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1. Nitric Acid

1.1. Introduction

Nitric acid is a strong acid that occurs in nature only in the form of nitrate salts. When large-scale production of nitric acid began, sodium nitrate (soda saltpeter, Chile saltpeter) was used as the feedstock. At the beginning of the 20th century the reserves of Chile saltpeter were thought to be nearing exhaustion, so processes were developed for replacing nitrogen from natural nitrates with atmospheric nitrogen. Three techniques were used industrially:

1. Production of nitrogen monoxide by reacting atmospheric nitrogen and oxygen at > 2000 °C (direct processes)
2. Production of ammonia by hydrolysis of calcium cyanamide under pressure
3. Production of ammonia from nitrogen and hydrogen

The direct combustion of air in an electric arc, developed by BIRKELAND and EYDE, was abandoned because of its poor energy efficiency. Later direct processes, such as thermal nitrogen monoxide synthesis with fossil fuels or nitrogen monoxide synthesis in nuclear reactors, did not gain widespread acceptance. Ammonia production from calcium cyanamide was of only transitory value. Ammonia produced from nitrogen and hydrogen by the Haber – Bosch process (→ Ammonia, 2. Production Processes) is, however, still used as feedstock for nitric acid production.

The crucial step in nitric acid production, the catalytic combustion of ammonia, was developed by OSTWALD around the turn of the century. The most important design parameters for a nitric acid plant were determined first in laboratory tests and later in a pilot plant. The first production facility employing the Ostwald process came on stream in 1906 at Gerthe in Germany [1–3].

Most of the nitric acid produced is used to form inorganic fertilizers (→ Phosphate Fertilizers); it is mostly neutralized with ammonia to form ammonium nitrate (→ Ammonium Compounds, Section 1.2.1.).

1.2. Properties

Nitric acid was known to the ancient Egyptians because of its special ability to separate gold and silver. Many well-known alchemists in the Middle Ages experimented with the acid. In the middle of the 17th century, GLAUBER reported its preparation from saltpeter and sulfuric acid.

Physical Properties. Nitric acid [7697-37-2], M_r 63.013, is miscible with water in all proportions. At a concentration of 69.2 wt %, it forms a maximum-boiling azeotrope with water. The azeotropic mixture boils at 121.8 °C. Pure anhydrous nitric acid boils at 83 – 87 °C; the reason a range of boiling points are cited in the literature is that the acid decomposes on heating [4]:



The nitrogen dioxide formed on decomposition colors the acid yellow or even red at higher concentrations. Because the vapors can also absorb moisture, the term “red fuming nitric acid” is used. In the pure anhydrous state, nitric acid is a colorless liquid.

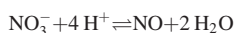
The most important physical properties of pure nitric acid follow:

<i>fp</i>	−41.59 °C
<i>bp</i>	82.6 ± 0.2 °C
Density, liquid	
at 0 °C	1549.2 kg/m ³
at 20 °C	1512.8 kg/m ³
at 40 °C	1476.4 kg/m ³
Refractive index n_D^{24}	1.3970
Dynamic viscosity	
at 0 °C	1.092 mPa · s
at 25 °C	0.746 mPa · s
at 40 °C	0.617 mPa · s
Surface tension	
at 0 °C	0.04356 N/m
at 20 °C	0.04115 N/m
at 40 °C	0.03776 N/m
Thermal conductivity (20 °C)	0.343 W m ^{−1} K ^{−1}
Standard enthalpy of formation	
Liquid	2.7474 J/g
Gas	2.1258 J/g

Heat of vaporization (20 °C)	626.3 J/g
Specific heat	
at 0 °C	1.7601 J g ^{−1} K ^{−1}
at 20 °C	1.7481 J g ^{−1} K ^{−1}

The decomposition of nitric acid makes its physical properties difficult to determine at higher temperature. Up to ca. 50 °C, conventional methods of measurement are possible; beyond this, indirect thermodynamic calculations or special short-time measuring methods must be employed. Figure 1 illustrates the vapor pressure curve of pure nitric acid. Table 1 lists important physical properties of aqueous nitric acid. A comprehensive review of the physical and chemical properties of nitric acid is given in [6].

Chemical Properties. Concentrated nitric acid, with nitrogen in the + 5 oxidation state, acts as a strong oxidizing agent. The reaction



goes to the right for all substances with oxidation potentials more negative than + 0.93 V [7]. For example, copper (+ 0.337 V) and silver (+ 0.799 V) are dissolved by nitric acid, whereas gold (+ 1.498 V) and platinum (+ 1.2 V) are resistant. In practice, 50 % nitric acid (aqua

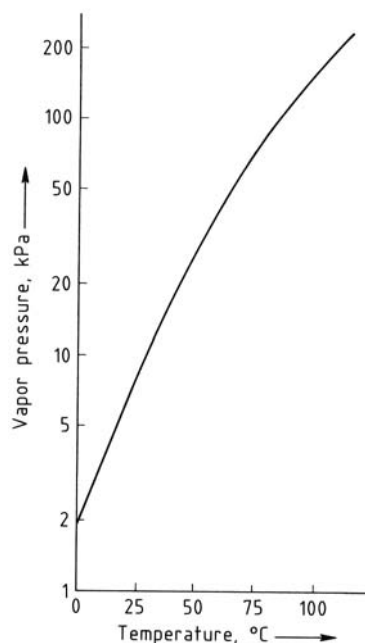


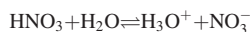
Figure 1. Vapor pressure curve for pure nitric acid

Table 1. Physical properties of aqueous nitric acid as a function of composition [5]

HNO ₃ concentration, wt %	Density (20 °C), g/cm ³	mp, °C	bp, °C	Partial pressure (20 °C), kPa	
				HNO ₃	H ₂ O
0	0.99823	0	100.0		2.23
10	1.0543	−7	101.2		2.26
20	1.1150	−17	103.4		2.02
30	1.1800	−36	107.0		1.76
40	1.2463	−30	112.0		1.44
50	1.3100	−20	116.4	0.03	1.05
60	1.3667	−22	120.4	0.12	0.65
70	1.4134	−41	121.6	0.39	0.35
80	1.4521	−39	116.6	1.4	0.12
90	1.4826	−60	102.0	3.6	0.03
100	1.5129	−42	86.0	6.0	0

fortis) is used for separating gold from silver. Some base metals, such as aluminum and chromium, are attacked by nitric acid only at their surfaces because a thin oxide layer is formed, which protects (i.e., passivates) the core against further oxidation. As a result of this passivation, alloyed steel equipment can be used in nitric acid technology.

Highly diluted nitric acid is almost completely dissociated



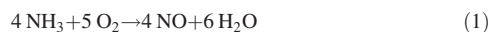
and does not attack copper and more noble metals. Due to its acid nature, however, it reacts with base metals, liberating hydrogen and forming nitrates.

A mixture (volume ratio 3 : 1) of concentrated nitric acid and concentrated hydrochloric acid (aqua regia) also dissolves gold.

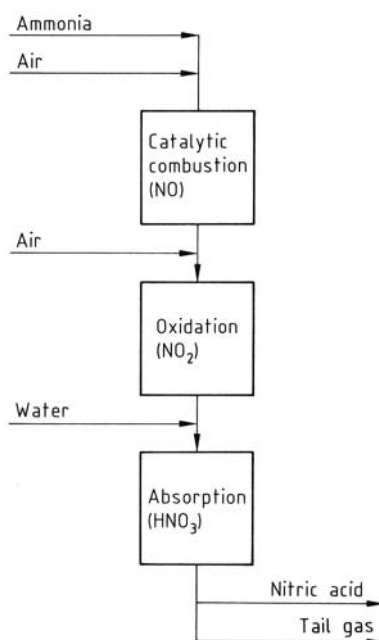
1.3. Industrial Production

The industrial production of nitric acid by the Ostwald process is described in this section. The process involves three chemical steps (Fig. 2):

1. Catalytic oxidation of ammonia with atmospheric oxygen to yield nitrogen monoxide:



Oxidation of the nitrogen monoxide product to nitrogen dioxide or dinitrogen tetroxide:

**Figure 2.** Ostwald process

2. Absorption of the nitrogen oxides to yield nitric acid:



The way in which these three steps are implemented characterizes the various nitric acid processes. In *monopressure (single-pressure) processes*, ammonia combustion and NO_x absorption take place at the same working pressure. These include medium-pressure (230 – 600 kPa) and high-pressure (700 – 1100 kPa) processes. Very few plants currently employ low pressure (100 – 220 kPa) for both combustion and absorption.

In *dual-pressure (split-pressure) processes*, the absorption pressure is higher than the combustion pressure. Modern dual-pressure plants feature combustion at 400 – 600 kPa and absorption at 900 – 1400 kPa. Some older plants still employ atmospheric combustion and medium-pressure absorption.

Intensive work on ammonia combustion as well as the oxidation and absorption of nitrogen oxides has been well documented since the early 1920s. Up to now the combustion of ammonia has been considered as a heterogeneous catalytic surface reaction with undesirable side reactions. The oxidation of nitrogen monoxide is a rare example of a homogeneous third-order gas-phase reaction. The absorption of NO_x is a heterogeneous reaction between fluid (i.e., gas and liquid) phases.

1.3.1. Oxidation of Ammonia

The oxidation of ammonia to nitrogen monoxide is described by the equation



Over a suitable catalyst, 93 – 98 % of the feed ammonia is converted to nitrogen monoxide. The remainder participates in undesirable side reactions leading to dinitrogen monoxide (nitrous oxide, laughing gas)



and to nitrogen



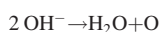
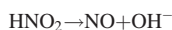
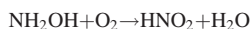
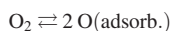
Other undesirable reactions are the decomposition of the nitrogen monoxide product



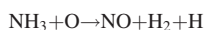
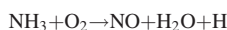
and its reaction with ammonia



Reaction Mechanism. Early theories of the mechanism for the oxidation of ammonia differed as to which intermediate product was formed. The classical theories were proposed by ANDRUSOV (nitroxyl theory, 1926), RASCHIG (imide theory, 1927), and BODENSTEIN (hydroxylamine theory, 1935) [3]. According to the hydroxylamine theory, ammonia reacts with atomic oxygen adsorbed on the catalyst to yield hydroxylamine. This in turn reacts with molecular oxygen to form nitrous acid, which then dissociates to nitrogen monoxide and hydroxyl ions:



In oxidation experiments under high vacuum, BODENSTEIN and coworkers detected both hydroxylamine and nitrous acid as intermediate products on the platinum catalyst. Later studies with a mass spectrometer showed that no such intermediate products are found above 400 °C [8]. In these tests, both molecular and atomic oxygen was found on the catalyst surface. A direct reaction between oxygen and ammonia was therefore postulated according to the following equations:



In fast reactions such as the combustion of ammonia (the reaction time for Eq. 4 is ca. 10^{-11} s), however, the possible intermediates most likely cannot be detected because they are very short-lived and present in very low concentrations. NOWAK [9] has compared the numerous theories of ammonia combustion. PIGNET and SCHMIDT present a classical Langmuir – Hinshelwood treatment of the process [10]. The possibility that the combustion of ammonia may be considered as a homogeneous catalytic reaction is now being discussed.

At low temperature (200 – 400 °C), the rate of ammonia oxidation is limited by the reaction kinetics. The byproducts nitrogen, and especially dinitrogen monoxide, are formed preferentially. Between 400 and 600 °C, the reaction rate becomes limited by mass transfer, which is then dominant above 600 °C. Control by mass transfer relates to the diffusion rate of ammonia through the gas film to the catalyst surface. The product in this reaction regime is nitrogen monoxide.

The catalyst surface experiences a very low partial pressure of ammonia and a diminished partial pressure of oxygen due to mass-transfer limitations. The catalytic side reaction between

ammonia and nitrogen monoxide is accelerated by an increase in the partial pressures of both species on the catalyst surface. If catalyst poisoning occurs, the number of active centers decreases and the partial pressure, particularly that of ammonia, increases at the remaining active centers. The result is increased formation of undesirable byproducts. In practice, this shift is offset by raising the temperature, i.e., the reaction is again displaced into the region limited by gas-film diffusion.

