounds. The following processes contribute to emissions to air:

- Digestion of phosphate rock including separation/washing of sand and filtration/washing of calcium nitrate tetrahydrate (CNTH),
- Conversion of CNTH
- Neutralisation/evaporation of NP-acid, and
- Slurry granulation.

Emission sources of NO_x and fluorine compounds are the digestion of phosphate rock, the separation of sand and the filtration of CNTH. NO_x is formed by redox reactions of HNO_3 with organic substances and/or ferrous salts. From the neutralisation/evaporation unit, emissions of NH_3 and fluorine compounds are released. Dust, NH_3 and fluorine compounds are released from slurry granulation.

3.1.1 Ammonia production

The major air emissions of ammonia production are nitrogen oxides (NO, NO_2), carbon monoxide (CO), ammonia (NH_3) and methane (CH_4). At the reference plant NO_x and CO emissions are monitored continuously, NH_3 emissions are measured four times per year. The emission limit values for these pollutants are 150 mg/Nm³ NO_x (as NO_2), 100 mg/Nm³ CO and 10 mg/Nm³ NH_3 at a reference oxygen content of 3 vol%. The measurement uncertainty for the measurement of NO_x is 4% at both lines and the measurement uncertainty for the measurement of CO is 2% for line 1 and 4% for line 2. Values reported to the competent authority have to be measured values. The emission limits are met, when after deducting the measurement uncertainty (validated values)

- all daily averages are below the emission limit value and
- all half hourly averages are below twice the emission limit value and
- 97% of the half hourly averages are below 1.2 times the emission limit value.

The daily average NO_x emissions to air for both plants are usually about 140 mg/Nm^3 and the daily average CO emissions are usually below 3 mg/Nm^3. Table 7, Table 8 and Table 9 give an overview of the air emissions from the ammonia production.

During the reference periods 2015 (plant 1) and 2016 (plant 2), the daily average of NO_x exceeded the emission limit value 1 out of 324 times at plant 1 and 2 out of 285 times at plant 2. At plant 2 half hourly averages of NO_x and CO were exceeded as well as one half hourly average of NH_3.

Table 7: Classification of daily averages and maximum half hourly averages of the day of NO_x emissions to air. (Source: Operator information 2016)

NO_x emissions [mg/Nm^3] (3% O_2) 1)	**Plant 1 (2015)**		**Plant 2 (2016)**	
	Daily average	**Maximum half hourly average 2)**	**Daily average**	**Maximum half hourly average 2)**
0 – 50	0	0	0	0
50 – 100	0	0	0	0
100 – 150 (ELV)	321	293	281	239
150 – 180 (1.2xELV)	2	27	4	36
180 – 300 (2xELV)	0	3	0	8
> 300	0	0	0	2[3]
Total	**323**	**323**	**285**	**285**

1) Standard conditions 0°C, 1,013 mbar and dry waste gas stream.

2) Maximum half hourly average in a day.

3) Maximum value: 322 mg/Nm^3

Table 8: Classification of daily averages and maximum half hourly averages of the day of CO emissions to air. (Source: Operator information 2016)

CO emissions [mg/Nm^3] (3% O_2) 1)	**Plant 1 (2015)**		**Plant 2 (2016)**	
	Daily average	**Maximum half hourly average 2)**	**Daily average**	**Maximum half hourly average 2)**
0 – 10	323	323	285	284
10 – 50	0	0	0	0
50 – 100 (ELV)	0	0	0	0
100 – 120 (1.2xELV)	0	0	0	0
120 – 200 (2xELV)	0	0	0	0
> 200	0	0	0	1[3]
Total	**323**	**323**	**290**	**290**

1) Standard conditions 0°C, 1,013 mbar and dry waste gas stream.

2) Maximum half hourly average in a day.

3) Maximum value: 239 mg/Nm^3

NH_3 emissions [mg/Nm³] (3% O_2) [1]	Plant 1 (2015)	Plant 2 (2016)
Q1	< 0.1	0.3
Q2	< 0.1	14.0
Q3	< 0.1	8.4; 9.8; 9.1
Q4	< 0.1	-

[1] Standard conditions 0°C, 1,013 mbar and dry waste gas stream.

Table 9: Half hourly averages of NH_3 emissions to air, measured four times a year. (Source: Operator information 2016)

3.1.2 Nitric acid production

The major air emissions of nitric acid production are nitrogen oxides (NO, NO_2) and nitrous oxides (N_2O).

3.1.2.1 Emissions of Nitrogen Oxides (NO_x)

At the production of weak nitric acid, the absorption step is essential for NO_x concentration of the waste gas. Crucial parameters for a high absorption efficiency resulting in low NO_x emission level are (VDI 1983; THIEMANN et al. 1991):

- Pressure: High absorption pressure favours high absorption efficiency and low NO_x emission level. Absorption yield in plants with high pressure absorption columns is above 99.8% [GRY, 1994];
- Temperature: Low absorption temperature favors high absorption efficiency;
- Reaction volume;
- Low solubility of the nitrogen monoxide in water or nitric acid;
- Partial pressures of nitrogen oxides and oxygen: Compared to waste gases of other industrial processes, molar rate of NO_2/NO in waste gas of a nitric acid plant is rather high.

For achieving low NO_x emission levels, nitric acid plants are equipped with end-of-pipe technologies. Among end-of-pipe measures, the selective catalytic reduction (SCR) process and the EnviNO$_x$ process can be considered state-of-the-art technology for the reduction of NO_x emissions.

SCR is used in line F. For N_2O reduction a secondary catalyst is used after the Pt/Rh nets in the ammonia compustion unit. No adustments in the construction was necessary as the catalyst replaces raschig packing. Preassure drop depends on the shape of the catalyst. With the second generation catalyst no preassure drop compared to the initial configuration (raschig rings) was obtained.

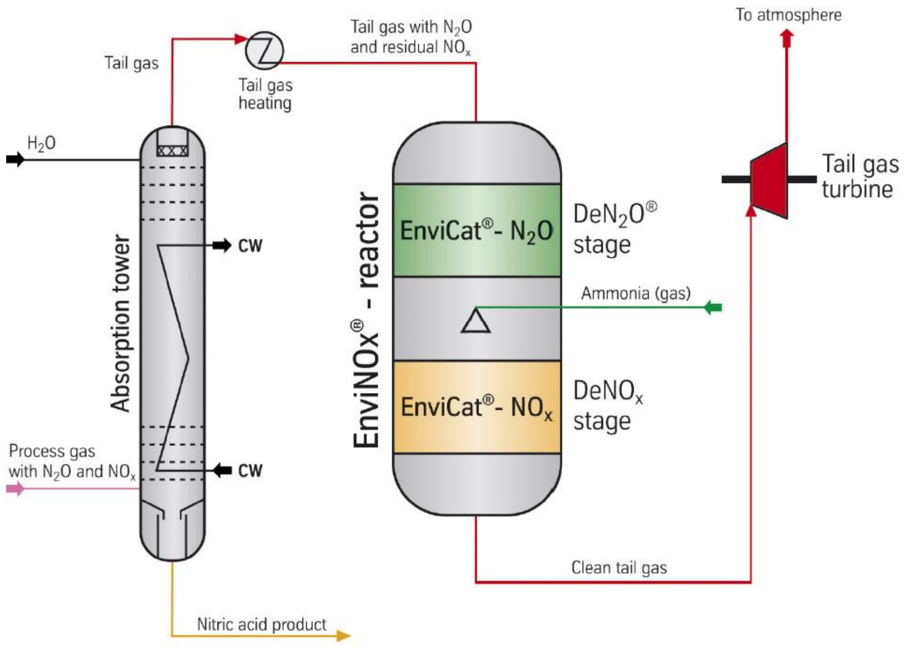
The initial decomposition rates of are approx. 93 – 94% and decline during an operation periode of about 6.5 years to approx. 80%. Replacement of the top layer of catalyst can delay the decline in catalyst activity. No effect of the secondary catalyst on product quality was observed.

The EnviNO$_x$ process (Line E) combines the abatement of NO_x and N_2O. The abatement reactor consists of two layers of iron-zeolite catalyst. Two different variants are available, one for plants with a tail gas temperature above 425 °C and one for plants with a tail gas temperature below 425 °C.

In the first variant N_2O is decomposed in the first step and the present NO_x acts as co-catalyst. Before entering the second stage, NH_3 is added and NO_x and residual N_2O react subsequently with the added reducing agent. (GROVES & FRANK 2009)

Figure 4: EnviNOx® process variant 1: Combined N_2O and NO_x abatement for nitric acid plants using N_2O decomposition and NO_x reduction with ammonia.

