

SNAP CODE: 040402

SOURCE ACTIVITY TITLE: PROCESSES IN INORGANIC CHEMICALS INDUSTRIES
Nitric Acid

NOSE CODE: 105.09.11

NFR CODE: 2 B 2

1 ACTIVITIES INCLUDED

This chapter covers emissions released from nitric acid production plants, whereby all process steps are taken into account.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from nitric acid plants to the total emissions in the countries of the CORINAIR90 inventory is given as follows:

Table 1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO ₂	NO _x	NMVOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃
Nitric Acid	040402	-	0.6	0.1	-	0	-	5.4	0.1

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

This activity is not believed to be a significant source of PM_{2.5} (as of December 2006).

3 GENERAL

3.1 Description

For the production of nitric acid, ammonia is oxidised catalytically. Nitrous gases are obtained, which are converted into nitric acid (together with oxygen and water). The following figure shows a flow sheet of a nitric acid plant:

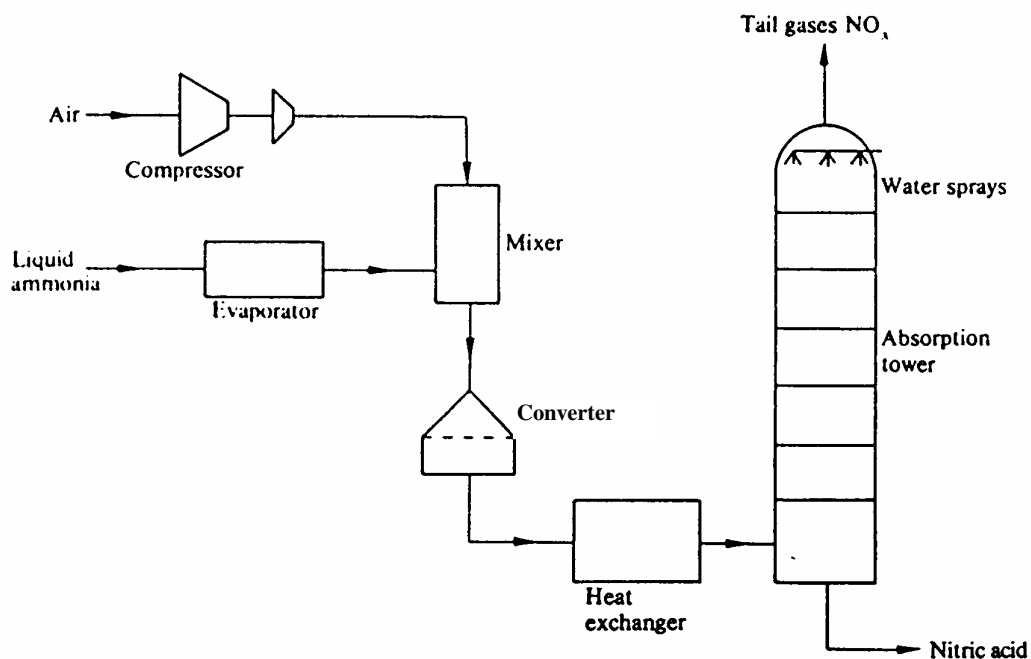


Figure 1: Nitric acid plant (weak acid about 50 wt.-%) - schematic (based on /5/)

For NO_x emissions the relevant process units are the absorption tower and the tail gas cleaning units (e. g. SCR, SNCR). Small amounts of NO_x are also lost for acid concentrating plants.

3.2 Definitions

Highly concentrated acid: nitric acid with a concentration of about 98 wt.-%.
 Weak acid: nitric acid with a concentration of about 50 to 75 -wt.-%.

3.3 Techniques

Nitrogen monoxide (NO) is formed by catalytic oxidation of ammonia with atmospheric oxygen. NO is oxidised to nitrogen dioxide (NO₂) by adding further air. The reaction of NO₂ with water and oxygen forms nitric acid (HNO₃) with a concentration of generally 50 to 75 wt.-% ("weak acid").

For the production of highly concentrated nitric acid (98 wt.-%), first nitrogen dioxide is produced as described above. It is then absorbed in highly concentrated acid, distilled, condensed and finally converted into highly concentrated nitric acid at high pressure by adding a mixture of water and pure oxygen. /cf. 3/

The following production steps should be distinguished /3/:

- Production of nitrogen monoxide:
Ammonia is oxidised with air in the presence of catalysts of platinum-rhodium alloy. The yield of nitrogen monoxide (normally between 95 and 98 % /1/) depends on the reaction conditions (such as pressure and temperature).
- Further treatment of nitric oxides:
Nitrogen monoxide is oxidised to nitrogen dioxide. Nitrogen dioxide is then absorbed and reacts with water to form nitric acid.
- Upgrading of nitric acid.

