

STATE OF THE ART IN THE INORGANIC CHEMICAL INDUSTRY

1 OVERVIEW

The aim of the report is to illustrate the level of environmental protection in the Austrian inorganic chemistry industry. Based on the assessment of applied techniques and the associated emission values, best available techniques for certain products and/or processes are described.

Aim of the study

The report was prepared to support the drafting of the BREF document on “Common Waste Gas Treatment in the Chemical Sector”. Therefore, data and information from installations under the regime of Industrial Emissions Directive IED, No 2010/75/EU, Annex I, activity 4.2 and 4.3 were analysed.

Content of the study

The Austrian inorganic chemical industry is a heterogeneous industrial sector regarding products, applied processes and the size of installations. A representative sample of data and information was collected to draw conclusions for the industry sector.

Depending on the product and the process used, different environmental parameters and emissions are relevant. Important environmental parameters are emissions to air and water, energy demand and usage, noise and waste generation. Emissions to air and water are often linked together, since several air emissions reduction measures are wet processes and transfer air emissions into water.

Relevant parameters for emissions to air are:

Relevant emission parameters to air

- Dust, NO_x, SO_x and CO from incineration;
- Dust when producing and/or handling solids including metals and metal oxides;
- SO₂ when using and/or producing sulphur containing chemicals;
- NO_x, N₂O and NH₃ when using and/or producing nitrogen containing chemicals;
- NH₃ when using NO_x abatement techniques (SCR and SNCR);
- Halogens and hydrogen halides when used in the process;
- Aerosols;
- Odour (sulphur compounds, etc.);
- Other parameters related to specific production processes and products, when used in the process or likely to be formed.

Wastewater emissions occur mainly due to wet process routes or waste gas treatments. Relevant parameters for emissions to water in dependence of the production process and the product manufactured are:

Relevant emission parameters to water

- Temperature, pH, TSS, settleable substances, metals (Cd, Hg, Zn), NH₄-N, total P, fluoride, nitrite, COD, TOC, BSB and AOX (inorganic fertilizer production).
- Potassium, COD and TOC (ammonia production).

- $\text{NH}_4\text{-N}$, total N and COD (urea production).
- Temperature, pH, TSS, aluminium, COD and total hydrocarbons (precipitated calcium carbonate)
- pH and metals (Pb, Al, As, Cd, Zn) (lead oxide production)

Furthermore, waste generation and waste disposal and energy consumption have to be considered.

The following Austrian inorganic chemistry plants were described.

2 REFERENCE PLANTS IN AUSTRIA

Sulphuric acid

In Austria sulphuric acid is produced on three sites and five installations are in operation. To produce sulphuric acid, sulphur or sulphur containing gases (e.g. CS_2 , H_2S) are incinerated to obtain SO_2 . SO_2 is oxidized by several layers of a catalyst to SO_3 which is absorbed resulting in sulphuric acid. The Austrian installations use different sulphur sources namely liquid sulphur and H_2S and/or CS_2 gases containing. The main environmental relevant emissions are SO_2 , SO_3 and aerosol (H_2SO_4) emissions to air. NO_x emissions are of low concern, when the combustion temperature is low enough to avoid thermal NO_x .

SO_2 emissions are reduced by optimising the production process and therefore the conversion rate, which ranges from 99.7% up to 99.9% (double contact process). The single contact process achieves significantly lower conversion rates from 99.0-99.5%.

Without further treatment SO_2 emissions are between 200 and 750 mg/Nm^3 ¹. One plant using a H_2O_2 scrubber achieves SO_2 emissions to air as low as 120 to 160 mg/Nm^3 ¹.

NO_x emissions were measured at one plant and ranged between 31 – 131 mg/Nm^3 ¹.

Aerosols containing SO_3 can be reduced with candle filters. The SO_3 emissions of Austrian sulphuric acid plants are between 7 and 51 mg/Nm^3 ¹.

No wastewater arises from the sulphuric acid production.

Fertilizer

Two plants in Austria produce fertilizers, one of them also producing ammonia, urea and nitric acid. Depending on the type of fertilizer different processes are used. In the first step usually inorganic phosphates react with sulphuric or nitric acid, respectively. In this process and in the following conversion processes the main environmental emissions are dust, NO_x , NH_3 , HCl and HF. Significant dust emissions originate from storage and granulation. NO_x emissions are only relevant when nitric acid is used for digesting the phosphate rock.

Scrubbers are commonly used to reduce dust, NO_x , NH_3 , HCl and HF. Scrubber liquids can be recycled into the production process. Usual emission levels achievable with scrubbers are less than 40 mg/Nm^3 ¹ dust, 140 to 400 mg/Nm^3 ¹ of NO_x , less than 30 mg/Nm^3 ¹ ammonia, less than 8 mg/Nm^3 of HCl and less

¹ At standard conditions (1,013.25 mbar, 0 °C), dry air, without startup/shutdown

than 5 mg/Nm^{3 2} of HF. Bag filters are usually used for dedusting the off-gasses containing only dry dust from e.g. storage and emissions are below 10 mg/Nm^{3 2}.