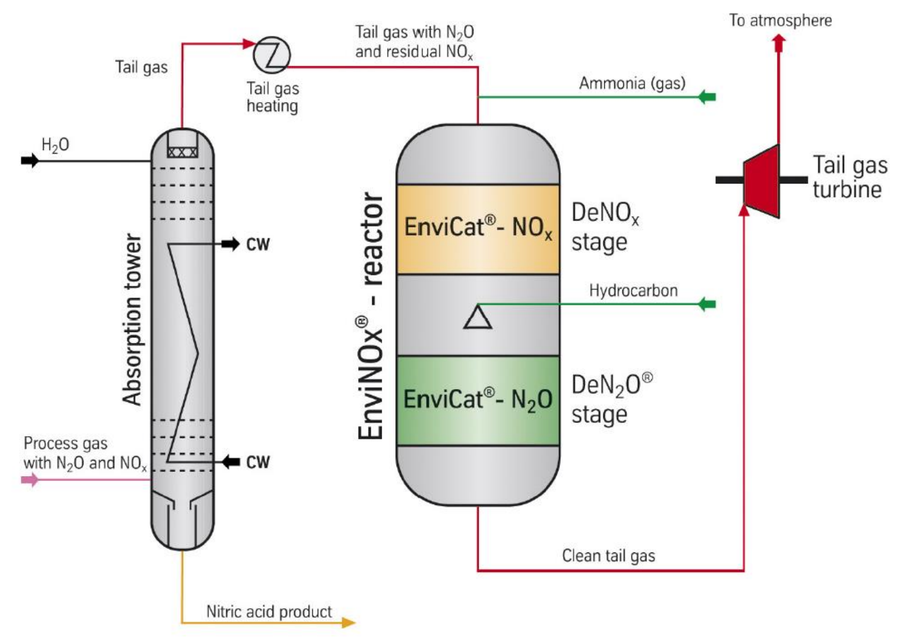
EnviNOx® process variant 1



Source: GROVES & FRANK *2009*

In the second variant, used when the tail gas temperature is below 425 °C and higher than ~340 °C, ammonia is added before entering the first catalyst bed to reduce NO_x and N_2O. After the first stage, hydrocarbons (e.g. methane, propane) are added to the virtually NO_x-free tail gas to reduce residual N_2O.

EnviNOx® process variant 2



Source: GROVES & FRANK *2009*

Figure 5: EnviNOx® process variant 2: Combined N_2O and NO_x abatement for nitric acid plants using N_2O reduction with hydrocarbons and NO_x reduction with ammonia (GROVES & FRANK 2009)

Table 10 presents NO_x emission levels of the Austrian reference plants and relevant operating parameters of the absorption processes. These plants are equipped with SCR and $EnviNO_x$ (variant 1) installations, respectively, for reduction of NO_x emissions. Detailed information of the reference installations operating parameter and emissions are given in Table 10 and Table 11.

Table 10: NO_x emissions and operation parameter relating to the reference installation. (Source: Operator information 2016)

	Line E **M/H process**	**Line F** **N/M process**
Pressure for absorption 1)	8.5 bar	4.5 bar
Absorption temperature	25 °C	25 °C
Absorption efficiency	99.6%	98.6%
NO_x reduction process	tertiary ($EnviNO_x$)	SCR
NO_x concentration before abatement	≤ 500 ppm	1,000 – 2,000 ppm
NO_x concentration after abatement 2) 3)	3 – 4 ppm 7 mg/Nm³ 0.02 kg/t HNO_3 4)	50 – 55 ppm 109 mg/Nm³ 0.33 kg/t HNO_3 4)
Permitted emission limit value 3) 5)	120 mg/Nm³	280 mg/Nm³
	Combined half hourly load < 38 kg/h	

1) *Pressure above atmospheric*

2) *As NO_2*

3) *O_2 levels as obtained with no correction to reference oxygen content. Oxygen content in the waste gas is usually below 1 vol%. ELVs refer to standard conditions (0 °C, 1,013 mbar) and dry air.*

4) *related to 100% HNO_3*

5) *The emission limits are met, when*
- *all daily averages are below the emission limit value and*
- *all half hourly averages are below twice the emission limit value and*
- *97% of the half hourly averages are below 1.2 times the emission limit value.*

Table 11: Classification of daily averages of NO_x emissions to air in 2015. (Source: Operator information 2016).

[mg/Nm³] [1)]	**Line E** **M/H process**		**Line F** **N/M process**	
< 50	357	100%	0	0%
50 – 100	0	0%	11	3%
100 – 150	0	0%	337	95%
150 – 200	0	0%	3	1%
200 – 250	0	0%	2	1%
> 250	0	0%	0	0%
[kg/d]				
< 50	347	97%	1	0%
50 – 100	10	3%	0	0%
100 – 150	1	0%	7	2%
150 – 200	0	0%	278	79%
200 – 250	0	0%	65	18%
> 250	0	0%	3[2]	1%

[1)] O_2 levels as obtained with no correction to reference oxygen content. Oxygen content in the waste gas is usually below 1 vol%. Emission values refer to standard conditions (0 °C, 1,013 mbar) and dry air.

[2)] Maximum value: 291 mg/Nm³

In 2003 the SCR of line E was replaced with an Uhde EnviNO$_x$ system. Thus, NO_x emissions could be reduced from below 200 mg/Nm³ to below 20 mg/Nm³. The usual daily average emissions of line E are between 0 and 15 mg/Nm³ (5th and 95th percentile respectively) with an annual average of 7 mg/Nm³. With the EnviNO$_x$ system the new drafted emission limit value of TA-Luft of 40 mg/Nm³ (half hourly averages) is met.

Daily average NO_x emissions of line F usually range from 101 to 126 mg/Nm³ (5th and 95th percentile respectively) with an annual average of 109 mg/Nm³. During the recorded periods the daily averages did not exceed the emission limit values.

Considering the emission values presented above, annual NO_x emissions of the Austrian nitric acid reference plants can be estimated at about 70 – 80 t/a.

3.1.2.2 Emissions of Nitrous Oxides (N_2O) [1]

Nitrous oxide forms by catalytic oxidation of ammonia. Ammonia reacts to NO; here, efficiencies of 93 and 98% are achieved. The conversion efficiency of ammonia to nitric oxide is a function of temperature, pressure, velocity of gas stream, volume of catalyst, and purity of the ammonia and air streams. Residual ammonia (2 – 7%) reacts in secondary reactions into nitrogen N_2 and at least partly into nitrous oxide (N_2O).

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[1] Nitrous oxide (N_2O) is a greenhouse gas with a greenhouse potential of about 298 times as high as CO_2 over a 100 year time horizon. Major polluters contributing to the N_2O emissions are agriculture, the energy sector (traffic and combustion processes) and industrial processes (production of adipic acid and nitric acid).

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 4\ O_2 \rightarrow 2\ N_2O + 6\ H_2O$$

Detailed information of the reference installations operating parameter and emissions are given in Table 12 and Table 13.

Table 12: N_2O emissions and operation parameter relating to the reference installation. (Source: Operator information 2016)

	Line E **M/H process**	**Line F** **N/M process**
Pressure for catalytic ammonia combustion [1]	3.9 bar	-0.01 bar
Combustion temperature	25 °C	25 °C
Efficiency of catalytic ammonia combustion	96%	94%
N_2O reduction process	tertiary (EnviNO$_x$)	secondary (intermediate catalyst)
N_2O concentration before abatement	800 – 1.400 ppm	600 – 700 ppm
N_2O concentration after abatement [2]	approx. 20 ppm 41 mg/Nm³ 0.117 kg/t HNO_3 [3]	approx. 90 ppm 180 mg/Nm³ 0.539 kg/t HNO_3 [3]
Permitted emission limit values [4]	600 mg/Nm³	600 mg/Nm³

[1] *Pressure above atmospheric*

[2] *O_2 levels as obtained with no correction to reference oxygen content. Oxygen content in the waste gas is usually below 1 vol%. ELVs refer to standard conditions (0 °C, 1,013 mbar) and dry air.*

[3] *related to 100% HNO_3*

[4] *The emission limits are met, when*

- *all daily averages are below the emission limit value and*
- *all half hourly averages are below twice the emission limit value and*
- *97% of the half hourly averages are below 1.2 times the emission limit value.*

Table 13: Classification of daily averages of N_2O emissions to air in 2015. (Source: Operator information 2016)

[mg/Nm³] [1]	**Line E** **M/H process**		**Line F** **N/M process**	
< 50	288	81%	0	0%
50 – 100	69	19%	38	11%
100 – 150	0	0%	42	12%
150 – 200	0	0%	112	32%
200 – 250	0	0%	161	46%
[kg/d]				
< 50	16	4%	1	0%
50 – 100	71	20%	2	1%
100 – 150	223	62%	16	5%
150 – 200	47	13%	31	9%
200 – 250	1	0%	42	12%
250 – 300	0	0%	21	6%
300 – 350	0	0%	40	11%
350 – 400	0	0%	172	49%
400 – 450	0	0%	30	8%

[1] *O_2 levels as obtained with no correction to reference oxygen content. Oxygen content in the waste gas is usually below 1 vol%. Emission values refer to standard conditions (0 °C, 1,013 mbar) and dry air.*

In 2003 the SCR of line E was replaced with an Uhde EnviNO$_x$ system (variant 1), which abates NO_x and N_2O in a two-step process. In the first stage N_2O is catalytically decomposed. Before entering the second stage, NH_3 is added and NO_x and residual N_2O reacts with the added reducing agent in the second stage.