Plants for the production of nitric acid can be designed as low pressure (< 1.7 bar), medium pressure (1.7 - 6.5 bar) and high pressure (> 8 bar) plants. New plants are only built for pressure ranges above 4 bar.

3.3.1 Weak Nitric Acid Production

Medium pressure plants (1.7 to 6.5 bar) can achieve NO_x contents (see Section 3.4) of 600 to 800 ppm by volume in the exhaust gas. High pressure plants (above 8 bar) can achieve NO_x contents of 200 to 400 ppm by volume in the exhaust gas. /cf. 3/ Taking into account the ammonia combustion as described above, two plant types can be further distinguished:

- single-pressure plant NH₃ oxidation and absorption take place at the same pressure; compression takes place before the NH₃ oxidation (medium pressure).
- dual-pressure plant Absorption takes place at a higher pressure than the NH₃ oxidation; an NO compressor is required.

3.3.2 High Strength Nitric Acid Production

The reaction of nitrogen dioxide with water and pure oxygen takes place at high pressure. The reaction water from the combustion gases has to be condensed by cooling and then discharged. Nitrogen monoxide (NO) is oxidised with air and then with highly concentrated nitric acid to form nitrogen dioxide. NO₂ is scrubbed by means of highly concentrated nitric acid. The nitrogen dioxide and the dinitric tetroxide (N₂O₄, obtained by dimerisation) are mixed with nitric acid containing water. This mixture is converted to nitric acid (98 to 99.5 wt.-%) at high pressure (e.g. 50 bar). The NO_x content of the waste gas depends on the temperature of the last absorption stage. /cf. 3/

3.3.3 Process-integrated emission reduction facilities

The two most common techniques used in order to control NO_x emissions are:

- extended absorption by alkali solutions, and
- catalytic reduction.

Here, controls refer to reduction facilities which are normally an integral part of a nitric acid plant (see Section 3.3).

Extended absorption reduces nitrogen oxide emissions by treatment of the waste gas either with sodium hydroxide or with ammonia.

By treatment of the waste gas with sodium hydroxide, NO and NO₂ are absorbed and sodium nitrite (NaNO₂) is formed. Under certain conditions a NO_x content in the waste gas of 200 ppm by volume can be achieved (absorption pressure of more than 4.5 bar, NO_x content by volume of less than 600 ppm etc.) /3/.

Catalytic purification can be divided into a non-selective and a selective process. Both processes for waste gas treatment require a minimum temperature and a minimum pressure, conditions which often cannot be achieved in old plants /3/.

In non-selective reduction processes, the waste gas reacts with a reduction agent (hydrogen and/or hydrocarbons e.g. natural gas, waste gas from ammonia plants or naphtha) by passing a catalyst (which contains platinum, rhodium or palladium). Depending on the reduction conditions (amount of reduction agent) the reduction product is either nitrogen monoxide or nitrogen. The utilisation of hydrocarbons has the disadvantage that the waste gas contains carbon monoxide as well as hydrocarbons in a non-converted or partially converted state. /3/

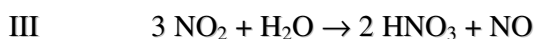
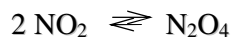
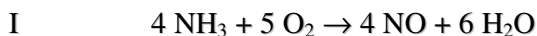
In the selective reduction process the reduction agent, ammonia, reacts with nitric oxides to form nitrogen and water. The catalysts used are for example vanadium pentoxide, platinum, iron/chromium oxides mixtures or zeolites. According to the stoichiometric conditions of the reaction an excess of ammonia is necessary. This process can offer economical advantages for plants with small capacities (less than 100 t of N per day). /3/

A seldom used alternative control device for the absorption of tail gas is the use of molecular sieves. This process can be used for nitric acid plants with high-pressure absorption, where nitrogen dioxide is absorbed from the waste gas at an ambient temperature. /3/

3.4 Emissions

Relevant pollutants are nitrogen oxides (NO_x) and nitrous oxide (N₂O). Emissions of ammonia (NH₃) and non-methane volatile organic compounds (NMVOC) are of less relevance. Emissions of carbon monoxide (CO) are not relevant.^{1, 2}

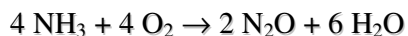
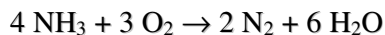
Basic reactions for the production of nitric acid, according to the "Ostwald"-process (oxidation of ammonia, see section 3.3), are:



¹ Trace amounts of HNO₃ can also be emitted.