The use of scrubbers for cleaning off gases generates wastewater. Since main pollutants in the wastewater are substances used in fertilizers, the wastewater can often be reused in the production process. Relevant emission parameters to water are: temperature, pH, TSS, settleable substances, metals (Cd, Hg, Zn), NH₄-N, total P, fluoride, nitrite, COD, TOC, BSB and AOX (inorganic fertilizer production).

Besides fertilizers, one plant produces several chemicals along the nitrogen chain too: ammonia, urea and nitric acid. The main pollutants from ammonia production are NO_x, NH₃, CH₄ and CO. Nitrogen oxides from flue gas from reformer are in the range from 125 to 150 mg/Nm^{3 3}. Ammonia emissions are below 10 mg/Nm^{3 3} and CO emissions from the steam reformer are up to 2.3 mg/Nm^{3 3}.

Ammonia

Wastewater from the ammonia production is treated via stripping in order to reduce the NH₃ content before being discharged and thereof gained NH₃ is reused in the process. Relevant emission parameters to water are: Potassium, COD and TOC.

The main pollutants from the production of nitric acid are nitrogen oxides (NO_x and N₂O) and ammonia from tail gas treatment. N₂O is catalytically decomposed and NO_x is catalytically reduced with ammonia.

Nitric acid

Very low NO_x (below 15 mg/Nm^{3 2}) and N₂O (18 to 55 mg/Nm^{3 2}) emissions are achievable using an EnviNOx ® technology. In this case ammonia slip is up to 6 mg/Nm^{3 2}. The applicability of the EnviNOx ® technology depends on the temperature and pressure used in the process (e.g. M/H-process).

When using a combination of intermediate catalyst for N₂O reduction (secondary measure) and a SCR system for NO_x reduction (tertiary measure), emissions of NO_x range from 100 to 130 mg/Nm^{3 2} and emissions of N₂O range from 90 to 240 mg/Nm^{3 2}. The ammonia slip is in this case below 3 mg/Nm^{3 2}.

No wastewater arises from the nitric acid production.

Dust and NH₃ emissions from urea production are reduced by acidic wet scrubbers and range from 2 to 30 mg/Nm^{3 1} and from 5 to 30 mg/Nm^{3 1}, respectively. Dust emission from handling solids (e.g. bagging) are reduced with bag filters and are below 5 mg/Nm^{3 2}.

Urea

Wastewater from the urea production is, together with other NH₃ contaminated process wastewaters, treated via stripping. The thereof gained NH₃ (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 CO₂ before being discharged. Relevant emission parameters to water are: NH₄-N, total N and COD.

² At standard conditions (1,013.25 mbar, 0 °C) and dry air, without startup/shutdown.

³ At standard conditions (1,013.25 mbar, 0 °C), dry air and reference oxygen content of 3%, without startup/shutdown.

Calcium chloride Calcium chloride, mostly used for defrosting, is produced by reacting calcium carbonate with hydrochloric acid. Environmental relevant pollutant is HCl which is reduced by scrubbers. Average emission during one batch, including refilling of the HCl tank, is below 8 mg/Nm³.

No wastewater emissions from the process occur. Process water from the scrubber is reused in production process. Relevant emission parameters to water are: temperature, pH, TSS, aluminium, COD and total hydrocarbons.

Metal oxides Austrian plants produce several metal compounds. Zinc oxide is melted in a first step and afterwards vaporized. Zinc vapour is reacted with air and the product is precipitated. Lead oxide is produced by melting lead and blowing air through the liquid lead. For both products the most relevant air emission is metal containing dust.

Bag filters are used to meet the emission limit value of 20 mg/Nm³ for zinc oxide production. With new filter media bag filters for the zinc oxide production achieve emissions below 5 mg/Nm³. Due to high temperatures the bag filters wear out despite the specially tailored material and the emissions rise to the emission limit value.

HEPA⁴ filters are state of the art for lead oxide production due to the much higher toxicity of lead. Half hourly averages in the lead oxide production using HEPA filters are below 0.1 mg/Nm³ and three hours averages are about one order of magnitude lower.

Accruing wastewater from the production of lead oxide is pre-treated (physical-chemical treatment) before being discharged into the public sewer system. Required cooling water is reused in the process. Relevant emission parameters to water are: pH and metals (Pb, Al, As, Cd, Zn).

Metal sulphides Metal sulphides are used as additives in a broad range of applications. Production is carried out in closed reactors. Metals or metal salts are heated in the reactor together with sulphur containing reactants. Relevant pollutants are dust and SO₂. The exhaust gas from the reactors is pre-cleaned in a fabric filter and subsequently cleaned together with other waste air streams in HEPA filters. The filter producer assures the emissions to be below 2 mg/Nm³.

Precipitated calcium carbonate The main application of PCC is as filler material in the paper industry. Compared to ground calcium carbonate PCC is more expensive but can be optimised in regard to purity, morphology, crystallite size and surface area.

In two steps quick lime (CaO) reacts to PCC. In the first step quick lime is slaked and reacts to calcium hydroxide (Ca(OH)₂). In a subsequent batch process carbon dioxide reacts with the slaked lime to PCC. The slurry is concentrated by a centrifuge and evaporator to adjust the solid content to customer needs and additives are added if needed.