Due to the EnviNO$_x$ system N_2O emissions could be reduced from over 2,000 mg/Nm³ in the raw gas to below 50 mg/Nm³. The daily average emissions of line E are between 18 and 55 mg/Nm³ (5th and 95th percentile respectively) with an annual average of 41 mg/Nm³. Daily average N_2O emissions of line F usually range from 90 to 234 mg/Nm³ (5th and 95th percentile respectively) with an annual average of 180 mg/Nm³. Considering the emission values presented above, annual N_2O emissions of the Austrian nitric acid reference plants can be estimated at about 150 – 160 t/a.

3.1.2.3 Emissions of ammonia (NH_3)

The use of ammonia in the abatement systems, i.e. SCR and EnviNO$_x$, causes secondary emissions of NH_3. Half hourly averages of ammonia emissions are monthly measured and are between 1 and 6 mg/Nm³ for line E and between 1 and 3 mg/Nm³ for line F. The emission limit value for half hourly ammonia emissions of 10 mg/Nm³ was not exceeded during the recorded period.

3.1.3 Urea production

3.1.3.1 Prilling tower

A wet scrubbing system was retro-fitted for the waste gas treatment of the prilling tower. The waste gas of the prilling tower, which has a volume of approx. 350,000 to 400,000 Nm³/h, is allocated to six scrubbers. Forced upward-draft has been necessary since the installation of wet scrubbers. For all six scrubbers together, approximately 400 m³/h acidc washing solution and approximately 4 m³/h fresh water are necessary. The circulating solution has a pH-value of 5.

The emission limit values for dust and ammonia compounds (calculated as NH_3) is 30 mg/Nm³. The compliance with permitted values has to be verified by measurements every three months at every operated scrubber (at least three).

The measured emissions values from urea production in 2015 are displayed in Table 14. The emission values were mostly compliant with the emission limit values.

Table 14: Dust and NH_3 emissions to air (HHA) in 2015. (Source: Operator information, 2016).

[mg/Nm³] 1)	Dust No. of values		NH_3 No. of values	
0 – 6	7	29%	1	4%
6 – 12	3	13%	7	29%
12 – 18	5	21%	9	38%
18 – 24	4	17%	4	17%
24 – 30 (ELV)	3	13%	2	8%
31 – 40	2	8%	1	4%

1) *Standard conditions 0 °C, 1,013 mbar and dry air.*

3.1.3.2 Bagging plant

Exhaust air from the urea bagging plant (approx. 10,000 – 12,000 Nm^3/h) is de-dusted in a bag filter. Compliance with emission limit values has to be validated once a year.

The emission limit value for dust is 20 mg/Nm^3 (standard prilled urea) and 30 mg/Nm^3 (fine prilled urea) respectively. In 2015 dust emissions were usually below 5 mg/Nm^3 with one out of 6 values below 15 mg/Nm^3.

The emission limit value for ammonia is 30 mg/Nm^3. Measured values in 2015 ranged from 2 to 10 mg/Nm^3.

All values (emission values and emission limit values) refer to half hourly averages, standard conditions 0 °C, 1,013 mbar, dry.

3.1.4 Emissions of N-fertilizer production

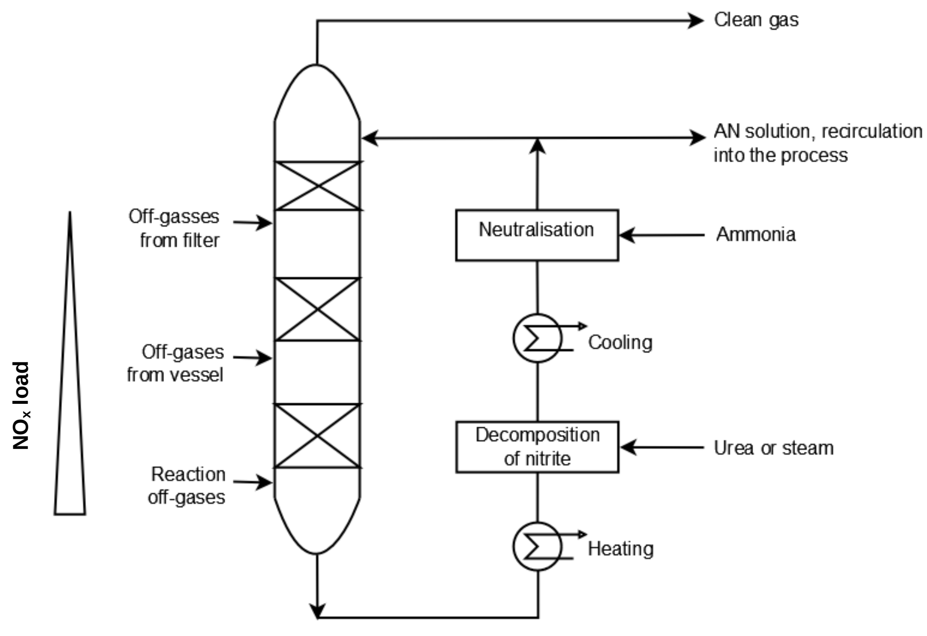
3.1.4.1 Digestion of phosphate rock and conversion of CNTH

Emissions of NO_x and fluorine compounds are collected from following sources

- phosphate rock digestion,
- separation/washing of sand,
- filtration/washing of CNTH.

In order to reduce these emissions, off-gases are combined and treated together by wet scrubbing. AN solution is used as scrubbing liquor. Figure 6 presents a block diagram of multi-stage NO_x waste gas scrubbing of the rock phosphate digestion at the ODDA process.

Multi-stage NO_x waste gas scrubbing



Source: Umweltbundesamt

Figure 6: Multi-stage NO_x waste gas scrubbing with AN solution of the phosphate rock digestion (ODDA process) and regeneration of the scrubbing solution.

Additionally to scrubbing, NO_x emissions can be reduced when using phosphate rock with low contents of organic substances and ferrous salts. Furthermore, digestion temperature has to be controlled accurately. If the digestion temperature is too high, excessive formation of NO_x will take place.

Waste gases arising from the separation and washing of the CNTH crystals are treated together with waste gases from the digestion of phosphate rock.

Other waste gases such as exhaust vapours arising from evaporation of the AN solution are treated together with the waste gases arising from a subsequent CAN production process.

The emission limits are 5 and 400 mg/Nm³ for HF and NO_x, respectively (0 °C, 1,013 mbar, dry air). Periodic monitoring is permitted every three months and three half hourly averages have to be determined. Currently, measurments are carried out every month. The emission limit value is met, when all half hourly averages are below the emission limit value. The flow rate is between 24,000 and 28,000 Nm³/h (dry air).

Table 15 presents half hourly emission averages for HF and NO_x emissions after the scrubber.

NO_x values, both measured and validated (talking into accout measurement uncertainty) values, are exceeding the emission limit value recently. This can be assigned to technical problems and end of lifetime of the abatement equipment (scrubber). Emission behaviour of the installation is currently optimised to ensure permanent compliance with the emission limit values.

Table 15: Half hourly averages of HF and NO_x emissions to air in 2015. (Source: Operator information 2016).

[mg/Nm³]	**HF No. of values**		**[mg/Nm³]**	**NO_x No. of values**	
0 – 1	11	46%	0 – 100	0	0%
1 – 2	2	8%	100 – 200	2	3%
2 – 3	4	17%	200 – 300	33	55%
3 – 4	3	13%	300 – 400(ELV)	13	22%
4 – 5 (ELV)	3	13%	400 – 500	0	0%
5 – 6	1	4%	500 – 600	1	2%
6 – 7	0	0%	600 – 700	3	5%
7 – 8	0	0%	700 – 800	3	5%
8 – 9	0	0%	800 – 900	0	0%
9 – 10	0	0%	900 – 1,000	1	2%
> 10	0	0%	> 1,000	4[1)]	7%

Standard conditions 0 °C, 1,013 mbar and dry air.