Precious-metal catalysts are usually employed in the form of closely stacked, fine-mesh gauzes. At the beginning of a campaign they have a smooth surface and therefore only slightly limit mass transfer in the gas phase. This gives an initially lower yield of nitrogen monoxide. After a short time in service, however, the surface area of the catalyst increases greatly because of microstructural changes and interactions with volatilizing constituents of the catalyst (Fig. 3). Catalyst growth increases the limitation of mass transfer in the gas phase and thus the yield of nitrogen monoxide.

Reaction Engineering. From an engineering standpoint, the combustion of ammonia is one of the most efficient catalytic reactions (maximum possible conversion 98 %). According to the stoichiometry of Equation (4), the ammonia – air reaction mixture should contain 14.38 % ammonia. A lower ammonia – air ratio is, however, employed for a variety of reasons, the most important being that conversion decreases with too high a ratio; ammonia and air also form an explosive mixture. Because the mixing of ammonia and air in industrial practice is incomplete, locally higher ratios may occur. A ratio that includes a safety margin below the explosion limit is therefore necessary. The explosion limit declines with pressure so that high-pressure burners can operate with up to 11 % ammonia, whereas 13.5 % ammonia is possible in low-pressure systems. The explosion limit also depends on the flow velocity (Table 2, see also [3]) and the water content of the reaction mixture [11].

According to Le Chatelier's principle, the increase in volume in Equation (4) implies that conversion declines as pressure rises (Fig. 4).

If the gas velocities are too high or the number of catalyst gauzes is insufficient, conversion to

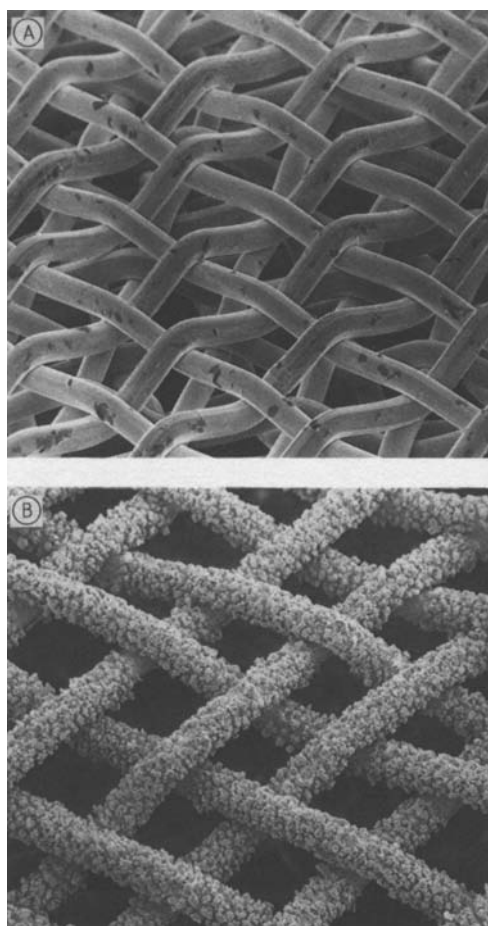


Figure 3. Photograph of platinum – rhodium gauze (Degussa, FRG) taken with a scanning electron microscope (enlargement 100 : 1) A) Initial stage; B) Highly activated stage

nitrogen monoxide decreases because of the slip (leakage) of ammonia which reacts with it according to Equation (8). If the gas velocities are too low or too many gauzes are used, decomposition of nitrogen monoxide according to Equation (7) is promoted. Table 3 gives typical gas velocities.

Table 2. Explosion limits of ammonia – air mixtures at atmospheric pressure

Flow velocity, m/s	Lower explosion limit, % NH ₃	Upper explosion limit, % NH ₃
0	15.5	27.5
3	28	38
5 – 8	30	40
12	32	37
14	none	none

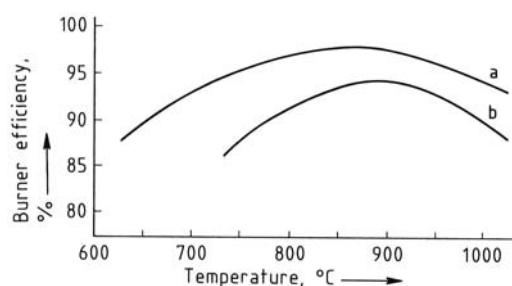


Figure 4. Conversion of ammonia to nitrogen monoxide on a platinum gauze as a function of temperature [5] a) 100 kPa; b) 400 kPa

A high reaction temperature promotes ammonia combustion (Fig. 4), but high temperature decreases the conversion. Maximum temperatures up to 950 °C have been realized, but catalyst losses, chiefly due to vaporization, increase greatly (Fig. 5). The usual way to maintain the conversion toward the end of a campaign in spite of catalyst deactivation and losses, is to raise the temperature. The ammonia – air ratio is directly related to the reaction temperature: a 1 % increase in the proportion of ammonia increases the temperature by ca. 68 K. If the temperature is too low, conversion to nitrogen monoxide decreases. The reaction temperature also depends on the temperature of the inlet gas mixture. The following formula provides an approximate value in °C:

$$t_{\text{reactor}} = t_{\text{gas mixture}} + r \cdot 68 \quad \text{where } r = \text{NH}_3 / (\text{NH}_3 + \text{air}) \quad (9)$$

Catalysts. [12]. Since the introduction of the industrial production of nitric acid by the Ostwald process, several hundred materials have been tested as catalysts for ammonia combustion. Platinum catalysts have proved most suitable and are used almost exclusively today. Oxides of non-noble metals can also be employed; these

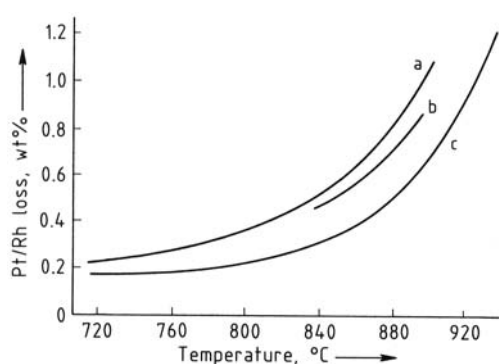


Figure 5. Losses of precious metals in the combustion of ammonia to nitrogen monoxide as a function of temperature and catalyst composition [5] a) Pt; b) Pt – Rh 98/2; c) Pt – Rh 90/10

cost less than platinum catalysts, but conversion is lower. Another disadvantage of non-noble-metal catalysts is that they are more quickly poisoned [13].

The usual form of catalyst is a fine-mesh gauze (standardized at 1024 mesh/cm²). Manufacturers offer wire diameters of 0.060 and 0.076 mm. The Johnson Matthey “Tailored Pack” combines gauzes made of different wire diameters [14]. The upstream gauzes have a wire diameter of 0.076 mm and the downstream ones 0.060 mm to optimize the catalyst surface area.

High-pressure plants also utilize “fiber packs” in which a fraction of the fibrous catalyst material is held between two gauzes [15]. The packs have the advantage of reduced platinum loss and thus longer run times. “Fiber packs” have not yet been used in medium-pressure ammonia combustion because fewer gauzes are used in medium-pressure than in high-pressure processes (see Table 3), so the lower pressure drop results in poorer distribution.

To reduce catalyst consumption, particularly in gauzes at the bottom of the reactor, ceramic grids coated with platinum – rhodium have also been developed [16].

Platinum is usually alloyed with 5 – 10 % rhodium to improve its strength and to reduce catalyst loss. During combustion, the metal surface becomes enriched in rhodium, thus improving catalytic activity [17]. Because rhodium is more expensive than platinum, a rhodium content of 5 – 10 % has proved optimal. Figure 6 shows the efficiency of conversion to nitrogen

Table 3. Typical design data for ammonia burners

Pressure, MPa	Number of gauzes	Gas velocity, m/s	Reaction temperature, °C	Catalyst loss, g/t HNO ₃
0.1 – 0.2	3 – 5	0.4 – 1.0	840 – 850	0.05 – 0.10
0.3 – 0.7	6 – 10	1 – 3	880 – 900	0.15 – 0.20
0.8 – 1.2	20 – 50	2 – 4	900 – 950	0.25 – 0.50

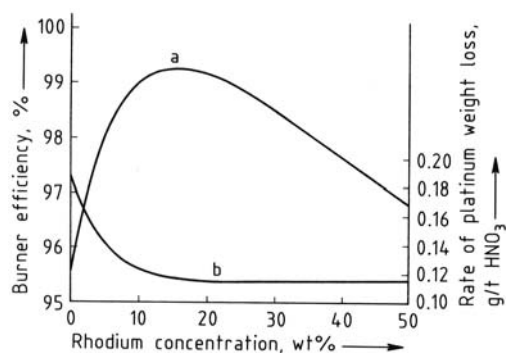


Figure 6. Conversion of ammonia to nitrogen monoxide on platinum gauze (a) and platinum losses (b) as a function of catalyst composition

monoxide and the platinum loss as a function of the rhodium content of the alloy [18].

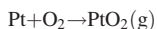
If a low reaction temperature ($< \text{ca. } 800^\circ\text{C}$) is unavoidable, a pure platinum catalyst should be employed, because otherwise rhodium(III) oxide would accumulate at the catalyst surface and decrease catalytic activity [18].

Palladium is also used in catalyst alloys. Laboratory studies on the catalytic activity of 90% Pt – 10% Rh and 90% Pt – 5% Rh – 5% Pd gauzes reveal no great differences in nitrogen monoxide yield [19]. The ternary catalyst is of economic interest because palladium costs much less than platinum or rhodium.

Platinum gauzes are pretreated by the manufacturer (Degussa and Heraeus, FRG; Johnson Matthey and Engelhard, UK) so that they do not need to be activated after installation in the burner. The reaction is ignited with a hydrogen flame until gauzes glow red. After the reaction has been initiated, crystal growth rapidly increases the surface area. The highest conversion on the catalyst is obtained after a few days use. Specially pretreated platinum gauzes that reach maximum activity after just a few hours are also on the market [20]. Start-up problems with platinum gauzes are discussed in [21]. The prolonged decline in activity after the conversion maximum is due to catalyst poisoning and platinum loss.

Catalyst poisons include iron oxide (rust) and dust in the process air, which is especially concentrated in the vicinity of fertilizer plants. Any material deposited on the catalyst surface acts as a poison. A multistage filter is used to prevent these substances from reaching the catalyst (see Section 1.3.3.1).

Platinum loss during operation is caused by vaporization and abrasion. Vaporization loss predominates, but if heavy vaporization loss weakens the structure then abrasion can substantially lower burner efficiency. Platinum loss due to vaporization is thought to involve the formation of short-lived platinum dioxide:



Mechanical losses are accelerated by impurities in the reaction mixture, which can lead to the formation of whiskers at the grain boundaries. The whiskers are more easily broken off by the flowing gas.

Recovery of Precious Metals. Precious-metal losses from the catalyst have a significant effect on the operating costs of a nitric acid plant. The approximate losses and resulting costs can be determined from the ammonia combustion temperature and the loading. Losses increase with temperature and loading; however, smaller losses may be measured at higher loadings because a more uniform incoming flow causes less movement of the gauzes relative to one another and thus reduces mechanical losses. Table 3 lists typical loss rates.

Platinum recovery systems are installed in most nitric acid plants to improve process economics.

Mechanical Filters. Mechanical filters are made of glass, mineral wool, or ceramic or asbestos fibers. They are normally installed where the gas temperature is $< 400^\circ\text{C}$. Their most important drawback is their large pressure drop, which can reach 25 kPa between filter changes.

Mechanical filters recover 10 – 20% platinum, but recovery rates up to 50% have been reported [22]. These filters have the advantage of low capital costs and the disadvantage of high operating costs resulting from the large pressure drop across the filter. For economic reasons, they are only employed in mono-high-pressure plants.