The production of PCC in the reference installation causes no emissions to air as only aqueous slurries are manufactured. Process water is treated by precipitation, flocculation and filtration. Cooling and splashing water is treated by carbon dioxide to adjust the pH and subsequent flocculation and filtration. Separat-

⁴ HEPA: High efficiency particulate air

ed calcium carbonate from the wastewater treatment is either reused in the production or disposed in a cement plant. The treated wastewater stream is directly discharged or reused in the production process.

3 AIR EMISSIONS

3.1 Monitoring and Reference Conditions

Emissions are listed stating the measurement period as mass concentrations of air polluting substances in milligrams per standard cubic metre (mg/Nm^3), referring to the exhaust air volume under standard conditions (273.15 K, 1,013.25 hPa) after deduction of a moisture content of water vapour. The corresponding reference oxygen content is indicated, when the exhaust air arise from an incineration process. Besides the emission parameters following operational parameters are usually recorded: temperature, flow rate, moisture content, pressure and oxygen content. Furthermore several production parameters (e.g. production rate, type of product produced, malfunctions) are usually recorded.

Reference conditions

As for the monitoring periods, half-hour mean values are given for periodic measurements and half-hour and/or daily mean values for continuous monitoring. In the case of periodic measurement at least three values should be obtained in each period.

Monitoring

Emission monitoring is done according to standards. Standards are specified preferably in ordinances or in permits. A change of the standard may result in different emission levels measured. The impact of a new standard applied should be discussed with the permitting authority.

Standards

The amount and type of parameters measured depends on the production process, as well as the decision between periodic or continuous measurement (cf. Table 3).

Table 1: Emission limit values for air emissions (Source: Operator information 2015 – 2016)

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Sulphuric acid			SO₂ <u>INSTALLATION 1:</u> ELV: 1,030 mg/Nm ³ ⁵ <u>INSTALLATION 2:</u> HHA: 1,000 mg/Nm ³ DA: 150 kg/d <u>INSTALLATION 3:</u> DA: 700 mg/Nm ³ <u>INSTALLATION 4:</u> DA: 625 mg/Nm ³ <u>INSTALLATION 5:</u> DA: 200 mg/Nm ³ (H ₂ O ₂ scrubber) SO₃ <u>INSTALLATION 1:</u> 0.4 kg/t H ₂ SO ₄ ⁵ <u>INSTALLATION 2:</u> HHA: 60 mg/Nm ³			

⁵ No averaging period given.

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Fertilizer	<p><u>INSTALLATION 1:</u> HHA: 50⁶ (scrubber)</p> <p><u>INSTALLATION 2:</u> CAN⁷ production: HHA: 25 (scrubber)</p> <p>CAN⁷ cooling drum: HHA: 20 (cyclone)</p> <p>AN⁸ prilling: HHA: 25 (scrubber)</p> <p>storage & building dedusting: HHA: 10 (bag filter)</p>	<p>NO_x</p> <p><u>INSTALLATION 1:</u> direct dryer: HHA: 250⁶</p> <p><u>INSTALLATION 2:</u> digestion & CNTH⁹ conversion: HHA: 400 (scrubber)</p>		<p><u>INSTALLATION 1:</u> granulation: HHA: 20 (scrubber)</p> <p><u>INSTALLATION 2:</u> CAN⁷ production: HHA: 30 (scrubber)</p> <p>CAN⁷ cooling drum: HHA: 30</p> <p>AN⁸ prilling: HHA: 20 (scrubber)</p>	<p>HCl</p> <p><u>INSTALLATION 1</u> granulation & den: HHA: 30 (scrubber)</p> <p>HF</p> <p><u>INSTALLATION 1:</u> granulation & den: HHA: 5⁶ (scrubber)</p> <p><u>INSTALLATION 2:</u> digestion & CNTH⁹ conversion: HHA: 5 (scrubber)</p> <p>CAN⁷ production: HHA: 1 (scrubber)</p>	<p>CO</p> <p><u>INSTALLATION 1:</u> direct dryer: HHA: 100⁶</p> <p>TOC</p> <p><u>INSTALLATION 1:</u> direct dryer: HHA: 50⁶</p>
Ammonia ¹⁰		<p>NO_x</p> <p>ELV: 150¹¹</p>		<p>ELV: 10¹¹ (purge gas treatment)</p>		<p>CO</p> <p>ELV: 100¹¹</p>

⁶ Reference oxygen content: 13%

⁷ CAN: calcium ammonium nitrate

⁸ AN: ammonium nitrate

⁹ CNTH: calcium nitrate tetrahydrate

¹⁰ Reference oxygen content: 3%

¹¹ ELV is met, when: 1) all daily averages are below the emission limit value and 2) all half hourly averages are below twice the emission limit value and 3) 97% of the half hourly averages are below 1.2 times the emission limit value.