Methods used: VDI 2456 and EN ISO 10304-1 for NO_x and VDI 2470/Sheet 1 and DIN 38405-4 for HF.

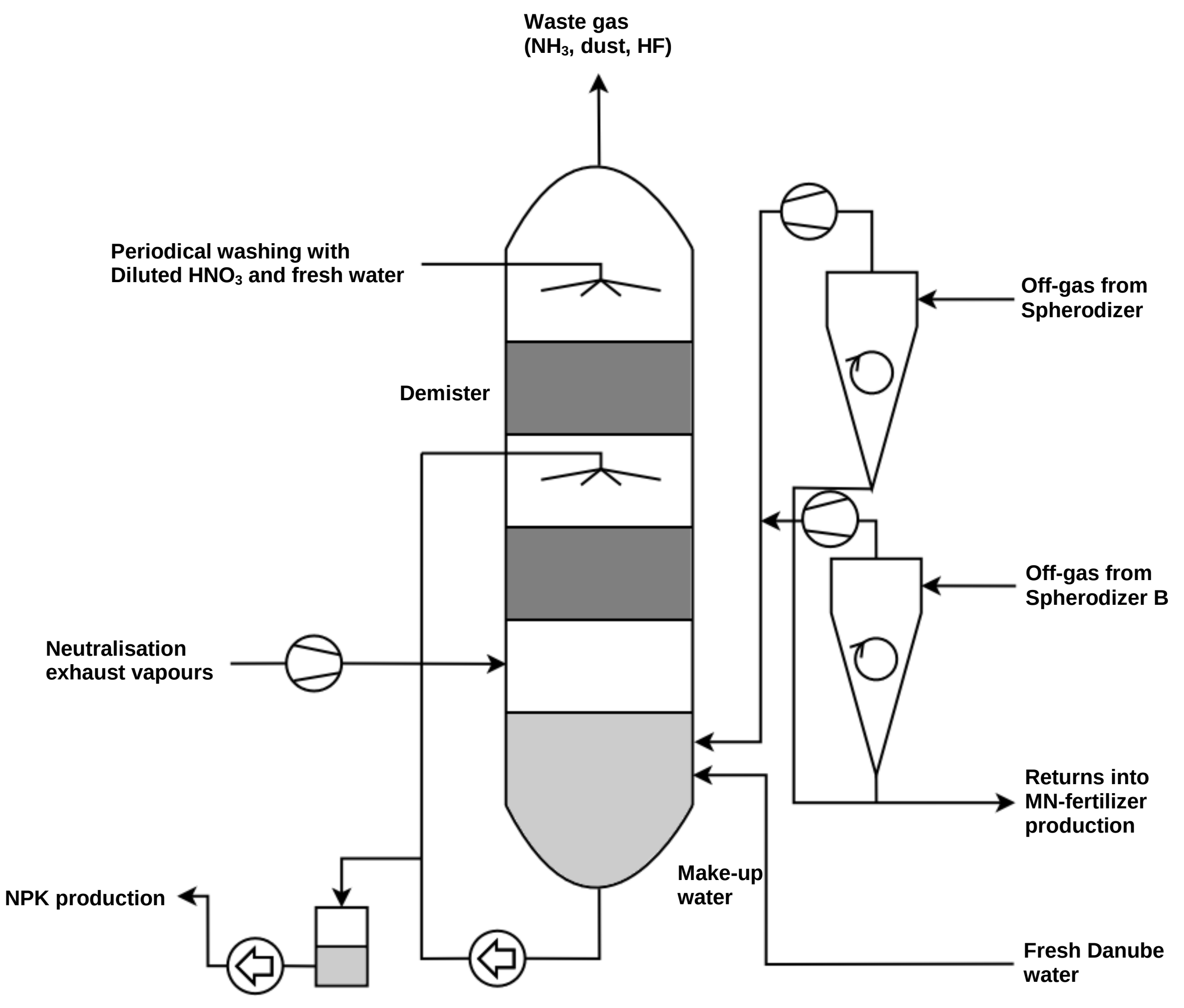
[1)] Maximum value: 8,700 mg/Nm³

3.1.4.2 Combined scrubbing of neutralisation and granulation off-gases

Instead of condensing the exhaust vapours from the NP neutralisation unit, they are introduced as they are in a scrubber, which at the same time cleans the off-gases of the Spherodizer(s). The hot off-gases of the Spherodizer (~100 °C) are not saturated with H_2O and the heat content is used to evaporate additional water in the scrubber. Thus, the combined scrubber works as an evaporator for liquid effluents without additional energy requirement. Concentrated scrubbing liquor can be recycled into the production process. This way avoids liquid effluents from both neutralisation/evaporation and granulation units. At the same time the main part of the nutrients normally lost in liquid effluents are recovered.

The total waste gas volume of the combined scrubber is about 250,000 Nm^3/h. Circulation of scrubbing liquor is about 1,800 m^3/h. About 1 m^3/h scrubbing liquor with an AN concentration of about 25 wt-% is drawn off and recycled into the MN-fertiliser production process. Liquid effluents from the MN fertiliser production, which are collected in a process water reservoir, are used as make-up water. The scrubber is equipped with a demister located above the scrubber packing. The combined scrubber has to be cleaned periodically, because insoluble compounds in the waste gas, such as dolomite, $CaSO_4$ and $Ca_3(PO_4)_2$, cause clogging of the scrubbing column. Figure 7 presents a schematic diagram of the combined scrubber.

Combined scrubber for the neutralisation exhaust vapours and the granulation off-gasses of the MN-fertilizer production



Source: Umweltbundesamt

Figure 7: Schematic diagram of the combined scrubber for the neutralisation exhaust vapours and the granulation off-gasses of the MN-fertilizer production

Table 17 presents the half hourly emission levels for dust, ammonia, HF and NO_x from the combined waste gas scrubbing in the year 2015 (0 °C, 1,013 mbar, dry air). Emission limit values, measurement frequency, sample number and rules for determination of compliance are given in Table 16. Dust emissions have to be monitored periodically and continuously. Although the emission limit value for both methods is the same, the rules for determining the compliance with the permit are different.

All measured values of NO_x and HF are below the emission limit value. Although few measured values of the NH_3 emissions exceed the emission limit value, the criteria for compliance are met.

Dust emission values, both measured and validated (talking into accout measurement uncertainty) values, exceed the emission limit value recently. This can be assigned to technical problems and end of lifetime of the abatement equipment (scrubber) as well as changes in analytical methods. Emission behaviour of the installation is currently optimised to ensure permanent compliance with the emission limit values.

Table 16: Parameter for determination of compliance with the emission limits.

	Emission limit value	**Measurement frequency**	**Sample**	**ELV is met, when**	**Methods**
NO$_x$	30 mg/Nm^3	Periodic every three months	3 half hourly averages	all measurements minus the measurement uncertainty are lower than the ELV.	VDI 3453 VDI 2450 Sheet 2 VDI 4200 ÖNORM EN 14792
HF	2 mg/Nm^3				VDI 3453 VDI 2450 Sheet 2 VDI 4200 VDI 2470
NH$_3$	30 mg/Nm^3	Periodic monthly	12 half hourly averages	the arithmetic average of the 12 samples minus the measurement uncertainty is lower than the ELV.	VDI 3453 VDI 2450 Sheet 2 VDI 4200 VDI 3496 Sheet 1
Dust *)	25 mg/Nm^3	Periodic monthly			VDI 3453 VDI 2450 Sheet 2 VDI 4200 ÖNORM EN 13284-1
		Continuous	Half hourly averages	● no validated half hourly average exceeds the ELV and ● at most 3% of the validated half hourly averages exceed the ELV more than 1.2 times the ELV and ● no validated daily average exceeds the ELV. The validated value is the measured value minus the measurement uncertainty.	n/a

**) Due to the properties of dust (thermally instable) special requirements for sampling and measurments are needed.*

Table 17: Half hourly averages of dust, NH_3, HF and NO_x emissions from periodic measurement in 2015. (Source: Operator information 2016)