In low-pressure burners, marble chips 3 – 5 mm in length were used immediately downstream of the catalyst gauzes [23]. At high reaction temperature, the marble is converted to calcium oxide, whose high absorption capacity for platinum and rhodium permits up to 94% recovery. During reactor shutdown, however, the

calcium oxide must be protected against moisture.

Recovery Gauzes. A technically elegant approach to platinum recovery is to install, just downstream of the catalyst gauzes, a material that is stable at high temperature and that can absorb platinum oxide vapor and form an alloy with it. The first recovery gauzes in production plants (supplied by Degussa in 1968) consisted of a gold – palladium alloy (20/80). Nowadays most such gauzes are gold-free but have a low content of nickel (ca. 5 %) to enhance their strength. The gauzes have 100 – 1350 mesh/cm² and are made of wire with a diameter of 0.2 – 0.06 mm. Several recovery gauzes with different specifications are usually installed. Loss of platinum from the catalyst is greater than that of rhodium; for example, the calculated loss composition for a 90/10 Pt – Rh gauze is 95/5. A “recovery factor” can be determined for each recovery gauze, indicating how much of the available platinum is retained by the gauze. This recovery factor depends on the specifications of the gauze, the operating pressure, and the loading. Figure 7 shows the dependence of the

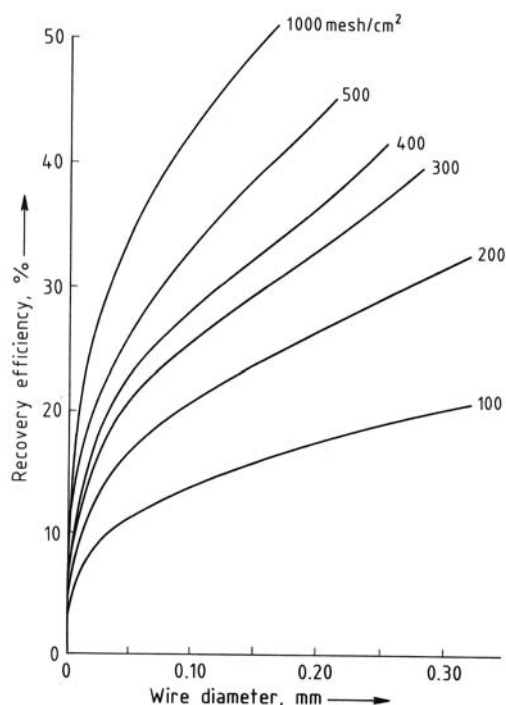


Figure 7. Performance of a palladium-based recovery gauze as a function of mesh size and wire diameter

recovery efficiency on wire diameter and mesh fineness [24]. A method for selecting the optimum platinum recovery gauze system for a particular nitric acid plant is described in [25].

The captured platinum diffuses into the palladium gauze and forms an alloy. The topmost gauze is often designed to reach saturation in one campaign, usually 180 d. Determining the economic optimum for a recovery system (the most important criterion is the weight of palladium required) necessitates taking into account the fact that palladium is lost. This loss corresponds to about one-third of platinum recovery.

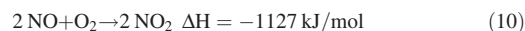
“Getter” systems can recover more than 80 % of the platinum lost from the catalyst. The mechanism of rhodium recovery has not yet been fully elucidated. Up to 30 % of rhodium from the catalyst is captured by recovery systems.

1.3.2. Oxidation and Absorption of Nitrogen Oxides

After the combustion of ammonia, the nitrogen monoxide product gas is cooled en route to absorption and, if necessary, compressed. As a result, part of the nitrogen monoxide is oxidized to nitrogen dioxide or dinitrogen tetroxide (Eq. 2), which is converted to nitric acid by absorption in water (Eq. 3).

Absorption is usually performed in plate columns where the nitrous gases are converted to nitric acid in the liquid phase on the plates. Nitrogen monoxide is constantly reformed in this step and prevents complete absorption of the inlet gases. Oxidation of nitrogen monoxide occurs mainly in the gas phases between the plates, but also in the gas phase of the bubble layer on them.

Gas Phase. The gas phase is the site of nitrogen monoxide oxidation



as well as nitrogen dioxide dimerization



and dinitrogen trioxide formation



Reaction of the oxidized nitrogen oxides with water vapor leads to formation of nitrous

and nitric acids. These reactions are of secondary importance from an engineering standpoint.

To describe the kinetics of nitrogen monoxide oxidation (Eq. 10), a third-order rate equation is used [26]:

$$r = \frac{k_p}{RT} p_{\text{NO}}^2 p_{\text{O}_2} \quad (13)$$

where

r = reaction rate, $\text{kmol m}^{-3} \text{s}^{-1}$

k_p = reaction rate constant, $\text{atm}^{-2} \text{s}^{-1}$

R = universal gas constant, $\text{m}^3 \text{atm kmol}^{-1} \text{K}^{-1}$

T = temperature, K

p = partial pressure, atm

The rate constant is defined by

$$\log k_p = \frac{652.1}{T} - 1.0366 \quad (14)$$

This reaction is unusual because it goes to the right faster at low temperature than at high temperature, i.e., the reaction rate has a negative temperature coefficient.

Because equilibrium in the nitrogen dioxide dimerization system is reached very quickly, an equilibrium formula

$$r = \frac{k_p}{RT} \left(p_{\text{NO}_2}^2 - \frac{p_{\text{N}_2\text{O}_4}}{K_p} \right) \quad (15)$$

can be assumed where K_p is the equilibrium constant. The dimerization rate is virtually independent of temperature [27], so the rate constant at 25 °C

$$k_p = 5.7 \times 10^5 \text{ atm}^{-1} \text{s}^{-1} \quad (16)$$

can be used at all temperatures of technical interest.

HOFTYZER and KWANTEN [28] give the following equation for the $\text{NO}_2 - \text{N}_2\text{O}_4$ equilibrium constant:

$$K_p = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{NO}_2}^2} = 0.698 \times 10^{-9} \exp\left(\frac{6866}{T}\right) \quad (17)$$

An equilibrium formula can also be written for dinitrogen trioxide formation:

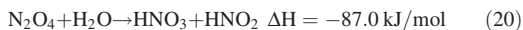
$$r = \frac{k_p}{RT} \left(p_{\text{NO}} p_{\text{NO}_2} - \frac{p_{\text{N}_2\text{O}_3}}{K_p} \right) \quad (18)$$

According to [27], the equilibrium constant can be determined as

$$K_p = \frac{p_{\text{N}_2\text{O}_3}}{p_{\text{NO}} p_{\text{NO}_2}} = 65.3 \times 10^{-9} \exp\left(\frac{4740}{T}\right) \quad (19)$$

Liquid Phase. The large number of reactive components in the gas phase (NO , NO_2 , N_2O_3 , N_2O_4) means that the reaction model for absorption is complicated. Figure 8 shows a sophisticated model devised by HOFTYZER and KWANTEN [28].

The main route for the formation of nitric acid in this model involves two steps in the liquid phase. First, dissolved dinitrogen tetroxide reacts with water, yielding nitric and nitrous acids:



Nitrous acid then dissociates to nitric acid, water, and nitrogen monoxide, the latter being transported across the interface into the bulk gas:



According to ANDREW and HANSON [29], a first-order equation can be written for the rate of dinitrogen tetroxide hydrolysis:

$$r = k c_{\text{N}_2\text{O}_4} \quad (22)$$

where $c_{\text{N}_2\text{O}_4}$ is the concentration of dinitrogen tetroxide in kmol/m^3 . The rate constant is given by

$$\log k = -\frac{4139}{T} + 16.3415 \quad (23)$$

The kinetics of nitrous acid dissociation were studied by ABEL and SCHMID [30], with the following result:

$$r = k \frac{c_{\text{HNO}_2}^4}{p_{\text{NO}}^2} = \frac{k}{H_{\text{NO}}^2} \frac{c_{\text{HNO}_2}^4}{c_{\text{NO}}^2} \quad (24)$$

where H_{NO} is the Henry coefficient for nitrogen monoxide in $\text{m}^3 \text{atm/kmol}$ and c is the concentration in kmol/m^3 . The rate constant is defined by

$$\log k = -\frac{6200}{T} + 20.1979 \quad (25)$$

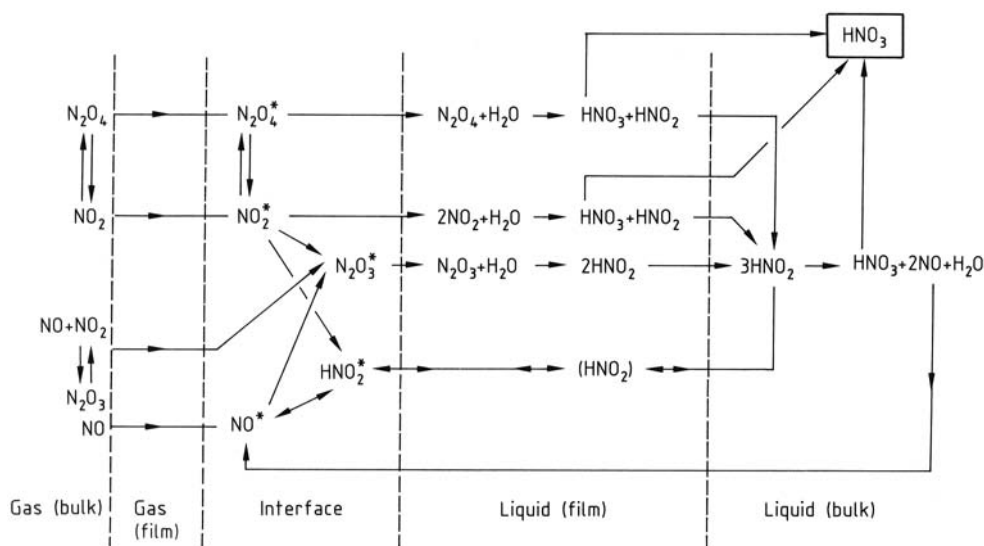


Figure 8. Nonstoichiometric model of absorption of nitrogen oxides in water [28]

Equations (23) and (25) were derived by HOFFMANN and EMIG [31] and are based on experimental data from [32].

Mass Transfer. For more than 50 years scientists have studied the transport of nitrogen oxides in water and in dilute and concentrated nitric acid. A variety of mechanisms have been proposed depending on the gas composition and the acid concentration. These are partly in agreement with the absorption model of Figure 8.

In the NO_x absorption region important for acid formation, dinitrogen tetroxide transport is considered to be the rate-limiting step. The quantity of dinitrogen tetroxide transported from the bulk gas to the interface depends chiefly on the $\text{NO}_2 - \text{N}_2\text{O}_4$ equilibrium [28], [33]:

$$J_{\text{N}_2\text{O}_4} = \frac{K_{\text{gNO}_2}}{2RT} (p_{\text{NO}_2}^0 - p_{\text{NO}_2}^i) + \frac{k_{\text{gN}_2\text{O}_4}}{RT} (p_{\text{N}_2\text{O}_4}^0 - p_{\text{N}_2\text{O}_4}^i) \quad (26)$$

where

J = absorption rate, $\text{kmol m}^{-2} \text{s}^{-1}$

k_{g} = gas-side mass-transfer coefficient, m/s

p^0 = partial pressure in the bulk gas, atm

p^i = partial pressure at the interface, atm

At higher $\text{NO}_2/\text{N}_2\text{O}_4$ concentrations in the reaction gas, primarily dinitrogen tetroxide crosses

the interface and reacts in the fast first-order reaction (Eq. 20) to form nitric and nitrous acids. Nitrous acid dissociates (Eq. 21), and the resulting nitrogen monoxide is transported back into the gas space.