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Nitric acid		<p>NO_x</p> <p><u>INSTALLATION 1:</u> ELV: 280¹² (SCR)</p> <p><u>INSTALLATION 2:</u> ELV: 120¹² (EnviNOx)</p> <p>N₂O</p> <p><u>INSTALLATION 1</u> ELV: 600¹² (intermediate catalyst)</p> <p><u>INSTALLATION 2</u> ELV: 600¹² (EnviNOx)</p>		<p><u>INSTALLATION 1&2:</u> HHA: 10</p>		
Urea	<p><i>prilling:</i> HHA: 20 (coarse prills) HHA: 30 (fine prills) (scrubber)</p> <p><i>bagging:</i> HHA: 20 (bag filter)</p>			<p><i>prilling:</i> HHA: 30 (scrubber)</p> <p><i>bagging:</i> HHA: 30</p>		
Calcium chloride					<p>HCl 30¹³ (scrubber)</p>	
Zinc oxide	HHA: 20 (high temperature fabric filter)					
Lead oxide	HHA: 0.05 – 0.1 (HEPA ¹⁴ filter)					

¹² ELV is met, when: 1) all daily averages are below the emission limit value and 2) all half hourly averages are below twice the emission limit value and 3) 97% of the half hourly averages are below 1.2 times the emission limit value.

¹³ No averaging period prescribed.

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Metal sulphides			SO ₂ DA: 100 ¹⁵ ; 150 ¹⁶ (2-stage lime scrubber)			

All values are in mg/Nm³ at 0 °C, 1,013.25 mbar and dry air. Reference oxygen content is given, if conversion to reference oxygen content is done.

HHA: half hourly average; 2h-AVG: two hours average; DA: daily average; ELV: emission limit value

¹⁴ HEPA: High efficiency particulate air

¹⁵ dry gas, standard conditions with 3°C, no reference oxygen content (O₂ as obtained)

¹⁶ dry gas, standard conditions, no reference oxygen content (O₂ as obtained).

Table 2: BAT-AELs according to Austrian plants –measured values (data from 2013, 2014, 2015, 2016 depending on monitoring reports).

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Sulphuric acid		NO_x <u>INSTALLATION 2:</u> HHA: 31 – 131 ¹⁷	SO₂ <u>INSTALLATION 1:</u> 2h-AVG: 300 – 700 Input ¹⁸ : 9.5 vol% CR: 99.82 – 99.85% <u>INSTALLATION 2:</u> HHA: 200 – 650 ¹⁹ Input ¹⁸ : 2 vol% CR: 99.0 – 99.5% <u>INSTALLATION 3:</u> DA: 512 – 700 *) Input ¹⁸ : 10 – 11 vol% CR: 99.9% <u>INSTALLATION 4:</u> DA: 457 – 625 *) Input ¹⁸ : 7 – 8 vol% CR: 99.8% <u>INSTALLATION 5:</u> DA: 120 – 160 (H ₂ O ₂ scrubber) Input ¹⁸ : n/a CR: 99.9% SO₃ <u>INSTALLATION 2:</u> HHA: 12 – 49 <u>INSTALLATION 3:</u> 4h-AVG: 9.1 – 22.4 <u>INSTALLATION 4:</u> 4h-AVG: 12.2 – 26.3 <u>INSTALLATION 5:</u> 4h-AVG: 7.6 – 50.6			

¹⁷ Oxygen content between 7.5 and 9.5%.¹⁸ SO₂ concentration before entering the converter.

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Fertilizer	<p><u>INSTALLATION 1:</u> <i>digestion:</i> HHA: < 0.5 – 6.6 (scrubber)</p> <p><i>granulation:</i> HHA: 14 – 36 (scrubber)</p> <p><i>granulation:</i> HHA: 0.3 – 2.7 (scrubber)</p> <p><i>storage & mill:</i> HHA: < 0.5 – 6.4 (bag filter)</p> <p><u>INSTALLATION 2:</u> <i>CAN²⁰ production:</i> HHA: <25^{21 *} (scrubber)</p> <p><i>CAN²⁰ cooling drum:</i> HHA: <5 (cyclone)</p> <p><i>AN²² prilling:</i> HHA: <5 (scrubber)</p> <p><i>storage & building dedusting:</i> HHA: <1 – 8.7 (bag filter)</p>	<p>NO_x</p> <p><u>INSTALLATION 2:</u> <i>digestion & CNTH²³ conversion:</i> 140 – 400^{21 *} (scrubber)</p>		<p><u>INSTALLATION 1:</u> <i>granulation:</i> HHA: 0.3 – 3.4 (scrubber)</p> <p><u>INSTALLATION 2:</u> <i>CAN²⁰ production:</i> HHA: <10 – 30 *) (scrubber)</p> <p><i>CAN²⁰ cooling drum:</i> HHA: <7</p> <p><i>AN²² prilling:</i> HHA: 2 – 9 (scrubber)</p>	<p>HCl</p> <p><u>INSTALLATION 1:</u> <i>digestion:</i> HHA: 6.4 – 7.4 (scrubber)</p> <p><i>granulation:</i> HHA: < 1 – 1.8 (scrubber)</p> <p><i>granulation:</i> HHA: < 1 – 1.2 (scrubber)</p> <p>HF</p> <p><u>INSTALLATION 1:</u> <i>digestion:</i> HHA: < 0.6 (scrubber)</p> <p><i>granulation:</i> HHA: < 0.6 (scrubber)</p> <p><i>granulation:</i> HHA: < 0.3 – 2.8 (scrubber)</p> <p><u>INSTALLATION 2:</u> <i>digestion & CNTH²³ conversion:</i> HHA: 0.1 – 4.7 (scrubber)</p> <p><i>CAN²⁰ production:</i> HHA: 0.1 – 0.9 (scrubber)</p>	