Dust			**NH_3**			**HF**			**NO_x**		
[mg/Nm^3]1)	**No. of values**		**[mg/Nm^3]1)**	**No. of values**		**[mg/Nm^3]1)**	**No. of values**		**[mg/Nm^3]1)**	**No. of values**	
0 – 5	3	1%	0 – 6	180	76%	0 – 0.4	8	67%	0 – 6	1	8%
5 – 10	13	5%	6 – 12	39	16%	0.4 – 0.8	2	17%	6 – 12	4	31%
10 – 15	27	11%	12 – 18	7	3%	0.8 – 1.2	2	17%	12 – 18	8	62%
15 – 20	28	12%	18 – 24	3	1%						
20 – 25	17	7%	24 – 30	5	2%						
25 – 30	19	8%	30 – 36	4	2%						
30 – 35	23	10%	36 – 42	1	0%						
35 – 40	8	3%									
40 – 45	17	7%									
45 – 50	23	10%									
50 – 55	15	6%									
55 – 60	17	7%									
60 – 65	11	5%									
65 – 70	4	2%									
70 – 75	7	3%									
> 75	7 2)	3%									

1) *Standard conditions with 0 °C, 1,013 mbar and dry air apply.*

2) *Maximum value: 97 mg/Nm^3*

3.1.4.3 Ammonium nitrate and Calcium ammonium nitrate production

Ammonium nitrate prilling

Exhaust air from the prill tower is cleaned by a scrubber. Permitted half hourly emission limit values for dust and ammonia are 25 and 20 mg/Nm^3, respectively. In 2015 half hourly measured dust emissions were below 5 mg/Nm^3 and ammonia emissions ranged from 2 to 9 mg/Nm^3 (0 °C, 1,013 mbar, dry air). The waste gas flow rate is approx. 12,000 Nm^3/h.

Periodic monitoring is done twice a year and three half hourly averages are measured. The emission limit is met, when all measured values reduced by the measurement uncertainty are below the emission limit value. Dust is measured according to ÖNORM M 5861-1, EN 13284-1 and VDI 2066/Sheet 1. Ammonia is measured according to VDI 3496/Sheet 1.

Main scrubber of CAN production

Permitted half hourly emission limit values for dust, ammonia and HF are 25, 30 and 1 mg/Nm^3 (0 °C, 1,013 mbar, dry air), respectively.

Periodic monitoring is permitted four times a year and three half hourly averages are measured. The emission limit is met, when all measured values reduced by the measurement uncertainty are below the emission limit value. Dust is measured according to ÖNORM M 5861-1, EN 13284-1 and VDI 2066/Sheet 1. Ammonia is measured according to VDI 3496/Sheet 1 and EN ISO 11732. HF is measured according to VDI 2470/Sheet 1 and DIN 38405-4.

The waste gas flow rate ranges from 90,000 to 111,000 Nm^3/h. Half hourly emission levels from periodic measurement are presented in Table 18.

In 2015 and 2016 some exceedances for the measured emission value of dust were recorded. Emissions of ammonia were usually below 10 mg/Nm^3, but were between 16 and 21 mg/Nm^3 in one measuring period, and exceeded the emission limit value in another. In both years emissions of HF were below the emission limit value.

Emission limit value exceedances can be assigned to technical problems and end of lifetime of the abatement equipment. Emission behaviour of the installation is currently optimised to ensure permanent compliance with the emission limit values.

Table 18: Half hourly averages of dust, NH$_3$ and HF emissions from periodic measurement in 2015. (Source: Operator information 2016)

Dust			**NH$_3$**			**HF**		
[mg/Nm^3]1)	**No. of values**		**[mg/Nm^3]1)**	**No. of values**		**[mg/Nm^3]1)**	**No. of values**	
0 – 10	7	23%	0 – 5	21	75%	0 – 0.1	3	14%
10 – 20	8	27%	5 – 10	1	4%	0.1 – 0.2	7	33%
20 – 30	6	20%	10 – 15	0	0%	0.2 – 0.3	3	14%
30 – 40	2	7%	15 – 20	2	7%	0.3 – 0.4	4	19%
40 – 50	1	3%	20 – 25	1	4%	0.4 – 0.5	2	10%
50 – 60	2	7%	25 – 30	0	0%	0.5 – 0.6	0	0%
60 – 70	2	7%	30 – 35	2	7%	0.6 – 0.7	1	5%
70 – 80	1	3%	35 – 40	1	4%	0.7 – 0.8	0	0%
80 – 90	0	0%	40 – 45	0	0%	0.8 – 0.9	1	5%
90 – 100	0	0%	45 – 50	0	0%	0.9 – 1.0	0	0%
> 100	1 2)	3%	> 50	0	0%	> 1.0	0	0%

1) *Standard conditions with 0 °C, 1,013 mbar and dry air apply.*

2) *Maximum value: 114 mg/Nm^3*

Rotary drum granulation of CAN production

Exhaust air of the rotary cooling drums is dedusted by cyclones. Half hourly emission limit values for the released exhaust air for dust and ammonia are 20 and 30 mg/Nm^3 (0 °C, 1.013,25 mbar, dry air), respectively. Periodic measurement is permitted twice a year and three half hourly averages have to be measured. The emission limit is met, when no half hourly average, with the measurement uncertainty added, exceeds the emission limit value. Dust emissions are measured according to ÖNORM M 5861-1, EN 13284-1 and VDI 2066/Sheet 1.

Dust emissions are usually below 5 mg/Nm^3, although in 2015 the emission limit was exceeded once. Ammonia emissions were below 7 mg/Nm^3 in 2015. The waste gas flow rate for each drum ranges from 59,000 to 150,000 Nm^3/h.

Dedusting of production building

Air from the production building is dedusted by bag filters. The half hourly emission limit value for dust is 10 mg/Nm^3 (0 °C, 1,013 mbar, dry air). In 2015 the measurement period dust emissions were usually below 5 mg/Nm^3, although one exceedance of the emission limit value was recorded (measured half hourly averages: 8.1, 12 and 13 mg/Nm^3).

3.1.4.4 Other emission sources

Several bunkers, used to store raw materials, and other facilities are equipped with fabric filters for dedusting. Periodic measurement is permitted once a year and three half hourly averages have to be measured. The emission limit of 10 mg/Nm^3 (0 °C, 1.013,25 mbar, dry air) is met, when no half hourly average, with the measurement uncertainty added, exceeds the emission limit value. Dust emissions are measured according to ÖNORM M 5861-1, EN 13284-1 and VDI 2066/Sheet 1.

Table 19: Dust emissions to air in 2015. (Source: Operator Information 2016)

Source	Flow rate [Nm^3/h]	Half hourly averages [mg/Nm^3]
$MgSO_4$ bunker	1,600 – 2,100	1.0 4.6 18 < 1 1.6 1.9
$CaCO_3$ bunker	1,200	1.1 1.4 8.9
$(NH_4)_2SO_4$ bunker	2,100	< 1 < 1
KCl deduster	6,500	1.5 2.9 3.3;
Powder bunker	3,700 – 4,800	7.0 8.7 11.0 3.5 3.8 4.2
Raw phosphate storage	3,700	<1.0 1.1 1.3
Raw phosphate sieving	5,100	< 1.0 < 1.0 3.1

Standard conditions with 0 °C, 1,013 mbar and dry air apply.

3.2 Water

Process wastewater arises at the NPK fertilizer production, the urea production, the ammonium nitrate production and the ammonia production.

Wastewater from the NPK fertilizer production is treated by neutralisation before being discharged into the river Danube.

Wastewater from the urea production is, together with other NH_3 contaminated process wastewaters, treated via stripping (Abwasser-Destillationskolonne). The thereof gained NH_3 (gaseous) is reused in the production process. Pre-treated wastewater (after stripping) is partly reused in the process (e.g. washing water for exhaust air purification). The remaining fraction of the pre-treated wastewater passes neutralisation with CO_2 before being discharged into the river Danube.

Wastewater from the ammonium nitrate production passes pressure neutralisation before being discharged into the river Danube.

Wastewater from the ammonia production is treated via stripping in order to reduce the NH_3 content before being discharged into the river Danube. The thereof gained NH_3 (gaseous) is reused in the process.

Process wastewater emissions are regulated by the wastewater ordinance on inorganic fertilizers (2/8/6/3/5 Anorganische Düngemittel), except for wastewater from the ammonia production which is regulated by the wastewater ordinance on technical gases (2/8/6/3/9 Technische Gase). Cooling water from the prilling tower (ammonium nitrate production) and the CAN production are regulated by the general wastewater ordinance (2/7/1 Allgemeine Abwasseremissionsverordnung). Emission limit values are set by permit. The permits are currently under revision.

Treated process wastewater and cooling water is collected in the cooling water sewer (Kühlwasserkanal) before being discharged into the river Danube. External-monitoring of the cooling water sewer has been conducted in 2016 and is presented in Table 45. External-monitoring reports of the individual plants (NPK fertilizer production, urea production, ammonium nitrate production and ammonia production) are not available.