² Emissions of NMVOC and CO reported in CORINAIR90 are not specified with regard to process technology.

Concerning the formation of N₂O only step I is of relevance. By using suitable catalysts about 93 - 98 % of the ammonia is converted into NO. The rest of the ammonia is converted into nitrogen, mostly in secondary reactions, but also to nitrous oxide according to /6/:



Based on literature data it can be assumed that about 1.5 % of the ammonia is converted to N₂O; modern processes need about 283 kg NH₃/Mg HNO₃ produced. /6/

Emissions released by the stacks contain mainly a mixture of nitrogen oxides (see section 9). In general, the quantity of NO_x emissions is directly related to the kinetics of the nitric acid formation reaction and the design of the reduction equipment. Here, NO_x emissions contain nitrogen monoxide (NO), dinitric trioxide (N₂O₃), nitrogen dioxide (N₂O), and dinitric tetroxide (N₂O₄). Emissions are mostly expressed as NO₂.

The design of the absorption process in a nitric acid plant is decisive for NO_x emissions. The process parameters of influence are for example pressure, temperature, the design of the reaction chamber, the (low) solubility of nitrogen monoxide in water or nitric acid, the efficiency of the absorption column etc. NO_x emissions may increase when there is for example an insufficient air supply to the oxidiser and absorber, low pressure (especially in the absorber), or high temperatures in the cooler condenser and absorber. NO_x emissions can also increase due to operation at high throughput rates or faulty equipment, such as compressors or pumps which lead to lower pressures or leaks and thus decreasing plant efficiency. /1, 3/

Comparatively small amounts of nitrogen oxides are lost from acid concentrating plants. These losses (mostly NO₂) originate from the condenser system, but the emissions are small enough to be easily controlled by absorbers. Acid mist emissions do not occur from the tail gas of a properly operated plant. The small amounts that may be present in the absorber exit gas streams are removed by a separator or collector before entering the catalytic reduction unit or expander. The acid production system and storage tanks are the only significant sources of visible emissions at most nitric acid plants. Emissions from acid storage tanks may occur during tank filling. /1/

A very high contribution to total emissions of nitrous oxide (N₂O) from nitric acid plants has been reported within the CORINAIR90 inventory (see Table 1). This high relevance of N₂O emissions has not yet been reported in the literature (except CORINAIR90).

3.5 Controls

Control measures are an integral part of the production process of nitric acid (see section 3.3.3). Control measures are e.g. the treatment of the waste gas with sodium hydroxide, non-selective catalytical purification (SNCR), selective catalytical purification (SCR) or the use of molecular sieves.

4 SIMPLER METHODOLOGY

For nitric acid plants only a simpler methodology is given; a detailed methodology is not proposed (see section 5). Here “simpler methodology” refers to the calculation of emissions based on emission factors and activities. The simpler methodology covers the relevant pollutants NO_x, N₂O and NH₃.

The annual emission is determined by an activity and an emission factor:

$$E_i = EF_i \cdot A \quad (1)$$

E_i annual emission of pollutant i

EF_i emission factor of pollutant i

A activity rate

The activity rate A and the emission factor EF_i have to be determined on the same level of aggregation by using statistical data (e.g. production of nitric acid, see Section 6).

Emission factors are given in Table 2 (section 8) based on literature data.

5 DETAILED METHODOLOGY

A detailed methodology is not proposed, due to the low relevance of emissions from nitric acid production compared to the total anthropogenic emissions (see section 2). Emission measurement appears to be not necessary for inventory purposes.

6 RELEVANT ACTIVITY STATISTICS

The activity rate according to CORINAIR90 should be reported in mass product/year [Mg/a]. The total production of nitric acid can be derived directly from statistics available on a European level. For point sources, individual data from national sources (e.g. association of chemical industries) should be used.

The following statistics contain data concerning the production of nitric acid:

- United Nations (ed.): Industrial Statistics Yearbook 1991; Volume I: Commodity Production Statistics; New York 1993; ISIC 3511-49 (production of nitric acid)

The following statistics on a European level contain only economic variables, such as the number of enterprises, number of employees, turnover, for the “Manufacture of basic industrial chemicals and manufacture followed by further processing of such products”:

- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992,
- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1994.

7 POINT SOURCE CRITERIA

According to the CORINAIR90 methodology, nitric acid plants have to be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 2 contains emission factors for relevant pollutants based on literature data. Nitrogen emission factors vary considerably depending on the type of control equipment and the process conditions.