¹⁹ 98th percentile of the half hourly averages in 2015: 500 mg/Nm³

²⁰ CAN: calcium ammonium nitrate

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Ammonia ²⁴		NO_x DA: 117 – 150 *)		HHA: < 0.1 – 10 *) (purge gas treatment)		CO DA: 0.0 – 6.7
Nitric acid		NO_x <u>INSTALLATION 1:</u> DA: 101 – 126 ²⁵ (SCR) <u>INSTALLATION 2:</u> DA: <1 – 15 ²⁵ (EnviNO _x) N₂O <u>INSTALLATION 1:</u> DA: 90 – 234 ²⁵ (intermediate catalyst) <u>INSTALLATION 2:</u> DA: 18 – 55 ²⁵ (EnviNO _x)		<u>INSTALLATION 1:</u> HHA: 1 – 3 (SCR) <u>INSTALLATION 2:</u> HHA: 1 – 6 (EnviNO _x)		
Urea	<i>prilling:</i> HHA: 2 – 30 *) (scrubber) <i>bagging:</i> HHA: <5 (bag filter)			<i>prilling:</i> HHA: 5 – 30 *) (scrubber) <i>bagging:</i> HHA: 2 – 10		
Calcium chloride					HCl 8 ²⁶ (scrubber)	

²¹ Some measured and validated emission values of this installation exceeded recently (due to technical problems and/or end of life time) the emission limit values. Emission behaviour is currently optimised to ensure permanent compliance with the emission limit values. Therefore, emission limit values and emission values may be updated after plant revision within the next years.

²² AN: ammonium nitrate

²³ CNTH: calcium nitrate tetrahydrate

²⁴ Reference oxygen content: 3%

²⁵ 5th and 95th percentile of daily averages in 2015

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Zinc oxide	HHA: <0.4 – 5 (new high temperature fabric filter) HHA: 10 – 20 *) (high temperature fabric filter at end of life time)					
Lead oxide	HHA: <0.1 (HEPA ²⁷ filter) 3h-AVG: 0.0090 – 0.0122 (HEPA ²⁷ filter)					
Metal sulphides	<2 (bag filter & HEPA ²⁷ filter)		SO₂ DA: 42.8 – 79.5 (2-stage lime scrubber)			

All values are in mg/Nm³ at 0 °C, 1,013.25 mbar and dry air. Reference oxygen content is given, if conversion to reference oxygen content is done.

HHA: half hourly average; 2h-AVG: two hours average; 3h-AVG: three hours average; 4h-AVG: four hours average; DA: daily average; CR: conversion rate

The values in this table represent measured emission values. Generally, the range displays the highest and lowest obtained values. Nevertheless, when the highest emission values were much higher compared to the entire continuously recorded data situation and therefore do not represent the general emission behaviour, percentiles were used. When indicated that measured values were recorded under OTNOC (other than normal operating conditions; start-up, shut-down and malfunctions), these values were not taken into account.

Measurement uncertainties were not subtracted from the measured values in table 2. In general measured values are reported to the competent authorities. To assess compliance with the emission limit value, measurement uncertainty may be deducted from the actual measured emission value (validated values).

In case of measured values higher than the emission limit value, the emission limit value was used as state of the art. These values are indicated with an (*) and measurement uncertainties were neither added nor subtracted.

²⁶ Average during one batch.

²⁷ HEPA: High efficiency particulate air

Table 3: Monitoring of air emissions. (Source: Operator information 2015 – 2016)

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Sulphuric acid		NO _x <u>INSTALLATION 2:</u> annually	SO ₂ <u>INSTALLATION 1 – 5:</u> continuously SO ₃ <u>INSTALLATION 2:</u> monthly <u>INSTALLATION 3&4:</u> four times a year <u>INSTALLATION 5:</u> monthly			