3.2.1 Urea

Table 20 compares the wastewater emissions of the urea production (2015; self-monitoring) with the emission limit values set by permit and by appendix A of the wastewater ordinance for inorganic fertilizers. For the calculation of specific loads the installed production capacity (related to one ton of nitrogen in the final product) is used. The installed N-production capacity is 653 t/d.

Wastewater from the urea production is, together with other NH_3 contaminated process wastewaters, treated via stripping. The thereof gained NH_3 (gaseous) is reused in the production process. Pre-treated wastewater (after stripping) is partly reused in the process. The remaining fraction of the pre-treated wastewater passes neutralisation with CO_2 before being discharged into the river Danube.

In 2015 the set ELV for NH_4-N has been exceeded on some occasions due to a malfunction of the urea production plant (OTNOC).

Table 21 illustrates the self-monitoring (2015) per parameter in a detailed way.

Table 20: Wastewater emissions (self-monitoring, 2015), ELV permit, ELV ordinance (Inorganic fertilizers, appendix A; 2/8/6/3/5 Anorganische Düngemittel, Anlage A). (Source: Operator Information 2016)

Urea production									
Parameter	**Daily min. (self-monitoring)**		**Daily max. (self-monitoring)**		**Annual average (self-monitoring)**		**ELV permit**	**Ordinance**	**Number of samples (self-monitoring)**
	kg/d	**kg/t N**	**kg/d**	**kg/t N**	**kg/d**	**kg/t N**	**kg/d**	**kg/t N**	
NH_4-N	19	0.029	300	0.46[2]	159	0.26	326	0.5	96
Total Kjeldahl N	49	0.07	590	0.9	210	0.32	1630	-	96
COD	10	0.02	79	0.12	36	0.06	362	0.5	96

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[2] NH_4-N exceedances, OTNOC – 0,75 kg/d (06.07.2015) und 1,34 kg/d (23.10.2015)

Table 21: Water emissions 2015. self-monitoring. (Source: Operator Information 2016)

Flow			**NH_4-N**		
[m^3/d]	**No. of values**		**[kg/d]**	**No. of values**	
0 – 140	0	0%	0 – 65.2	5	5%
140 – 280	2	2%	65.2 – 130.4	26	27%
280 – 420	3	3%	130.4 – 195.6	35	36%
420 – 560	60	63%	195.6 – 260.8	22	23%
560 – 700	31	32%	260.8 – 326	6	6%
> 700	0	0%	> 326	2	2%

COD			**TKN**		
[kg/d]	**No. of values**		**[kg/d]**	**No. of values**	
0 – 72.4	93	97%	0 – 326	83	86%
72.4 – 144.8	3	3%	326 – 652	13	14%
144.8 – 217.2	0	0%	652 – 978	0	0%
217.2 – 289.6	0	0%	978 – 1,304	0	0%
289.6 – 362	0	0%	1,304 – 1,630	0	0%
> 362	0	0%	> 1,630	0	0%

3.2.2 NPK

Table 21 compares the wastewater emissions of the NPK fertilizer production (2015; self-monitoring) with the emission limit values set by permit and by appendix B of the wastewater ordinance for inorganic fertilizers.

Table 22: Wastewater emissions (self-monitoring, 2015), ELV permit, ELV ordinance (Inorganic fertilizers, appendix B; 2/8/6/3/5 Anorganische Düngemittel, Anlage B). (Source: Operator Information 2016)

NPK fertilizer production							
Parameter	**Unit**	**Daily min. (self-monitoring)**	**Daily max. (self-monitoring)**	**Annual average (self-monitoring)**	**ELV permit**	**Ordinance**	**Number of samples (self-monitoring)**
Q	m³/d	289	3,451	2,306	10,177		365
Q inlet (neutralisation)	m³/d	0	3,301	2,163	3,380		365
Cooling water	m³/d	121	32,033	17,945	32,400		365
T	°C	6.6	32.7	17	30	30	365
pH		2.1	9.3	7.3	6.5 – 8.5	6.5 – 8.5	365
TSS	mg/l	5	1,308	61			362
TSS load	kg/d	5	3,089	129	525		362
TSS specific load	kg/t					50	
NH_3-N	mg/l	2	450	39	450		362
NH_3-N load	kg/d	3	581	86			362
NO_2-N	mg/l	0.3	1.89	0.47	2		362
NO_2-N load	kg/d	0.1	4	1.1	15		362
NO_3-N	mg/l	7	571	63			362
NO_3-N load	kg/d	10	710	138	600		362
PO_4	mg/l	1	515	20	550		362
PO_4 load	kg/d	3	634	42	193		362
Fluoride	mg/l	1	51	15	60		362
Fluoride load	kg/d	2	174	34	105		362
Fluoride specific load	kg/t					3	
Cadmium	µg/l	0.1	0.6	0.4	1		12
Cadmium load	g/d	0.1	1.8	0.9	21		365
Cadmium specific Load	g/t					0.1	
Mercury	µg/l	0.1	0.2	0.1	0.5		12
Mercury load	g/d	0	0.4	0.2	25		365

NPK fertilizer production

Parameter	Unit	Daily min. (self-monitoring)	Daily max. (self-monitoring)	Annual average (self-monitoring)	ELV permit	Ordinance	Number of samples (self-monitoring)
Mercury specific load	g/t					0.02	
Zinc	µg/l	12	57	30	60		12
Zinc load	g/d	7	182	69	200		365
Zinc specific load	g/t					2	
Potassium oxide	mg/l	1	110	4			362
Potassium oxide load	kg/d	0	110	8			362
Sulfate	mg/l	22	94	45			12
Sulfate load	kg/d	9.2	324.4	100.1			365
COD	mg/l	5	12	8	20		12
COD load	kg/d	1.4	39.3	18.8	210		365
COD specific load	kg/t					0.6	

In 2015 several exceedances occurred in the course of self-monitoring which are discussed in detail in the following. According to the operator the permit and therefore the emission limit values (ELV) for wastewater emissions from the NPK fertilizer production are currently under revision.

3.2.2.1 Feed

The ELV for water feed is 3,380 m³/d. no exceedance has been observed in 2015.

Table 23: Water feed 2015. self-monitoring. (Source: Operator Information 2016)

[m³/d]	No. of values	
0 – 676	13	4%
676 – 1,352	16	4%
1,352 – 2,028	56	15%
2,028 – 2,704	251	69%
2,704 – 3,380	29	8%
> 3380	0	0%

3.2.2.2 Discharge

The ELV for water discharge is 10,177 m³/d. no exceedance has been observed in 2015.

Table 24: Water discharge 2015. self-monitoring. (Source: Operator Information 2016)

[m³/d]	No. of values	
0 – 2,035.4	70	19%
2,035.4 – 4,070.8	295	81%
4,070.8 – 6,106.2	0	0%
6,106.2 – 8,141.6	0	0%
8,141.6 – 10,177	0	0%
> 10,177	0	0%

3.2.2.3 Cooling water

The ELV for cooling water is 32,400 m³/d. no exceedance has been observed in 2015.

Table 25: Water discharge 2015. self-monitoring. (Source: Operator Information 2016)

[m³/d]	No. of values	
0 – 6,480	12	3%
6,480 – 12,960	48	13%
12,960 – 19,440	168	46%
19,440 – 25,920	78	21%
25,920 – 32,400	59	16%
> 32,400	0	0%

3.2.2.4 Max. temperature

The permitted ELV for temperature (30 °C) was exceeded twice in 2015 – 31.6 °C (01.09.2015) and 32.7 °C (17.09.2015). According to the “4 out of 5” rule the monitored emission values are, however, complying – Wastewater ordinance for inorganic fertilizers (§4.(2)Z2; 2/8/6/3/5 Anorganische Düngemittel): “For the parameter temperature the “4 out of 5” is to be applied to the spot sample of a day; the measurement is not allowed to exceed the ELV by 1.2 times.”.

Table 26: Water temperature 2015. self-monitoring. (Source: Operator Information 2016)

[°C]	No. of values	
0 – 6	0	0%
6 – 12	59	16%
12 – 18	104	28%
18 – 24	192	53%
24 – 30	8	2%
> 30	2	1%

3.2.2.5 pH

The permitted ELV for pH (6.5 – 8.5) was 23 times not met in 2015. Out of which the measurements fell 15 times below the permitted ELV and exceeded the permitted ELV 8 times. According to the “4 out of 5” rule a deviation from the permitted pH interval of not more than 0.5 units is allowed (§4.(2)Z3; 2/8/6/3/5 Anorganische Düngemittel). After applying the “4 out of 5” rule 10 self-monitoring measurements are not complying with the permitted ELV for pH. Out of which 9 fell (more than 0.5 units) below the permitted interval and 1 exceeded the permitted interval (by more than 0.5 units).