The following equation can be written for the absorption rate of dinitrogen tetroxide [34]:

$$J_{\text{N}_2\text{O}_4} = H_{\text{N}_2\text{O}_4} p_{\text{N}_2\text{O}_4} \sqrt{k D_{\text{N}_2\text{O}_4}} \quad (27)$$

where

H = Henry coefficient, $\text{m}^3 \text{atm/kmol}$

k = rate constant, s^{-1}

D = diffusion constant, m^2/s

Numerous measurements in laboratory absorbers support this mechanism. Interpretations of measurements in absorption columns have given the following correlations for the mass-transfer coefficients [35]:

1. Bubble-cap trays

$$H_{\text{N}_2\text{O}_4} \sqrt{k D_{\text{N}_2\text{O}_4}} = \exp \left(-\frac{1500}{T} - 4.3790 - 23.279 W_{\text{HNO}_3} + 130.42 W_{\text{HNO}_3}^2 - 370.87 W_{\text{HNO}_3}^3 + 486.94 W_{\text{HNO}_3}^4 - 236.54 W_{\text{HNO}_3}^5 \right) \text{ kmol m}^{-2} \text{ kPa}^{-1} \text{ s}^{-1} \quad (28)$$

2. Sieve trays

For $W_{\text{HNO}_3} > 0.05$

$$H_{\text{N}_2\text{O}_4} \sqrt{k D_{\text{N}_2\text{O}_4}} = \exp \left(-\frac{1500}{T} - 2.7648 - 39.614 W_{\text{HNO}_3} + 181.98 W_{\text{HNO}_3}^2 - 429.65 W_{\text{HNO}_3}^3 + 496.99 W_{\text{HNO}_3}^4 - 223.24 W_{\text{HNO}_3}^5 \right) \quad (29a)$$

$\text{kmol m}^{-2} \text{ kPa}^{-1} \text{ s}^{-1}$

For $W_{\text{HNO}_3} < 0.05$

$$H_{\text{N}_2\text{O}_4} \sqrt{k D_{\text{N}_2\text{O}_4}} = \exp \left(-\frac{1500}{T} + 0.2548 - 315.73 W_{\text{HNO}_3} + 9256.2 W_{\text{HNO}_3}^2 - 95.602 W_{\text{HNO}_3}^3 \right) \quad (29b)$$

$\text{kmol m}^{-2} \text{ kPa}^{-1} \text{ s}^{-1}$

where

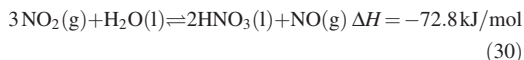
H = Henry coefficient, $\text{m}^3 \text{ kPa} / \text{kmol}$

T = temperature, K

W = mass fraction

The absorption of $\text{NO}_2 - \text{N}_2\text{O}_4$ in concentrated nitric acid can be treated as pure physical absorption [36]. Deviations from the described chemisorption also occur at low gas-phase $\text{NO}_2 - \text{N}_2\text{O}_4$ concentrations [29].

Absorption Equilibrium. Equilibrium considerations allow determination of the maximum possible acid concentration for a given composition of the inlet gas. For example, suppose the overall reaction is



and the equilibrium constant is defined as

$$K_p = \frac{p_{\text{HNO}_3}^2 p_{\text{NO}}}{p_{\text{NO}_2}^3 p_{\text{H}_2\text{O}}} \quad (31)$$

with the partial pressures of nitrogen monoxide (p_{NO}) and nitrogen dioxide (p_{NO_2}) in the gas phase and the vapor pressures of nitric acid (p_{HNO_3}) and water ($p_{\text{H}_2\text{O}}$) over the dilute acid. In industrial absorption the equilibrium constant depends only on temperature. The equilibrium constant is conventionally split into two terms:

$$K_p = K_1 \cdot K_2$$

where $K_1 = \frac{p_{\text{NO}}}{p_{\text{NO}_2}^3}$ and $K_2 = \frac{p_{\text{HNO}_3}^2}{p_{\text{H}_2\text{O}}} \quad (32)$

K_2 depends on the acid concentration and the temperature. Gases (N_2O_4 , N_2O_3 , HNO_2) dis-

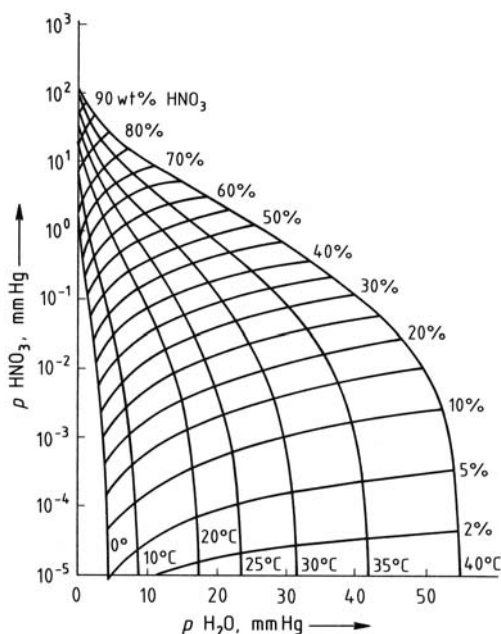
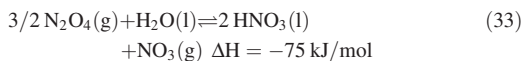


Figure 9. Vapor pressures of nitric acid and water as a function of acid strength and temperature [28] 1 mm Hg = 133.2 mPa

solved in the dilute acid affect the activities of nitric acid and water. Up to a nitric acid concentration of 65 wt % and an inlet nitrogen oxide partial pressure of 100 kPa, however, the vapor pressures from the binary system $\text{HNO}_3 - \text{H}_2\text{O}$ can be used to determine K_2 (Fig. 9).

Figure 10 shows how K_1 depends on the acid concentration and the temperature. This parameter is particularly interesting from an engineering standpoint because it allows the acid strength to be determined if the gas concentration is known.

If the equilibrium is based on the overall reaction



the equilibrium constant is

$$K_p = K_1 \cdot K_2$$

where $K_1 = \frac{p_{\text{NO}}}{p_{\text{N}_2\text{O}_4}^{3/2}}$ and $K_2 = \frac{p_{\text{HNO}_3}^2}{p_{\text{H}_2\text{O}}} \quad (34)$

Again Figure 9 gives the K_2 values. In this formulation, K_1 is a function of the acid

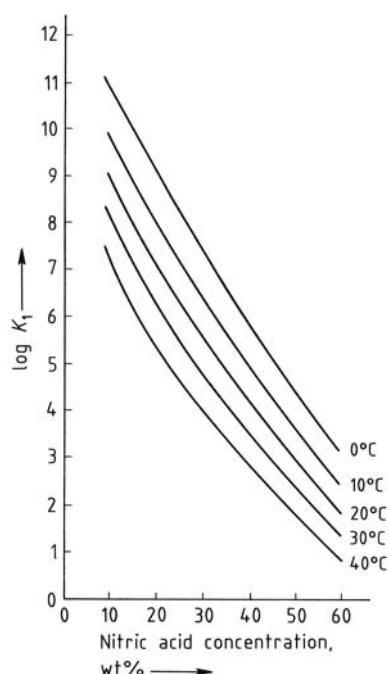


Figure 10. Value of K_1 from Equation (32) as a function of acid concentration and temperature [28]

concentration and does not depend on temperature (Fig. 11). The curve of Figure 11 can be fitted by an empirical equation [37]:

$$\log K_1 = 7.412 - 20.29W_{\text{HNO}_3} + 32.47W_{\text{HNO}_3}^2 - 30.87W_{\text{HNO}_3}^3 \quad (35)$$

where W denotes the mass fraction.

Another way of describing the absorption equilibrium is to start with the hypothetical component NO_2 denoted as “chemical NO_2 ”:

$$p_{\text{NO}_2} = p_{\text{NO}_2} + 2p_{\text{N}_2\text{O}_4} \quad (36)$$

The nitrogen dioxides, considered as completely dissociated, are assumed to react according to



This hypothetical reaction leads to the equilibrium relation

$$K_p = K_1 \cdot K_2$$

where $K_1 = \frac{p_{\text{NO}}}{p_{\text{NO}_2}^3}$ and $K_2 = \frac{p_{\text{HNO}_3}^2}{p_{\text{H}_2\text{O}}}$ (38)

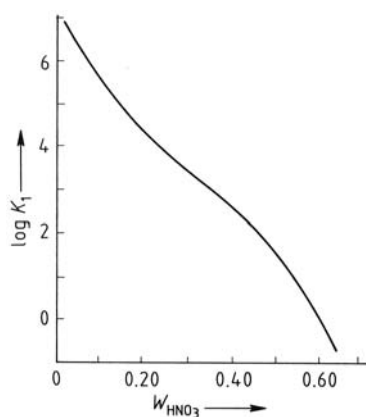


Figure 11. Value of K_1 from Equation (34) as a function of acid concentration

The equilibrium constant K_p can be estimated with the following equation [38]:

$$\log K_p = -7.35 + \frac{2.64}{T} \quad (39)$$

Then K_1 can be determined from K_p , and the K_2 values obtained from Figure 9. The parameter K_1 determines the equilibrium curves for constant temperature and constant acid concentration when p_{NO_2} is plotted against p_{NO} (Fig. 12). The K_1 values are necessary to calculate the absorption of nitrous gases according to TONIOLO [39]. The application of the Toniolo diagram is described in [40].

Modeling of the Absorption Tower. The literature offers many methods for calculating the absorption of nitrous gases; they can be classified according to the number of reactions, the reaction kinetics, or the type of mathematical method:

1. *Number of Reactions.* The simplest calculation model uses Equation (30) to describe the events on an absorption plate and a kinetic formula to describe nitrogen monoxide oxidation between two oxidation plates [41]. Extended models [42–45] also take into account the dimerization of nitrogen dioxide to dinitrogen tetroxide. In this way it is possible to describe nitric acid formation not just via nitrogen dioxide but also via dinitrogen tetroxide [46–49].

Models that include the formation and dissociation of nitrous acid in the liquid phase give

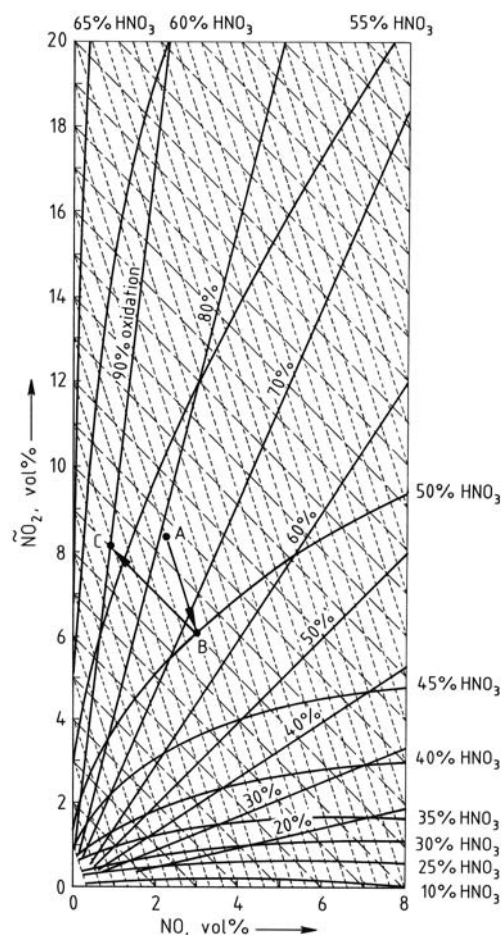


Figure 12. Toniolo diagram for an absorption tower [39]
A \rightarrow B absorption process; B \rightarrow C oxidation process

the best description of known chemical events [50], [50]. A model that permits nitrous acid formation in the gas phase has also been proposed [51].

2. *Reaction Kinetics.* Most design computations use equilibrium equations for the basic reactions. These static methods have the drawback of requiring the introduction of efficiency factors [51] that take into account limitation of transport of the reactants across the interface. Dynamic methods do not need empirical efficiency factors because they describe mass transfer in terms of physical and chemical laws [28], [31], [50], [52].
3. *Mathematical Methods.* In view of the large number of nonlinear equations to be solved in both equilibrium and dynamic models, plate-

to-plate calculations are generally described in the literature. The relaxation method [31] and a special stage-to-stage calculation [52], however, have also been used for the design of absorption towers.

By way of example, an equilibrium model and a transport model are described in more detail.