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Fertilizer	<p><u>INSTALLATION 1:</u> annually ÖNORM M 5861</p> <p><u>INSTALLATION 2:</u> CAN²⁸ production: four times a year EN 13284-1 ÖNORM M 5861-1 VDI 2066 Sheet 1</p> <p>CAN²⁸ Fehler! Textmarke nicht definiert. cooling drum: twice a year EN 13284-1 ÖNORM M 5861-1 VDI 2066 Sheet 1</p> <p>AN²⁹ prilling: twice a year</p> <p>storage dedusting: annually EN 13284-1 ÖNORM M 5861-1 VDI 2066 Sheet 1</p> <p>building dedusting: four times a year EN 13284-1 ÖNORM M 5861-1 VDI 2066 Sheet 1</p>	<p>NO_x</p> <p><u>INSTALLATION 1:</u> annually</p> <p><u>INSTALLATION 2:</u> digestion & CNTH³⁰ conversion: four times a year VDI 2456 EN ISO 10304-1</p>		<p><u>INSTALLATION 1:</u> annually</p> <p><u>INSTALLATION 2:</u> CAN²⁸ Fehler! Textmarke nicht definiert. production: four times a year VDI 3496 Sheet 1 EN ISO 11732</p> <p>CAN²⁸ Fehler! Textmarke nicht definiert. cooling drum: twice a year VDI 3496 Sheet 1 EN ISO 11732</p> <p>AN²⁹ Fehler! Textmarke nicht definiert. prilling: twice a year</p>	<p>HCl</p> <p><u>INSTALLATION 1:</u> annually ÖNORM EN 1911</p> <p>HF</p> <p><u>INSTALLATION 1:</u> annually ÖNORM EN 1911</p> <p><u>INSTALLATION 2:</u> digestion & CNTH³⁰ Fehler! Textmarke nicht definiert. con- version: four times a year VDI 2470 Sheet 1 DIN 38405-4</p> <p>CAN²⁸ Fehler! Textmarke nicht definiert. production: four times a year VDI 2470 Sheet 1 DIN 38405-4</p>	<p>CO</p> <p><u>INSTALLATION 1:</u> annually</p> <p>TOC</p> <p><u>INSTALLATION 1:</u> annually</p>
Ammonia		<p>NO_x</p> <p>continuously³¹</p>		<p>four times a year</p>		<p>CO</p> <p>continuously Fehler! Textmarke nicht definiert.</p>

²⁸ CAN: calcium ammonium nitrate

²⁹ AN: ammonium nitrate

³⁰ CNTH: calcium nitrate tetrahydrate

Product	Dust [mg/Nm ³]	NO _x , N ₂ O [mg/Nm ³]	SO _x [mg/Nm ³]	NH ₃ [mg/Nm ³]	HCl, HF [mg/Nm ³]	Other [mg/Nm ³]
Nitric acid		NO _x <i>INSTALLATION 1&2:</i> continuously <small>Fehler! Textmar- ke nicht definiert.</small>		<i>INSTALLATION 1&2:</i> monthly		
		N ₂ O <i>INSTALLATION 1&2:</i> continuously <small>Fehler! Textmar- ke nicht definiert.</small>				
Urea	<i>prilling:</i> four times a year <i>bagging:</i> twice a year			<i>prilling:</i> four times a year <i>bagging:</i> twice a year		
Calcium chloride					HCl once at acceptance measurement	
Zinc oxide	every three years					
Lead oxide	continuously annually ÖNORM EN 13284-1, VDI 2066-1					
Metal sulphides	continuously		SO ₂ continuously			

All values are in mg/Nm³ at 0 °C, 1,013.25 mbar and dry air. Reference oxygen content is given, if conversion to reference oxygen content is done.

HHA: half hourly average; 2h-AVG: two hours average; 3h-AVG: three hours average; 4h-AVG: four hours average; DA: daily average; CR: conversion rate

³¹ ELV is met, when: 1) all daily averages are below the emission limit value and 2) all half hourly averages are below twice the emission limit value and 3) 97% of the half hourly averages are below 1.2 times the emission limit value.

4 WATER EMISSIONS

4.1 Averaging periods

For the majority of parameters a monitoring regime is implemented that allows an expression of emission parameters as **daily average values**. A daily average value is defined as average over a sampling period of 24 hours taken as a flow proportional unsettled homogenised daily composite sample.

Certain parameters are **continuously measured** (such as Q, T and pH), whereas some parameters are monitored (for analytical reasons) by taking **spot samples** (such as total suspended solids, settleable substances).

All other parameters (e.g. COD, TN_b, ...) are measured as flow proportional unsettled homogenised daily composite samples over a sampling period of 24 hours.

4.2 Monitoring

The monitoring of emissions to water can be performed by the operator.

Self-monitoring

If monitoring is carried out by the operator, external-monitoring has to take place at least once a year. External-monitoring has to be carried out on representative production days.

External-monitoring

Table 4: Wastewater emission levels arising from urea production (self-monitoring) and emission limit values of the Wastewater Emission Ordinance for inorganic fertilizer Annex A for direct discharge.

Parameter	Wastewater Emission Ordinance		Wastewater Emissions
Ammonium (reported as N)	kg/t	0.5	0.029 – 0.46
Total Kjeldahl nitrogen (reported as N)	kg/t		0.07 – 0.9
COD (reported as O ₂)	kg/t	0.5	0.02 – 0.12

Table 5: Wastewater emission levels arising from fertilizer production (installation 1, external-monitoring) and emission limit values of the Wastewater Emission Ordinance for inorganic fertilizer Annex B for indirect discharge.