Table 27: pH value 2015. self-monitoring. (Source: Operator Information 2016)

	pH_{min}		pH_{max}	
[-]	No. of values		No. of values	
< 6.5	15	4%	0	0%
6.5 – 7	192	52%	0	0%
7 – 7.5	154	42%	124	34%
7.5 – 8	4	1%	179	49%
8 – 8.5	0	0%	54	15%
> 8.5	0	0%	8	2%

3.2.2.6 Total suspended solids

The permitted ELV for TSS (525 kg/d) was 11 times exceeded in 2015. Due to the “4 out of 5” rule (§4.(2)Z5; 2/8/6/3/5 Anorganische Düngemittel) 4 measurements are not complying – 1336 kg/d (03.07.2015); 1594 kg/d (02.10.2015); 3089 kg/d (23.10.2015); 2384 kg/d (30.12.2015).

§4.(2)Z5; 2/8/6/3/5 Anorganische Düngemittel: “TSS emissions are complying with the permitted ELV if the average of seven consecutive measurement’s are not exceeding the permitted ELV and no measurement exceeds the permitted ELV by 100%.”.

Table 28: TSS discharge 2015. self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values	
0 – 105	247	68%
105 – 210	66	18%
210 – 315	26	7%
315 – 420	8	2%
420 – 525	4	1%
> 525	11	

3.2.2.7 NH_3-N

The ELV for NH_3-N discharge (load) is 600 kg/d. for NH_3-N (concentration) is 450 mg/l. no exceedance has been observed in 2015.

Table 29: NH_3-N discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 120	296	82%	0 – 90	339	94%
120 – 240	49	14%	90 – 180	16	4%
240 – 360	11	3%	180 – 270	4	1%
360 – 480	3	1%	270 – 360	1	0%
480 – 600	3	1%	360 – 450	2	1%
> 600	0	0%	> 450	-	-

3.2.2.8 NO_2-N

The ELV for NO_2-N discharge (load) is 15 kg/d. for NH_3-N (concentration) 2 mg/l. no exceedance has been observed in 2015.

Table 30: NO_2-N discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 3	356	98%	0 – 0.4	161	44%
3 – 6	6	2%	0.4 – 0.8	153	42%
6 – 9	0	0%	0.8 – 1.2	37	10%
9 – 12	0	0%	1.2 – 1.6	9	2%
12 – 15	0	0%	1.6 – 2	2	1%
> 15	0	0%	> 2	-	-

3.2.2.9 NO_3-N

The ELV for NO_3-N discharge (load) is 600 kg/d. for NO_3-N (concentration) 600 mg/l. two exceedances have been observed in 2015 – 710 kg/d (01.01.2015) and 616 kg/d (25.09.2015).

Table 31: NO_3-N discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 120	183	51%	0 – 120	337	93%
120 – 240	149	41%	120 – 240	19	5%
240 – 360	19	5%	240 – 360	4	1%
360 – 480	8	2%	360 – 480	1	0%
480 – 600	1	0%	480 – 600	1	0%
> 600	2	1%	> 600	-	-

3.2.2.10 PO_4

The ELV for PO_4 discharge (load) is 193 kg/d. for PO_4 (concentration) 550 mg/l. four exceedances have been observed in 2015. The PO_4 emissions on July 2nd 2015 (634 kg/d) and October 23rd 2015 (598 kg/d) are not complying with the ELV. The increased emissions are due to a complete shut-down of the plant (02.07.2015) and a malfunctioning of the limewash doser (23.10.2015). The exceedances on July 3rd 2015 and September 25th 2015 are complying with the ELV due to the “4 out of 5” rule (§4.(2)Z1; 2/8/6/3/5 Anorganische Düngemittel).

§4.(2)Z1; 2/8/6/3/5 Anorganische Düngemittel: “ A measurement is complying if four out of five consecutive below or equal to the permitted ELV and one measurement is not exceeding the ELV by 50%.”

Table 32: PO_4 discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 38.6	235	65%	0 – 110	356	98%
38.6 – 77.2	100	28%	110 – 220	4	1%
77.2 – 115.8	17	5%	220 – 330	1	0%
115.8 – 154.4	4	1%	330 – 440	0	0%
154.4 – 193	2	1%	440 – 550	1	0%
> 193	4	1%	> 550	-	-

3.2.2.11 F

The ELV for fluorine discharge (load) is 105 kg/d. for fluorine (concentration) 60 mg/l. four exceedances (load) have been observed in 2015.Due to the “4 out of 5” rule (§4.(2)Z1; 2/8/6/3/5 Anorganische Düngemittel) one of the four exceedances (load) is not complying with the permitted ELV – 174 kg/d (30.12.2015).

§4.(2)Z1; 2/8/6/3/5 Anorganische Düngemittel: “ A measurement is complying if four out of five consecutive below or equal to the permitted ELV and one measurement is not exceeding the ELV by 50%.”

Table 33: Fluorine discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 21	51	14%	0 – 12	149	41%
21 – 42	240	66%	12 – 24	187	52%
42 – 63	55	15%	24 – 36	19	5%
63 – 84	8	2%	36 – 48	6	2%
84 – 105	4	1%	48 – 60	1	0%
> 105	4	1%	> 60	-	-

3.2.2.12 Cd

The ELV for Cadmium discharge (load) is 21 g/d. for Cadmium discharge (concentration) 1 µg/l. no exceedance has been observed in 2015.

Table 34: Cadmium discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[g/d]	No. of values		[µg/l]	No. of values	
0 – 4.2	365	100%	0 – 0.2	1	8%
4.2 – 8.4	0	0%	0.2 – 0.4	9	69%
8.4 – 12.6	0	0%	0.4 – 0.6	2	15%
12.6 – 16.8	0	0%	0.6 – 0.8	1	8%
16.8 – 21	0	0%	0.8 – 1	0	0%
> 21	0	0%	> 1	-	-

3.2.2.13 Hg

The ELV for Mercury discharge (load) is 25 g/d. for Mercury discharge (concentration) 0.5 µg/l. no exceedance has been observed in 2015.

Table 35: Cadmium discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[g/d]	No. of values		[µg/l]	No. of values	
0 – 5	365	100%	0 – 0.1	12	92%
5 – 10	0	0%	0.1 – 0.2	1	8%
10 – 15	0	0%	0.2 – 0.3	0	0%
15 – 20	0	0%	0.3 – 0.4	0	0%
20 – 25	0	0%	0.4 – 0.5	0	0%
> 25	0	0%	> 0.5	-	-

3.2.2.14 Zn

The ELV for Zinc discharge (load) is 200 g/d. for Zinc discharge (concentration) 60 µg/l. no exceedance has been observed in 2015.

Table 36: Zinc discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[g/d]	No. of values		[µg/l]	No. of values	
0 – 40	76	21%	0 – 12	1	8%
40 – 80	196	54%	12 – 24	4	31%
80 – 120	38	10%	24 – 36	5	38%
120 – 160	53	15%	36 – 48	1	8%
160 – 200	2	1%	48 – 60	2	15%
> 200	0	0%	> 60	-	-

3.2.2.15 COD

The ELV for COD discharge (load) is 210 kg/d. for COD discharge (concentration) 20 mg/l. no exceedance has been observed in 2015.

Table 37: COD discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 42	365	100%	0 – 4	0	0%
42 – 84	0	0%	4 – 8	6	46%
84 – 126	0	0%	8 – 12	6	46%
126 – 168	0	0%	12 – 16	1	8%
168 – 210	0	0%	16 – 20	0	0%
> 210	0	0%	> 20	-	-

3.2.2.16 K_2O

Furthermore, K_2O is monitored. Emission values are displayed in Table 38.

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 24	350	97%	0 – 24	355	98%
24 – 48	6	2%	24 – 48	5	1%
48 – 72	2	1%	48 – 72	0	0%
72 – 96	3	1%	72 – 96	0	0%
96 – 120	1	0%	96 – 120	2	1%
> 120	0	0%	> 120	-	-

Table 38: Potassium Oxide discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

3.2.2.17 SO_4

Furthermore, SO_4 is monitored. Emission values are displayed in Table 39.