Equilibrium Model. The equilibrium model is based on Equations (11) and (33). If a gas of known composition is fed to the plate and an acid of known strength leaves the plate, the calculation begins at the bottom of the tower. If the gas throughput is taken to be constant (because of the high content of inerts), the following mass balance is obtained for the n -th plate:

$$3(y_{n,\text{NO}} - y_{n-1,\text{NO}}) = (y_{n-1,\text{NO}_2} + 2y_{n-1,\text{N}_2\text{O}_4}) - (y_{n,\text{NO}_2} + 2y_{n,\text{N}_2\text{O}_4}) \quad (40)$$

where y is the mole fraction in the vapor phase.

Equilibrium Equations (34) for K_{p_1} and (17) for K_{p_2} give the equation

$$ay_{n,\text{NO}_2}^3 + by_{n,\text{NO}_2}^2 + y_{n,\text{NO}_2} + d = 0$$

with $a = 3(K_{p_1}\sqrt{p})(K_{p_2}p)^{1.5}$

$$b = 2(k_{p_2}p)$$

$$d = -(3y_{n-1,\text{NO}} + y_{n-1,\text{NO}_2} + 2y_{n-1,\text{N}_2\text{O}_4})$$
(41)

This formula allows the compositions of the gas leaving the n -th plate and the acid arriving at the n -th plate to be determined.

Before the $(n + 1)$ -th plate is calculated, the oxidation of nitrogen monoxide must be determined. The flow behavior of the nitrous gases in an absorption tower is not known exactly, so the oxidation space can be described as either a tubular or a stirred-tank reactor. Actual conditions probably lie somewhere between the two [28], but trends can be identified on the basis of plate type. The stirred-tank model is preferred for bubble-cap trays [47], but flow-through conditions can be expected in the case of sieve plates. Because virtually all absorption towers today are fitted with sieve plates, only these are discussed.

When the reaction is carried out isothermally, integration of the rate equation

$$-\frac{dp_{\text{NO}}}{dt} = kp_{\text{NO}}^2p_{\text{O}_2} \quad (42)$$

gives a solution

$$\theta = \frac{2}{k(2p_{O_2} - p_{NO})} \cdot \left\{ \frac{x}{p_{NO}(1-x)} - \frac{1}{2p_{O_2} - p_{NO}} \ln \left[\frac{2p_{O_2} - p_{NO}x}{2p_{O_2}(1-x)} \right] \right\} \quad (43)$$

where

θ = residence time, s

k = rate constant, $\text{atm}^{-2} \text{s}^{-1}$

p = partial pressure, atm

t = time, s

x = fraction of oxidized nitrogen monoxide

in which x must be determined by iteration from the residence time θ and the inlet partial pressures of nitrogen monoxide (p_{NO}) and oxygen (p_{O_2}) [47]. The partial pressures of the other components leaving the reactor can be calculated from the fraction x of oxidized nitrogen monoxide.

If an excess of oxygen is assumed to be present, the rate equation can be simplified [53] as

$$-\frac{dp_{NO}}{dt} = kp_{NO}^2 \quad (44)$$

so that the partial pressure of nitrogen monoxide at the reactor outlet (p'_{NO}) can be determined:

$$\frac{1}{p'_{NO}} = \frac{1}{p_{NO}} + (2p_{O_2} - p_{NO}) \frac{k\theta}{2} \quad (45)$$

Because the oxidation reaction is highly exothermic, the tubular reactor can be designed for isothermal operation only when conversion is very low (e.g., when the tail gas contains little NO). Otherwise, adiabatic reaction conditions must be assumed. To describe the reaction under adiabatic conditions the oxidation space is divided into n layers, in each of which the reaction is isothermal. The temperature increase from one layer to the next is given by [33]

$$\Delta T = 1/2 \frac{C_{NO,0}(-\Delta H_R)}{Q_0 C_p} \frac{G_{NO,0} - G_{NO}}{G_{NO,0}} \quad (46)$$

where

$C_{NO,0}$ = initial concentration of NO, kmol/m^3

C_p = molar heat capacity, $\text{kJ kmol}^{-1} \text{K}^{-1}$

G_{NO} = molar gas flow rate, kmol/s

$G_{NO,0}$ = initial gas flow rate, kmol/s

ΔH_R = reaction enthalpy, kJ/kmol

Q_0 = initial density, kg/m^3

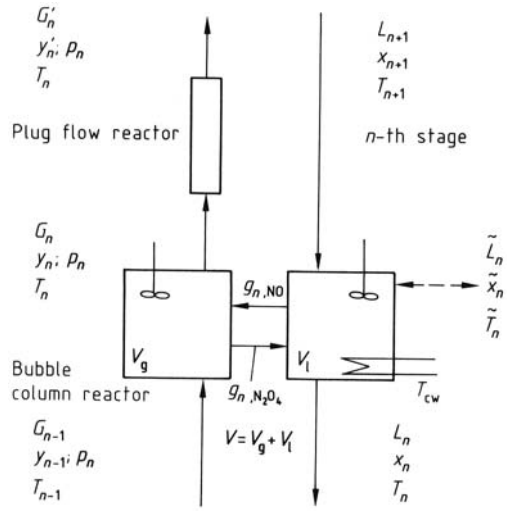


Figure 13. Hydrodynamic model of absorption tower g = molar gas flow rate of a component; G = molar flow rate of gas; L = molar flow rate of liquid; p = pressure; T = temperature; T_{cw} = temperature of cooling water; V = volume; x = mole fraction in liquid phase; y = mole fraction in gas phase

Transport Model. A transport model for the absorption tower is based on a series of units, each containing a bubble-column reactor and an adiabatic plug flow reactor (Fig. 13) [52]. The bubble-column reactor, modeled as two ideal stirred-tank reactors, simulates the liquid with gas bubbles on a tray (absorption space). The adiabatic plug flow reactor simulates oxidation between plates (oxidation space).

The balances are carried out with the equations

$$G_n y_{n,i} - G_{n-1} y_{n-1,i} - k_{g,i} a V \frac{p_n}{RT_n} (y_{n,i}^* - y_{n,i}) = V_g \sum_{j=1}^{M_g} v_{g,ij} r_{g,j} \quad (47)$$

$i = N_2, O_2, NO, NO_2, N_2O_4$ and $\sum_{i=1}^k y_{n,i} = 1$ for the components in the gas phase (subscript g) where

a = interfacial area per unit volume, m^2/m^3

G = molar gas flow rate, kmol/s

k_g = gas-side mass-transfer coefficient

M_g = number of reactions in the gas phase

n = plate number

r = reaction rate, $\text{kmol m}^{-3} \text{s}^{-1}$

V = volume of bubble layer

V_g = volume of gas phase in bubble layer

become overloaded and cause an excessive pressure drop. Filter life depends on the particulate load in the air (typically 0.8 mg/m^3). In areas where sandstorms may occur (maximum loading 500 mg/m^3), the use of a sand separator (a centrifugal collector) as a prefilter is recommended.

Ammonia Filters. The liquid ammonia filter removes solid contaminants, especially small rust particles; 99.9 % of all particles larger than $3 \text{ }\mu\text{m}$ should be eliminated. Selection of a liquid ammonia filter requires consideration of the fact that traces of oils and chlorides are also present in ammonia. Proven filter materials are Teflon and sintered metals. Polypropylene and ceramic filter candles (cartridges) are also employed. Magnetic filters have found some use but have limited capacity.

Filtration of ammonia gas should remove 99.9 % of oil and solid particles larger than $0.5 \text{ }\mu\text{m}$. The principal filter media are glass fibers, sintered metals, and ceramics. The pressure drop is up to 10 kPa, depending on filter type.

Filters for the Mixed Gas. The mixed-gas filter provides final cleaning of the ammonia – air mixture and improves the mixing of the air and ammonia; it should remove 99.8 % of all particles larger than $1.5 \text{ }\mu\text{m}$. Contaminants in the gas mixture not only originate externally (in the process air and ammonia) but are also formed by corrosion inside the system (rust). The gas mixture filter should therefore be installed as near as possible to the burner. Ceramic filter cartridges are generally used in which silicon dioxide is the dominant constituent. For a filter cartridge with a surface loading of $250 \text{ m}^3/\text{m}^2$, the maximum pressure drop in the clean state is 10 kPa.

Mixers. Static gas mixers are used for two purposes in nitric acid plants:

1. To mix ammonia and air in a ratio of ca. 1 : 10 for catalytic oxidation (see Section 1.3.1)
2. To mix ammonia and tail gas in a ratio of 1 : 100 for the catalytic reduction of NO_x as part of tail-gas treatment (see Section 1.4.2.3).

From an economic standpoint, homogeneous mixing of the gas streams upstream of the reactor

is important in both cases. Local ammonia excesses in the burner are a risk for plant safety (explosion limit) and may also cause overheating of the catalyst gauze. Poor mixing lowers the conversion of ammonia to nitrogen monoxide and increases platinum loss from the catalyst.

The efficiency of a given mixing operation is described by the standard deviation σ of measured samples from the theoretical value \bar{x} a certain distance downstream from mixing. In nitric acid plants, the deviation should be $< 1 \%$. If the theoretical ammonia concentration in a mixture is 10 %, for example, measured values fluctuate between 9.9 and 10.1 % [54]. Only static mixers are used (e.g., the Uhde tubular mixer or the Sulzer three-element mixer).

1.3.3.2. Burners and Waste-Heat Boilers

The heat of reaction liberated during ammonia combustion is utilized to produce steam and preheat the tail gas. Steam is produced in a waste-heat boiler located immediately below the burner (Fig. 15). The burner consists of a burner basket packed with filling material to ensure uniform distribution of the downward flowing reaction gas. Platinum recovery gauzes (Section Recovery of Precious Metals) are located above the filling material. The catalyst gauzes (Section Catalysts) are located above the recovery gauzes. The burner basket is clamped between the flanges of the burner head and the waste-heat boiler. To ensure better distribution of the reaction mixture, the burner head also contains a perforated plate or honeycomb grid. Hydrogen burners rotating above the surface are often used for ignition. The gauze temperature is measured, and the space above the gauze can be observed through inspection glasses. The gauzes glow bright red during catalysis. The throughput per element can produce up to 1200 t of 100 % nitric acid per day.

Waste-heat boilers up to 6 m in diameter are used. Figure 15 shows a waste-heat boiler for medium-pressure burning. The preevaporator is located directly below the burner basket and protects the downstream superheater against excessive temperature. The superheater is followed by the main evaporator. Evaporator tubes are also installed at the wall to cool it and protect it from excessive temperature.

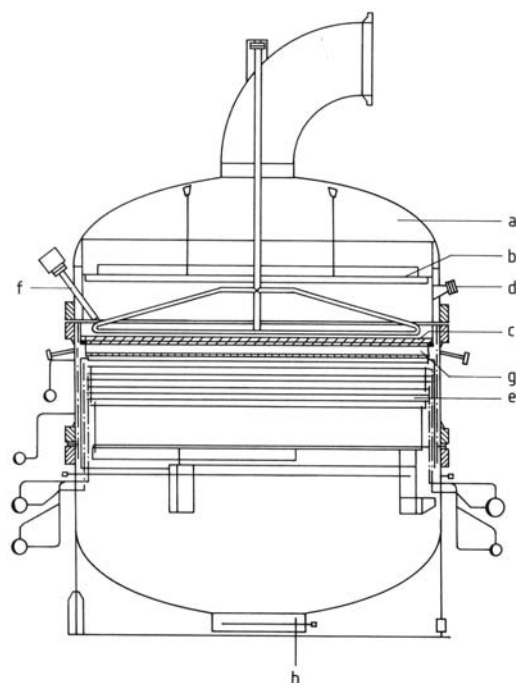


Figure 15. Reactor for catalytic ammonia oxidation with waste-heat recovery system (Lentjes) a) Burner head; b) Perforated plate; c) Platinum gauzes and platinum recovery gauzes; d) Inspection glass; e) Superheater and evaporator tubes; f) Hydrogen ignition; g) Refractory packing; h) Nitrous gas outlet

Figure 16 shows how heat from the waste-heat boiler is used to raise steam. Boiler feedwater is led through the economizer (b) into a steam drum (c). Water at thermal equilibrium with the steam is pumped from the drum through the evaporators. Steam from the drum goes first to the lower superheater (g) and is then cooled in the drum so that the desired temperature can be attained in the upper superheater (f).