Parameter		Wastewater Emission Ordinance	Wastewater Emissions
Temperature	°C	35	8.3 – 17.7
Settleable substances	ml/l		0.3
pH		6 – 9.5	7.1 – 7.3
Cadmium (reported as Cd)	mg/l	¹⁾	0.01
Mercury (reported as Hg)	mg/l	²⁾	0.0001
Zinc (reported as Zn)	mg/l	³⁾	0.01 – 0.038
Ammonium (reported as N)	mg/l	⁴⁾	1.2 – 3.6

Parameter		Wastewater Emission Ordinance	Wastewater Emissions
Fluoride (reported as F)	mg/l	⁵⁾	0.1 – 0.6
Nitrite (reported as N)	mg/l		0.024 – 0.033
Total phosphorous (reported as P)	mg/l	⁶⁾	0.6 – 1.7
COD (reported as O ₂)	mg/l		< 15

¹⁾ 0.1 g/t P based on the production capacity and based on the mass of P in the product

²⁾ 0.02 g/t P based on the production capacity and based on the mass of P in the product

³⁾ 2 g/t P based on the production capacity and based on the mass of P in the product

⁴⁾ 2 kg/t P based on the production capacity and based on the mass of P in the product

⁵⁾ 3 kg/t P based on the production capacity and based on the mass of P in the product

⁶⁾ 0.6 kg/t P based on the production capacity and based on the mass of P in the product

Table 6: Wastewater emission levels arising from NPK-fertilizer production (installation 2, internal and external-monitoring) and emission limit values of the Wastewater Emission Ordinance for inorganic fertilizer Annex B for direct discharge.

Parameter		Wastewater Emission Ordinance	NPK-Fertilizer production Self-monitoring	Cooling water & treated process water External-monitoring
Temperature	°C	30	6.6 – 30	25.4 – 26.3
TSS	mg/l		5 – 150 ¹⁾	25.1 – 26.8
pH		6 – 8.5	6 – 8.5	8 – 8.1
Cadmium (reported as Cd)	mg/l	²⁾	0.0001 – 0.0006	0.00005
Mercury (reported as Hg)	mg/l	³⁾	0.0001 – 0.0002	< 0.0001
Zinc (reported as Zn)	mg/l	⁴⁾	0.012 – 0.057	0.005
Ammonium (reported as N)	mg/l	⁵⁾		0.06 – 0.08
Fluoride (reported as F)	mg/l	⁶⁾	1 – 51	0.2
Nitrite (reported as N)	mg/l		0.3 – 1.89	0.18 – 0.42
TOC (reported as C)	mg/l			4 – 4.9
COD (reported as O ₂)	mg/l	⁷⁾	5 – 12	16 – 16.9
BOD ₅ (reported as O ₂)	mg/l			2.6 – 2.8
AOX (reported as Cl)	mg/l			0.041 – 0.058

¹⁾ 150 mg/l corresponds to the 95th percentile. Maximum values in the range of 260 – 1,300 mg/l.

²⁾ 0.1 g/t P based on the production capacity and based on the mass of P in the product

³⁾ 0.02 g/t P based on the production capacity and based on the mass of P in the product

⁴⁾ 2 g/t P based on the production capacity and based on the mass of P in the product

⁵⁾ 2 kg/t P based on the production capacity and based on the mass of P in the product

⁶⁾ 3 kg/t P based on the production capacity and based on the mass of P in the product

⁷⁾ 0.6 kg/t P based on the production capacity and based on the mass of P in the product

Parameter		Wastewater Emission Ordinance	Wastewater Emissions
Temperature	°C	30	15 – 27
TSS	mg/l	100	32 – 38
pH		6.5 – 9.5	8.03 – 8.22
Aluminium (reported as Al)	mg/l	2	0.669 – 2
COD (reported as O ₂)	mg/l	75	22 – 32
Sum of hydro carbons	mg/l	5	0.09 – 0.1
Anionic tensides	mg/l		< 0.1
Non-ionic tensides	mg/l		< 0.1

Table 7:
Wastewater emission levels arising from precipitated calcium carbonate production (external-monitoring) and emission limit values of the Wastewater Emission Ordinance for industrial minerals Annex A for direct discharge.

Parameter		Wastewater Emission Ordinance	Wastewater Emissions
pH		6.5 – 9.5	8.4 – 8.7
Aluminium (reported as Al)	mg/l	¹⁾	0.15 – 10.6
Arsenic (reported as As)	mg/l	0.1	0.03 – 0.1
Lead (reported as Pb)	mg/l	0.5	0.1 – 0.5
Cadmium (reported as Cd)	mg/l	0.1	0.01 – 0.1
Zinc (reported as Zn)	mg/l	1	0.006 – 0.019

¹⁾ Limited by TSS

Table 8:
Wastewater emission levels arising from lead oxide production (external-monitoring) and emission limit values of the Wastewater Emission Ordinance for production of inorganic acids, basis and salts Annex B for indirect discharge.

5 ENERGY

The chemical industry is a major industrial sector in Austria with high energy demand.

Sulphuric acid production is in general an exothermic process. Energy input into the system comes from the chemical energy of the sulphur (elemental or as sulphur containing waste gases) and the electrical energy from the fans.

Depending on the sulphur content the process is not always autotherm which means that in such a case overall more heat is needed than excess heat is produced.

Process waste heat recovered from the combustion gases after the incinerator, the steam superheater after catalyst layers, the heat exchanger and the economizer can be converted to superheated steam. Some heat recovered after the catalyst layer is used to reheat the reaction gas after the intermediate absorber in the intermediate heat exchanger.