[kg/d]	No. of values		[mg/l]	No. of values	
0 – 70	122	33%	0 – 20	0	0%
70 – 140	180	49%	20 – 40	8	62%
140 – 210	32	9%	40 – 60	3	23%
210 – 280	24	7%	60 – 80	0	0%
280 – 350	7	2%	80 – 100	2	15%
> 350	0	0%	> 100	-	-

Table 39: Sulfate discharge 2015 (load & concentration). self-monitoring. (Source: Operator Information 2016)

3.2.3 Ammonium nitrate and calcium ammonium nitrate

3.2.3.1 AN production – pressure neutralization plant

Wastewater from the AN production passes pressure neutralisation before being discharged into the river Danube. Table 40 compares the wastewater emissions of the AN production (2015; self-monitoring) with the emission limit values set by permit. The emission limit value for the daily waste water volume load is 840 m³/d, for total nitrogen load 108 kg/d. As total nitrogen is not regulated by the wastewater ordinance for inorganic fertilizer a comparison with the ordinance has been left out in Table 40. Table 41 presents a detailed analysis of the wastewater emissions.

Table 40: Wastewater emissions (self-monitoring, 2015), ELV permit. (Source: Operator Information 2016)

AN production self-monitoring 2015						
Parameter	**Unit**	**Daily min.**	**Daily max.**	**Annual average**	**ELV permit**	**Number of samples**
Q	m³/d	0	575	228	840	365
Total N	mg/l	0	440	41		365
Total N load	kg/d	0	89	10	108	365

Table 41: Total nitrogen discharge (concentration and load) and waste water volume in 2015. (Source: Operator Information 2016)

Waste water volume		**Total nitrogen**			
[m³/d]	**No. of values**	**[mg/L]**	**No. of values**	**[kg/d]**	**No. of values**
0 – 100	25	0 – 100	348	0 – 20	332
100 – 200	114	100 – 200	13	20 – 40	24
200 – 300	167	200 – 300	2	40 – 60	6
300 – 400	48	300 – 400	0	60 – 80	2
400 – 500	7	400 – 500	2	80 – 100	1
500 – 600	4				

3.2.3.2 AN production – prilling tower

Cooling water from the prilling tower is discharged into the river Danube. The daily cooling water usage for the prilling tower is given in Table 42. Permitted is a maximum temperature of 30 °C and a maximum flow of 6,000 m³/d. Wastewater from cooling systems is regulated by the general wastewater ordinance (2/7/1 Allgemeine Abwasseremissionsverordnung) and not regulated by the specific wastewater ordinance for inorganic fertilizers. Due to the “4 out of 5” rule the wastewater temperature is complying with the permitted ELV (general wastewater ordinance, §7.(2)Z2, 2/7/1 AAEV).

Table 42: Temperature and daily volume of cooling water used for prilling. (Source: Operator Information 2016)

Daily volume		**Daily average temperature**		**Daily maximum temperature**	
[m³/d]	**No. of values**	**[°C]**	**No. of values**	**[°C]**	**No. of values**
< 500	128	< 5	1	< 5	1
500 – 1,000	50	5 – 10	53	5 – 10	39
1,000 – 2,000	62	10 – 15	88	10 – 15	52
2,000 – 3,000	46	15 – 20	94	15 – 20	75
3,000 – 4,000	46	20 – 25	101	20 – 25	119
4,000 – 5,000	25	25 – 30	24	25 – 30	52
5,000 – 6,000	8	30 – 35	4	30 – 35	22
				35 – 40	4

3.2.3.3 CAN production

Cooling water from the CAN production is discharged into the river Danube. The daily cooling water usage in the CAN production is given in Table 43. Permitted are a maximum temperature of 30 °C and a maximum flow of 24.000 m³/d. Wastewater from cooling systems is regulated by the general wastewater ordinance (2/7/1 Allgemeine Abwasseremissionsverordnung) and not regulated by the specific wastewater ordinance for inorganic fertilizers. Due to the “4 out of 5” rule the wastewater temperature is complying with the permitted ELV (general wastewater ordinance, §7.(2)Z2, 2/7/1 AAEV). The permitted wastewater quantity has been exceeded 4 times in 2015 (self-monitoring).

Combined daily volume		Temperature of line 1 and 2		
[m³/d]	No. of values	[°C]	No. of values	No. of values
< 5,000	23	< 20	4	3
5,000 – 10,000	135	20 – 24	55	143
10,000 – 15,000	111	24 – 28	241	162
15,000 – 20,000	55	28 – 32	65	41
20,000 – 25,000	37	32 – 36	0	16
25,000 – 30,000	4		0	0

Table 43: Usage of cooling water and temperature in 2015. (Source: Operator Information 2016)

Details of the usage of cooling water for cooling the finished product are given in Table 44.

	Emission limit value	Maximum value measured
Cooling water per hour	300 m³/h	273 m³/h
Cooling water per week	50,400 m³/weak	44,455 m³/week
Cooling water per year	900,000 m³/a	813,000 m³/a
Temperature (hourly average)	30 °C	< 30 °C

Table 44: Usage of cooling water and temperature in 2015 for plate cooler. (Source: Operator Information 2016)

3.2.4 Ammonia production

Wastewater from the ammonia production is treated via stripping in order to reduce the NH_3 content before being discharge into the river Danube. The thereof gained NH_3 (gaseous) is reused in the process. Wastewater from the ammonia production is regulated by the wastewater ordinance on technical gases (2/8/6/3/9 Technische Gase).

3.2.5 External-monitoring

Treated process wastewater and cooling water is collected in the cooling water sewer (Kühlwasserkanal) before being discharged into the river Danube. External-monitoring of the cooling water sewer has been conducted on October 20th 2016. Table 45 presents the measured emission values, the applied methods and the emission limit values defined by permit (Wa-1177/5-1978/Kre; Wa-1460/6-1979/Re; Wa-310/8-1985/Spe).

Table 45: External-monitoring of the cooling water sewer (20.10.2016). (Source: Operator Information 2016)

External-monitoring of the cooling water sewer					
Parameter	**Unit**	**External-monitoring 29.09.2015**	**External-monitoring 20.10.2016**	**ELV permit**	**Method**
Q	m³/d	22,000	26,047	35,500	
T	°C	26.3	25.4	30	DIN 38404-4
Electric conductivity	µS/cm	396	440	800	DIN EN 27888
TSS	mg/l	26.8	25.1	100	ÖNORM M 6274
pH		8.1	8	6.5 – 8.5	DIN 38404-5
NO_3	mg/l	11.7	10.9	60	DIN EN ISO 10304-1
NO_3 load	kg/h	257	283	1500	calculated
NO_2	mg/l	0.18	0.42	5	DIN EIN 26777
NO_2 load	kg/h	4	10.9	125	calculated
NH_4-N	mg/l	0.06	0.08	30	DIN EN ISO 14911
NH_4-N load	kg/h	1.32	2.08	750	calculated
F	mg/l	0.22	0.2	5	DIN 38405-4
F load	kg/h	4.84	5.21	125	calculated
PO_4	mg/l	0.036	0.039	10	DIN EN ISO 11885
PO_4 load	kg/h	0.8	1.02	250	calculated
Cu	µg/l	2.8	3.5	20	DIN EN ISO 11885
Ni	µg/l	< 1	1	20	DIN EN ISO 11885
Cr	µg/l	1.0	< 1.0	20	DIN EN ISO 11885
Zn	mg/l	0.005	< 0.005		DIN EN ISO 11885
Co	µg/l	< 1	< 1		DIN EN ISO 11885
Mn	mg/l	< 0.005	< 0.005		DIN EN ISO 11885
Hg	µg/l	< 1	< 1	10	DIN EN ISO 11885
Cd	µg/l	< 0.5	< 0.5	10	DIN EN ISO 11885
Pb	µg/l	2.7	2.9	10	DIN EN ISO 11885
CN	mg/l	< 0.01	< 0.01	0.01	DIN 38405-13

External-monitoring of the cooling water sewer

Parameter	Unit	External-monitoring 29.09.2015	External-monitoring 20.10.2016	ELV permit	Method
Lipids	mg/l	10	< 10	20	DIN 38409-17
Cl	mg/l	19.0	19.3		DIN EN ISO 10304-1
SO_4	mg/l	32.1	28.6		DIN EN ISO 10304-1
COD	mg/l	16.9	16		DIN 38409-43
TOC	mg/l	4.0	4.9		DIN EN 1484
BOD_5	mg/l	2.6	2.8		DIN 38409-52
AOX	µg/l	41	58		DIN 38414-17
Na	mg/l	21.0	14.8		DIN EN ISO 11885
K	mg/l	2.7	2.5		DIN EN ISO 11885
Ca	mg/l	55.3	56.4		DIN EN ISO 11885
Mg	mg/l	14.1	14.8		DIN EN ISO 11885

4 REFERENCES

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