Systems with an economizer integrated in the waste-heat boiler have also proved serviceable (Fig. 17). Here, as in the waste-heat boiler of Figure 15, the heat-exchanger tubes can be arranged spirally in disk form or in a square pack.

A shell-and-tube evaporator with natural circulation can also be used (Fig. 18). The superheater tubes (e) are again arranged as a flat spiral. These waste-heat boilers are particularly suitable for smaller plants or those using low steam pressure.

Stress cracking corrosion is a special threat to economizer tubes. Start-up always leads to the formation of ammonium salts; nitrous and nitric acids may also condense. To prevent very rapid corrosive attack, the equipment is therefore heated before start-up and the feedwater is preheated to a high temperature.

Waste-heat boilers can be designed for pressures up to 10 MPa and temperatures up to 550 °C in the superheater. The steam is used to drive a turbine or is exported.

1.3.3.3. Compressors and Turbines

Machines on a common shaft are used to deliver and compress the gases and supply the drive power needed for this purpose. Power sources are the tail-gas turbine and a steam turbine or electric motor. The tail-gas turbine can supply 35 – 100 % of the compression energy required for the process, depending on the degree of preheating; the remainder comes from the steam turbine. The machinery used depends on the nitric acid process and may consist of an air compressor, a nitrous gas compressor, a tail-gas turbine, and a steam turbine or an electric motor.

Figure 19 shows the nitric acid process with atmospheric combustion and medium-pressure (400 – 600 kPa) absorption. The nitrous gas compressor (b) sucks the reaction mixture through the burner and simultaneously provides the pressure needed for absorption. This compressor does not have interstage cooling and can be of radial or axial design. The tail gas from the absorption column is expanded in a tail-gas turbine (d), usually a single-stage device. The rest of the power required to drive the nitrous gas compressor is supplied by the steam turbine or an electric motor.

Figure 20 shows a medium-pressure process (400 – 600 kPa), as preferred for small- or medium-capacity plants (≤ 600 t/d 100 % HNO_3). The machinery for this process includes a radial or axial air compressor (a) without interstage cooling, a single-stage tail-gas turbine (d), and a steam turbine (e) or electric motor.

A dual-pressure process with medium-pressure combustion and high-pressure absorption calls for both an air compressor and nitrous gas compressor (Fig. 21). The air for combustion is delivered at 400 – 600 kPa by an uncooled radial

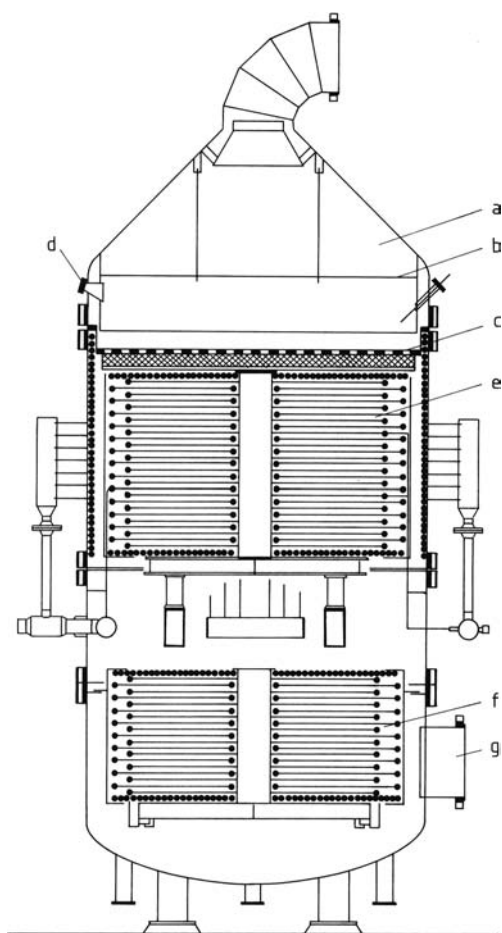


Figure 17. Reactor for catalytic ammonia oxidation with integrated waste-heat recovery system (Steinmüller) a) Burner head; b) Perforated plate; c) Platinum gauzes and platinum recovery gauzes; d) Inspection glass; e) Superheater and evaporator tubes; f) Feedwater preheater; g) Nitrous gas outlet

Tail-gas turbines can be single-stage or multistage devices of axial or radial design. For part-load operation, these machines are equipped with a group of valve-controlled nozzles or adjustable guide vanes in the inlet.

Steam turbines may be condensing or back-pressure machines with or without an extraction/side stream.

1.3.3.4. Heat Exchangers and Columns

Heat Exchangers. The shell-and-tube design predominates for tail-gas heat exchangers,

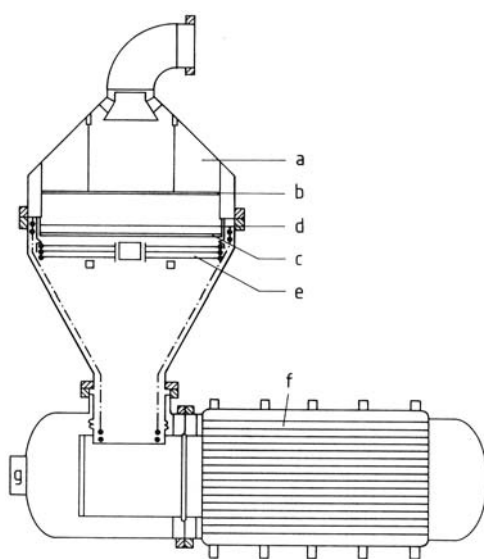


Figure 18. Reactor for catalytic ammonia oxidation with integrated waste-heat recovery system (Steinmüller) a) Burner head; b) Perforated plate; c) Platinum gauzes; d) Packing; e) Superheater tubes; f) Evaporator; g) Nitrous gas outlet

with hot nitrous gas on the tube side and cool tail gas on the shell side. The pressure drop should be kept as low as possible to secure a favorable energy balance for the plant as a whole.

Ammonia Evaporator. Various types of equipment can be used for ammonia evaporation. Figure 23 shows a shell-and-tube heat exchanger with mist collector. Cooling water on the tube side is cooled on evaporation. In medium-pressure plants, the heat of vaporization is also taken from chilled water used as coolant in the absorption step. The shell-side heat-transfer coefficients for ammonia can be calculated according to [57].

Gas Cooler – Condenser. In the cooler – condenser, the temperature is lowered below the dew point of the inlet nitrous gas. The nitric acid condensate has a concentration of, for example, ca. 40 wt % at medium pressure. Suitable materials of construction are discussed in Section 1.3.3.5. The thermal design of a gas cooler – condenser is difficult because the cooling step involves chemical reactions in both the gas and the condensed liquid phases. In the apparatus shown in Figure 24, nitrous gas passes into the shell side through two inlets; each of the partial

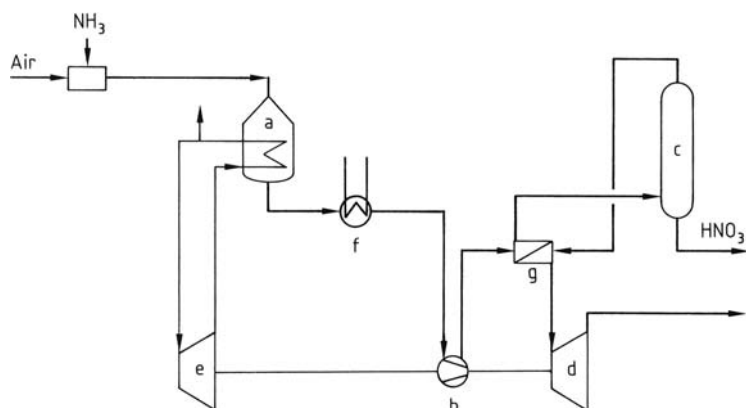


Figure 19. Flow sheet of a nitric acid process with atmospheric combustion and medium-pressure absorption a) Reactor with waste-heat recovery system; b) Nitrous gas compressor; c) Absorption tower; d) Tail-gas turbine; e) Steam turbine; f) Cooling system; g) Heat exchanger network

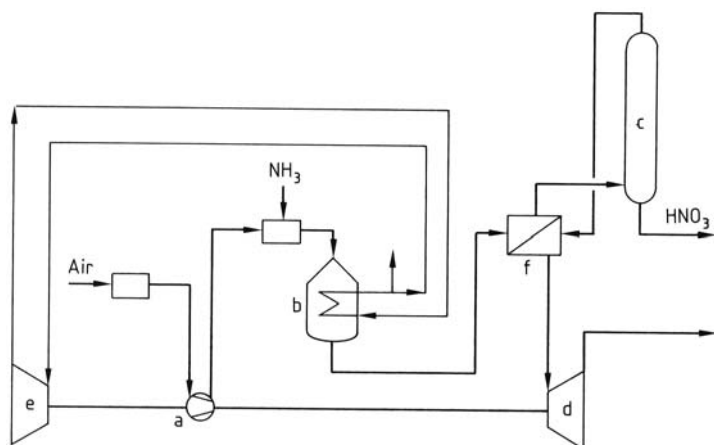


Figure 20. Flow sheet of a nitric acid process with medium-pressure combustion and medium-pressure absorption a) Air compressor; b) Reactor with waste-heat recovery system; c) Absorption tower; d) Tail-gas turbine; e) Steam turbine; f) Heat exchanger network

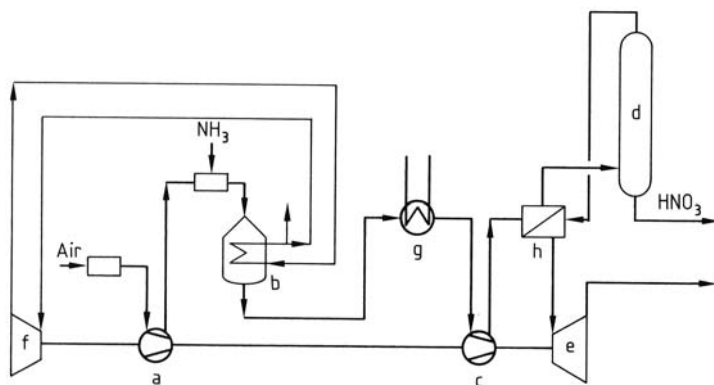


Figure 21. Flow sheet of a nitric acid process with medium-pressure combustion and high-pressure absorption a) Air compressor; b) Reactor with waste-heat recovery system; c) Nitrous gas compressor; d) Absorption tower; e) Tail-gas turbine; f) Steam turbine; g) Cooling system; h) Heat exchanger network

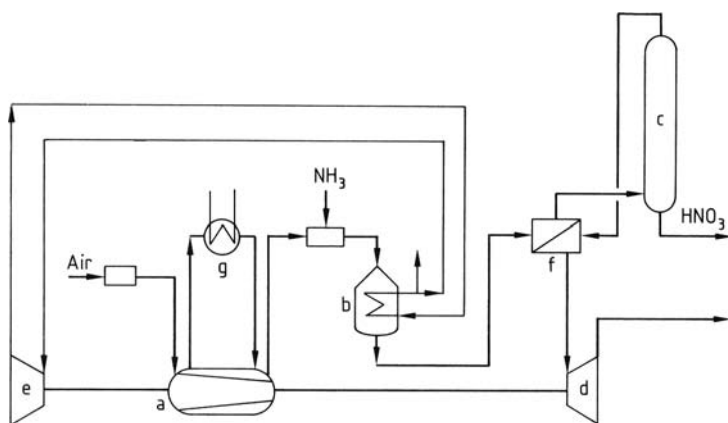


Figure 22. Flow sheet of a nitric acid process with high-pressure combustion and high-pressure absorption a) Air compressor; b) Reactor with waste-heat recovery system; c) Absorption tower; d) Tail-gas turbine; e) Steam turbine; f) Heat exchanger network; g) Interstage cooler

streams reverses direction four times. Heat is absorbed by cooling water.