Ammonia production requires, even though catalysts are used, high temperature, high pressure and an upstream steam reforming to obtain hydrogen for the synthesis of NH₃. Therefore, it is an energy intensive process.

Relevant environmental parameters for the production of ammonia are the consumption of energy for heating the primary reformer, and the existence of an efficient heat recovery system.

Sulphuric acid production

Ammonia production

Nitric acid production Nitric acid production according to state-of-the-art technology is characterised by a high degree of energy recovery.

Part of the high-pressure steam produced in the waste heat boiler (ammonia oxidation) is used for supply of the compression energy. Excess is exported as product steam. A set of gas/gas heat exchangers transfers energy from the gas leaving the waste heat boiler to the waste gas leaving the absorption column. In dual pressure plants energy is furthermore recovered by expansion of the waste gas to atmosphere using a gas turbine.

Waste heat arising from the compression of secondary air is used in an ammonia super-heater for preheating ammonia, thereby cooling the secondary air. Low level energy of the nitrous gas stream can also be used for preheating primary air and for preheating boiler feedwater.

Urea production Urea is produced by reacting ammonia and carbon dioxide at elevated temperature and pressure. The condensation energy of the high pressure section is recovered for steam production and of the medium pressure section for heat integration.

Fertilizer production Energy for the production of fertilizers is mainly required for grinding of the phosphate rock and for the waste gas scrubbing system.

For the production of calcium ammonium nitrate steam is recovered after the neutralisation of HNO_3 and NH_3 . The steam can be used for concentrating the ammonium nitrate solution in the first evaporation step. Excess steam is used for other heating purposes.

6 WASTE GENERATION

Waste generation and the kind of waste generated are dependent on the production process and the abatement technique used.

Residues which can be recycled in the process are obtained in dedusting from zinc oxide production. Furthermore, calcium carbonate wastes are also reused onsite if possible or otherwise discharged externally into cement plant.

Production waste from fertilizer plants (e.g. dust, particles too big or small) are milled or reused in the granulation process.

Waste from abatement techniques such as gypsum, which is formed due to the use of calcium hydroxide in scrubbers to reduce SO_2 in metal sulphide production, is disposed to a landfill site.

Production process related wastes are spent catalysts for the conversion of SO_2 to SO_3 in the contact tower for the sulphuric acid production. Furthermore, insoluble silicates in the limestone are filtered off and disposed when producing calcium chloride. When producing lead oxide and lead stabilisers contaminated packaging material and lead salts are disposed as hazardous waste.

7 CONCLUSIONS

Emissions to air

- Few pollutants are regulated in the permits or are relevant for the respective process/products.
- Specific processes require specific sets of emission-parameters.
- Emission levels for pollutants are dependent on the process/ abatement technique used and the product manufactured.
- Abatement technologies are often designed and optimised for the specific processes to achieve feasibility for reducing the targeted pollutants. Requirements are determined by the composition of the waste gas stream, e.g. wet gas, corrosiveness, temperature, etc.
- “very good technologies” compared to broadly applied abatement systems, e.g.:
 - Peroxide scrubber for SO₂ (sulphuric acid) when diluted H₂SO₄ with residual H₂O₂ can be used in the production process: 120 – 160 mg/Nm³ ³².
 - EnviNOx ® (nitric acid) for NO_x (tailgas temperature and pressure determines the applicability of technology): 1 – 15 mg/Nm³ compared to 100 – 130 mg/Nm³ and N₂O: 15 – 70 mg/Nm³ compared to 70 – 250 mg/Nm³ ³².
 - HEPA filters (dusts with high environmental impact) <0.01 – <0.1 mg/Nm³ ³³ compared to <5 – 10 mg/Nm³ (bag filter).

Emissions to water

- Amount and kind of pollutants regulated dependent on production process. The range is from zero parameters regulated/monitored (e.g. sulphuric acid, nitric acid) to 3 – 6 parameters (e.g. urea production, lead oxide production) up to more than 10 parameters (e.g. fertilizer production).
- Emission limit values are expressed as concentrations or as product specific loads. However, comparability is low and may cause problems in the permitting/compliance process. Concentrations should be given preference.
- Avoidance of wastewater streams due to recycling into the production process when possible (e.g. fertilizer production, PCC production).

Energy and crossmedia effects

- High degree of energy recovery in energy intensive processes (e.g. ammonia production, urea production) and exothermic reactions (e.g. sulphuric and nitric acid production, ammonium nitrate production)
- Different cross media effects as some processes/products require e.g. wet scrubbing for abating dust emissions. Wastewater can be reused in the process in some processes (e.g. fertilizer production).

³² daily average at standard conditions (1,013.25 mbar, 0 °C), dry air

³³ average over 30 min till 3h at standards conditions (1,013.25 mbar, 0 °C), dry air.

Waste generation

- Different level of waste generation and type of wastes according to the product manufactured and the respective process used.
- Internal recycling into the process when possible (e.g. dust from ZnO production, sludge from PCC wastewater treatment).