Table 2: Emission factors for nitric acid production (expressed in 100% acid)

Type of process	Emission factors in mass/mass 100 % acid [g/Mg]					
	NO _x ¹⁾		N ₂ O ⁹⁾		NH ₃	
	range	value	range	value	range	value
Low pressure	10,000 - 20,000 ²⁾⁵⁾⁶⁾ 3,600 - 8,600 ³⁾	12,000 ²⁾⁵⁾⁶⁾ 3,500 ³⁾		800 ²⁾⁷⁾		
Medium pressure	5,000 - 12,000 ²⁾⁵⁾⁶⁾	7,500 ²⁾⁵⁾⁶⁾		800 ²⁾⁷⁾		
High pressure	1,500 - 5,000 ²⁾⁵⁾⁶⁾	3,000 ²⁾⁵⁾⁶⁾		800 ²⁾⁷⁾		
Direct strong acid process	100 - 1,000 ²⁾	5,000 ³⁾				
No specification	664-75,000 ⁸⁾		1,000-79,000 ⁸⁾		1- 5,000 ⁸⁾	10 ⁸⁾

¹⁾ no specification into NO, NO₂, etc. has been reported

²⁾ CORINAIR /2/; data are from French and W.-German plants

³⁾ EPA data /1/

⁴⁾ Swedish data /4/

⁵⁾ Control by catalytic reduction: range 10 - 800 g/Mg; value 400 g/Mg

⁶⁾ Control by extended absorption: range 400 - 1,400 g/Mg; value 900 g/Mg

⁷⁾ French value as used for the "taxe parafiscale"; not further specified as low, medium or high pressure process

⁸⁾ CORINAIR90 data

⁹⁾ Emission measurements from the so called DuPont Process have led to emission factor ranges of 2 - 9 g N₂O/kg HNO₃ /7/.

9 SPECIES PROFILES

The NO_x emissions ("nitrous gases") contain a mixture of nitric oxide (NO) and nitrogen dioxide (NO₂), dinitric oxide (N₂O₃) and dinitric tetroxide (N₂O₄). Emissions of N₂O have to be reported separately (see also section 3.4).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors. Technic specific emission factors are provided in Table 2. CORINAIR90 data can only be used in order to give a range of emission factors. Further work should be invested in the analysis of measured data in order to decrease the range of emission factors given or to provide a further split of emission factors.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) provides a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from nitric acid plants can be obtained by taking into account the time of operation of different process types (see table 2).

However, data for the annual time of operation should take into account, that nitric acid plants produce during the whole year, and that the production of nitric acid is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on "Concepts for Emission Inventory Verification" different verification procedures can be recommended. Verification procedures considered here are principally based on the verification of emission data on a national level and on a plant level. Verification on a plant level takes into account e.g. the number of nitric acid plants considered and relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

Emission data for the nitric acid production can be verified on national level by comparing annual emissions related to the territorial unit to independently derived emission estimates (e.g. obtained by using population equivalents).

17 REFERENCES

- /1/ US-EPA (ed.): Compilation of Air Pollutant Emission Factors, Vol. 1: Stationary Point and Area Sources; 1986; AIR CHIEF Version 2.0 Beta; 1992
- /2/ CITEPA (ed.): CORINAIR - Emission Factor Handbook, part 1: Default Emission Factors from stationary sources; 1992
- /3/ Verein Deutscher Ingenieure (ed.): Emission Control Nitric Acid Production; Nr. 2295; Düsseldorf (Germany); 1983
- /4/ Ms. Froste; Mr. Kvist; Ms. Haclund; personal communication; February 1995 (Swedish EPA)
- /5/ Parker, Albert: Industrial Air Pollution Handbook; London; 1978
- /6/ Schön, M.; Walz, R.: Emissionen der Treibhausgase Distickstoffoxid und Methan in Deutschland; Umweltbundesamt (Hrsg.); Berlin, 1993
- /7/ Olivier, J. G. J.: Nitrous oxide emissions from industrial processes; *in*: Methane and Nitrous Oxide - Methods in National Emission Inventories and Options for Control; Proceedings of an international IPCC Workshop; Amersfoort (The Netherlands); 3-5 February 1993

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version : 2.1

Date : December 1995

Source : Otto Rentz, Dagmar Oertel
University of Karlsruhe

Updated with particulate matter details by:
Mike Woodfield
AEA Technology
UK
December 2006

20 POINT OF ENQUIRY

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