Absorption Tower. Absorption tower design is governed by the calculations for the oxidation process (i.e., tower height, see also Section 1.3.2) and thermal design. Because oxidation proceeds more slowly as the NO_x content in the tower decreases, the spacing between plates increases. Figure 25 shows an absorption tower for a plant with a daily production capacity of 1830 t of 100 % nitric acid. Acid formation takes place chiefly in the bottom third of the

tower, whereas NO_x is reduced in the upper two-thirds. As a result, most of the heat must be withdrawn in the lower third; this is done with cooling coils on the plates. The coils on the upper plates primarily cool the nitrogen monoxide gas against chilled water, because oxidation proceeds faster at lower temperature. Most modern absorption towers have sieve plates. Compartments built into the bottom of the tower separate acid of medium strength from weak acid in case of plant shutdown. The collected acids are pumped back to the tower at restart so that a steady state is reached more quickly. Before the

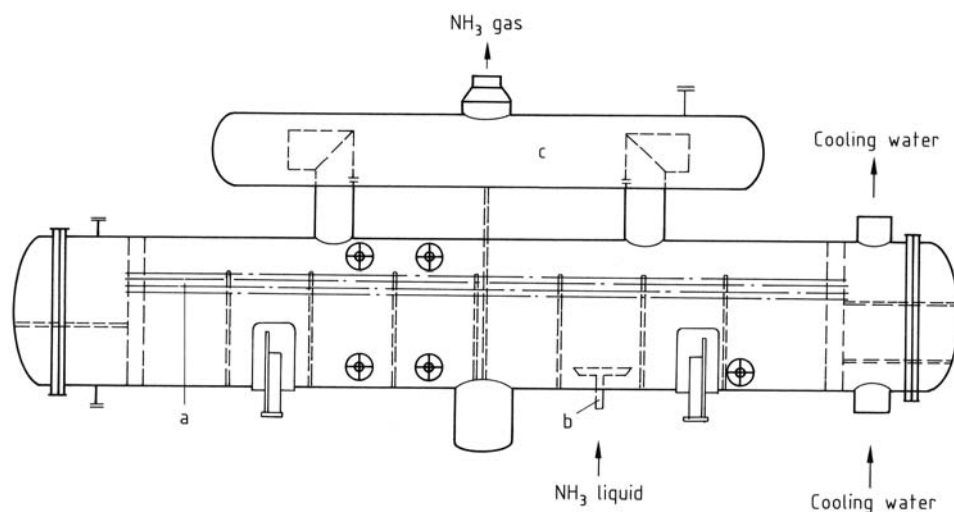


Figure 23. Ammonia evaporator a) Evaporator tubes; b) Sparger; c) Drop separator

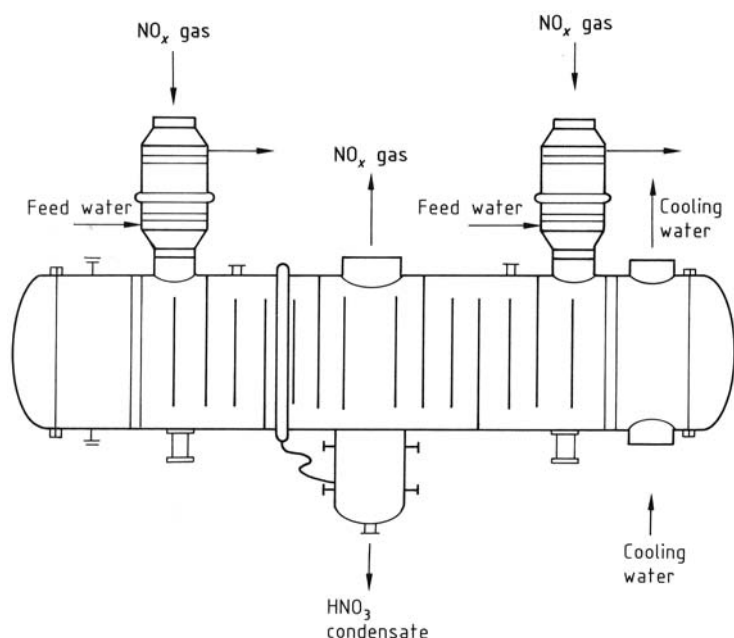


Figure 24. Cooler – condenser with feedwater preheaters attached to nitrous gas inlets

tail gas leaves the tower, entrained acid droplets are collected in the demister.

Bleacher. The NO_x gases contained in the acid are stripped out with secondary air in the bleacher. A distribution tray delivers the acid evenly onto the Raschig ring packing. The packing rings are made of stainless steel, material no. 1.4301 (AISI 304) or 1.4306 (AISI 304L).

1.3.3.5. Construction Materials

Because of the special behavior of nitric acid toward metals (see Section 1.2), materials of construction for nitric acid plants must be selected very carefully. When industrial production began, acid-resistant masonry linings were used for plant components that came in contact with the product. By the 1920s, materials technology had advanced to the point that high chromium contents could be incorporated into alloy steels. Today, the principal materials of construction in nitric acid plants ($< 70\% \text{HNO}_3$) are austenitic chromium – nickel steels containing 18% chromium and 10% nickel. The corrosion resistance of these steels decreases with increasing temperature. Normal austenitic steels are generally not stable above 70%. The chromium content de-

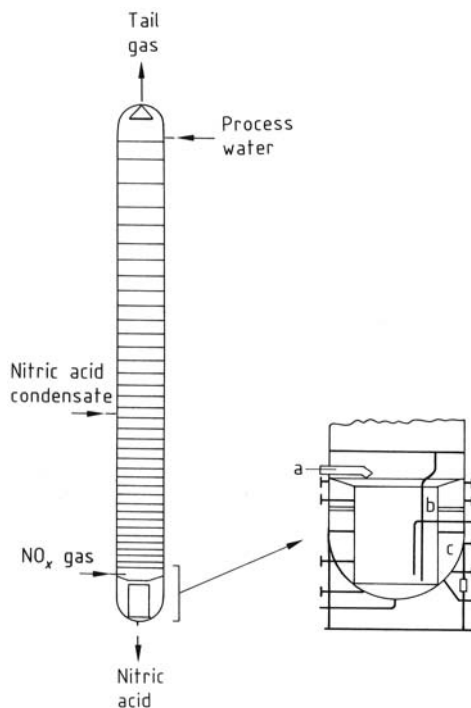


Figure 25. Absorption tower a) Nitrous gas inlet; b) Inner compartment; c) Outer compartment

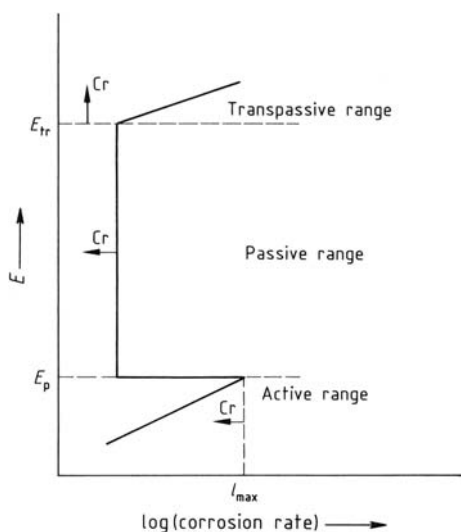


Figure 26. Anodic polarization curve for stainless steel Cr denotes the effect of chromium on the anodic polarization rate

termines the corrosion resistance; its anticorrosive action is influenced by the carbon content of steel. The chromium in the alloy forms a carbide (Cr_3C_2) at the grain boundaries; only small amounts of free chromium remain at high carbon contents, and the steel is therefore less corrosion resistant. If excess chromium remains after the amount needed for carbide formation is consumed, only this excess is responsible for the anticorrosion properties.

The effect of chromium on the corrosion rate is shown in the anodic polarization curve of Figure 26. When chromium is present in the alloy, the passive region E_p (see Section 1.2) is reached sooner. Furthermore, chromium lowers the corrosion rate in the passive state and raises the transpassive potential E_{tr} . The last

point is important because the corrosion potential of stainless steel in strong (highly concentrated) nitric acid often reaches the limit of the transpassive potential. In the transpassive range the passive layer starts to dissolve. A steel with too little chromium or with elements that lower the transpassive potential tends to corrode at a high rate [58].

Steels of a given specification behave differently under nitric acid attack because of permitted batch-to-batch variations in composition. The only way to be sure that a selected steel is suitable for an apparatus in contact with nitric acid is to perform tests. The best known method is the Huey test, in which a clean, polished piece of steel is immersed in boiling 65 % nitric acid at ambient pressure [59]. The specimen is exposed to these conditions for five successive 48-h periods, the acid being renewed at the beginning of each test period. The Huey test gives a good indication of how individual alloy constituents affect intergranular corrosion.

To ensure good weldability, the carbon content is limited to 0.03 %; alternatively, titanium or niobium is added as a stabilizer.

The stainless steels generally used in nitric acid plants are those classified under material no. 1.4306 (AISI 304L); in the Federal Republic of Germany, however, the corresponding stabilized qualities, material no. 1.4541 (AISI 321) and 1.4550 (AISI 347), are also employed (Table 4). These steels are usually specified for towers and heat-exchanger shells, and also for many heat-exchanger tubes. The 1.4335 steel (AISI 310L) has a very low corrosion rate and is used particularly where corrosive attack is severe, for example, if the temperature is below the dew point of nitrous gas, even at higher

Table 4. Chemical analyses (wt %) of standard and special stainless steels [59]

Type of steel		C max.	Si max.	P max.	S max.	Cr	Ni	Other
AISI	304L	0.035	0.75	0.040	0.030	18 – 20	8 – 13	
	321	0.08	0.75	0.040	0.030	17 – 20	9 – 13	Ti
	347	0.08	0.75	0.040	0.030	17 – 20	9 – 13	Nb
ISO	1.4306	0.03	1.0	0.045	0.030	17 – 20	10 – 12.5	
	1.4541	0.10	1.0	0.045	0.030	17 – 19	9 – 11.5	Ti
	1.4550	0.10	1.0	0.045	0.030	17 – 20	9 – 11.5	Nb
Sandvik	3R12*	0.030	0.60	0.030	0.030	18.5	10.5	
	2R12*	0.020	0.10	0.015	0.010	18.5	11	
	2RE10**	0.020	0.30	0.020	0.015	24.5	20.5	

* ISO material no. 1.4306.

** ISO material no. 1.4335.

temperatures [59]. These conditions normally occur at the inlet to the tail-gas preheater, in the dew point region of the cooler – condenser, and at the outlet of the feedwater preheater. Corrosion at these locations is caused mainly by reevaporation of nitric acid condensate, which brings the acid concentration up to the azeotropic level (69 % HNO_3). The acid is then very aggressive, even in the vapor phase. Corrosion can take place in the boiler feedwater preheater if condensate forms at the outlet. Reheating of the condensate by the hot process gas can lead to critical conditions. Process design parameters should normally be selected so as to avoid condensation; material no. 1.4306 is then adequate. If, however, condensation or reboiling occurs and this steel cannot be used, 1.4335 should be employed [60].

In plants producing concentrated nitric acid, aluminum (99.8 %), ferrosilicon, tantalum, and special austenitic steels are used. Because tantalum is very expensive, it is employed only with boiling concentrated nitric acid. Ferrosilicon can be used only in castings because of its brittleness.

1.3.4. Processes

Figure 14 illustrates the steps necessary for implementation of the Ostwald process. Industrial processes differ in the sequence and design of these steps. This section describes processes for the production of weak acid [61, pp. 61 – 98] and strong acid [61, pp. 99 – 130].

1.3.4.1. Weak Acid Processes

The first industrial plants for the production of weak acid employed atmospheric combustion and low-pressure absorption [3]. This type of plant is no longer built. It was followed by a process employing atmospheric combustion and absorption at medium pressure. This process has the advantage of lower absorption costs because the marked improvement in absorption obtained with the pressure generated by a nitrous gas compressor allows the apparatus to be downsized. The energy of compression can be partially recovered with a tail-gas turbine. To circumvent the difficulty of operating a compressor for nitrous gas and obtain a further decrease in plant volume, to ammonia was also oxidized at medi-

um pressure. This type of process is particularly economical for smaller capacities and is thus described first.

As plant capacities continued to grow and lower tail-gas levels of NO_x were necessary the absorption pressure was increased still further. Lower energy costs and shorter depreciation periods in the United States have led to a preference for the high-pressure process, whereas more favorable consumption and production figures in Europe have favored the dual-pressure process with medium-pressure combustion and high-pressure absorption.

The principle of medium- and high-pressure (monopressure) plants is that air for ammonia oxidation and NO_x absorption is compressed to the desired pressure. The “primary” air for oxidation is then mixed with ammonia and forced through the burner. The “secondary” air for stripping dissolved NO_x out of the raw acid and oxidizing the intermediate nitrogen monoxide is supplied upstream of the absorption tower. The tail gas is heated and then expanded in a turbine (on a common shaft with the compressor) to produce mechanical energy. The remaining drive power is supplied by a steam turbine running on process steam.

Medium-Pressure Process. Figure 27 is a flow sheet of a medium-pressure process (ca. 550 kPa). Liquid ammonia is evaporated at ca. 700 kPa in the ammonia evaporator (a). The cold generated can be used in the absorption step. Water is removed from liquid ammonia in an ammonia stripper (b). The ammonia – water blowdown mixture is evaporated batchwise with steam. Residual aqueous ammonia can be used in fertilizer production. The ammonia vapor is heated with steam to ca. 90 °C in the ammonia preheater (c) and then filtered (d). If necessary, a small stream of ammonia is diverted to tail-gas treatment.

All the air needed for the process is sucked in through the air filter (f) by the air compressor (g). The compressed air is divided into two sub-streams in a tail-gas preheater (h). The secondary air goes to the bleacher (x) for stripping raw acid. The secondary airstream exiting the bleacher is laden with NO_x and is added to the nitrous gas before it enters the absorption tower (p). The greater part of the process air, the primary air, is mixed with the superheated ammonia in the

Cooling water flowing through coils on the sieve trays removes heat generated by the oxidation of nitrogen monoxide to nitrogen dioxide and its further conversion to nitric acid. Part of the heat absorbed by the cooling water is utilized to evaporate ammonia. A demister in the head of the tower collects liquid droplets entrained in the tail gas; the condensate runs back to the last tray of the absorption tower.

The tail gas absorbs heat from the secondary air and the nitrous gas in three tail-gas preheaters. In the BASF catalytic tail-gas treatment (r; see also Section 1.4.2.3), ca. 60 vol % of the NO_x in the tail gas is selectively reacted with ammonia. Hot tail gas containing < 200 ppm NO_x goes to the tail-gas expansion turbine (s), in which mechanical energy is produced to drive the air compressor. Finally, the tail gas is discharged to the atmosphere via the stack.

The tail-gas expansion turbine supplies part of the power needed to drive the air compressor. The

rest is generated by a condensing steam turbine supplied with product steam. The turbine may be bled. The steam turbine condensate goes to the boiler feedwater preheater (n) where it absorbs heat from the NO_x gas and then flows through the deaerator into the feedwater tank (t). Nondeaerated feedwater from the battery limit also flows via a preheater into the feedwater tank. The boiler feedwater pump raises the pressure of the deaerated feedwater to the requisite boiler pressure. Product steam is raised with heat from ammonia combustion in the waste-heat boiler (j).

Most of the steam generated in the waste-heat boiler drives the condensing steam turbine. The remainder can be utilized in the ammonia preheater and stripper and for deaerating the feedwater; any excess is exported as product steam.

High-Pressure Process. Figure 28 shows a high-pressure process running at ca. 1 MPa.

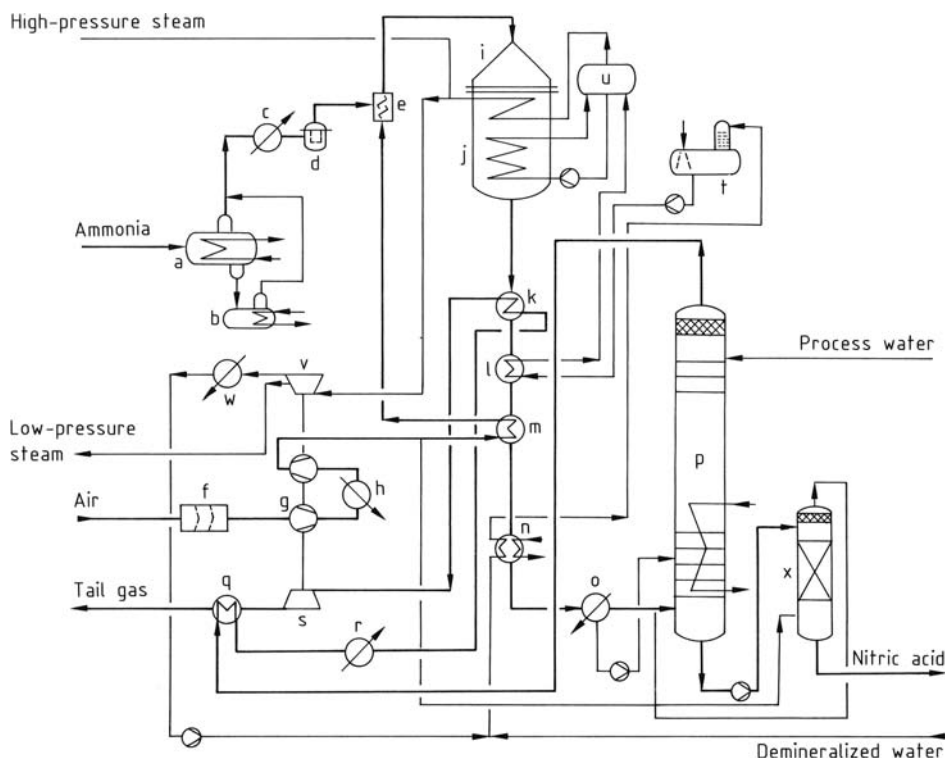


Figure 28. Simplified flow sheet of a high-pressure process a) Ammonia evaporator; b) Ammonia gas filter; c) Ammonia preheater; d) Ammonia gas filter; e) Ammonia – air mixer; f) Air filter; g) Air compressor; h) Interstage cooler; i) Reactor; j) Waste-heat boiler; k) Tail-gas preheater; l) Economizer; m) Air preheater; n) Feedwater and warm-water preheaters; o) Cooler – condenser; p) Absorption tower; q) Tail-gas preheater; r) Tail-gas preheater; s) Tail-gas expansion turbine; t) Feedwater tank with deaerator; u) Steam drum; v) Steam turbine; w) Steam turbine condenser; x) Bleacher

Liquid ammonia is fed into the evaporator (a), where it is evaporated at ca. 1.15 MPa against warm water. The evaporation temperature rises slightly above 35 °C as the water content builds up in the evaporator. The ammonia – water blowdown mixture is evaporated with low-pressure steam in the ammonia stripper (b). The residual ammonia concentration is ca. 2.5 %.

Ammonia exiting the evaporator system is heated to ca. 130 °C in the ammonia preheater (c), and contaminants are removed in the ammonia gas filter (d).

Air is sucked in through the air filter (f) and compressed to ca. 1 MPa in an air compressor (g) with interstage cooling (h). The primary air (ca. 80 % of the total) is heated to ca. 180 °C against nitrous gas in the air heater (m) and then fed to the ammonia – air mixer (e). The mixed gas stream has a temperature of ca. 175 °C and contains 10.7 vol % ammonia. It passes through a filter (not illustrated) into the reactor (i) where the ammonia and atmospheric oxygen react over the platinum – rhodium catalyst at ca. 900 °C to form mainly nitrogen monoxide and water.

The reaction gases next pass through the waste-heat boiler (j), where they are cooled to ca. 400 °C. The heat is used to raise high-pressure steam and superheat it to 500 °C in the preevaporator, superheater, and reevaporator of the boiler.

The boiler system is fed with condensate from the steam turbine condenser (w) plus demineralized water from the battery limit. Both streams are led to a tank and from there go through the feedwater preheater (n) to the deaerator mounted on the feedwater tank (t) and operating at a slight gauge pressure. The tank serves as suction vessel for the feedwater pumps, which deliver water through the economizer into the boiler drum (u).

The water – steam mixture in the evaporator is circulated by the boiler circulation pump. Saturated steam and water are separated in the boiler drum (u).

After leaving the waste-heat boiler (j), the nitrous gas is cooled to ca. 260 °C in a tail-gas preheater (k). After passing through a run of piping for oxidation, nitrous gas gives up more useful heat in the economizer (l), and its temperature falls to ca. 210 °C. After another oxidation run, the stream is led into the air heater (m) and cooled to ca. 180 °C. The heat recovered is used to preheat the primary air.

Before the nitrous gas is led into the gas cooler – condenser (o), it passes through feed-water preheaters and through the warm-water heater (n) both mounted on the two inlets of the cooler – condenser. The nitrous gas is cooled to ca. 115 °C and partly condensed before entering the cooler – condenser.

In the water-cooled cooler – condenser (o), the gas is cooled to < 50 °C so that water formed during ammonia oxidation condenses to produce ca. 45 % acid. This product is delivered to the appropriate tray of the absorption tower (p) by the acid condensate pump. The NO_x-laden secondary air recycled from the bleacher (x) is mixed with the nitrous gas stream before it is fed into the tower (p).

In the sieve-tray absorption tower (p) the nitrous gas flows countercurrently to the process water fed at the column head, and nitric acid is formed. Heat from the absorption tower is transferred to the cooling water. Raw acid from the absorption tower is treated with secondary air in the bleacher (x), then delivered to battery limit with the aid of the system pressure.

Tail gas exits the absorption tower at ca. 20–30 °C. It is heated to ca. 80 °C in a tail-gas preheater (q) against the tail-gas stream from the expansion turbine. The tail gas is further heated to 140 °C against low-pressure steam (r) and then to ca. 375 °C in a tail-gas preheater (k). It is subsequently expanded in the tail-gas turbine (s); this step produces ca. 70 % of the energy required to drive the air compressor.

Tail gas exits the turbine at ca. 135 °C and is led to a tail-gas preheater (q), where it is cooled to ca. 90 °C before being discharged through the stack.

The rest of the power needed to drive the air compressor can be supplied by a pass-out condensing steam turbine (v). The superheated steam is delivered to the steam turbine or exported. Part of the steam supplied to the turbine is withdrawn as low-pressure steam before admission to the condensing section. This low-pressure steam is used in the plant or exported. The rest of the steam supplied to the turbine passes through the condensing section and is condensed in the steam turbine condenser (w).

Dual-Pressure Process. The dual-pressure process combines the favorable economics of

medium-pressure combustion with the efficiency of high-pressure absorption. Figure 29 is a flow sheet of such a plant with ammonia combustion at 0.5 MPa and absorption at 1.1 MPa.

Liquid ammonia is fed to the ammonia evaporator (a), which is under a pressure of ca. 0.65 MPa. The entire stream then goes to ammonia evaporator I, where ca. 80 % of the ammonia is evaporated against cold water at a constant temperature of ca. 12 °C. Residual liquid ammonia is fed to ammonia evaporator II (not illustrated) and evaporated at varying temperatures against cooling water. The evaporation temperature increases from 12 °C to ca. 20 °C as water content builds up in the evaporator. Ammonia evaporator II is designed so that the entire ammonia stream can be evaporated in it, if necessary, at a maximum temperature of 20 °C. If the water content or the evaporation temperature in ammonia evaporator II is too high, the

ammonia – water mixture is blown down and fed to the ammonia stripper (b). Ammonia is stripped to a residual content of ca. 2.0 % as the temperature is raised to 150 °C with low-pressure steam. The residue, greatly depleted in ammonia, is discharged.

Gaseous ammonia from the evaporator system is passed through the ammonia gas filter (c) to remove contaminants, then heated to ca. 150 °C in the ammonia preheater (d).

Air is sucked through the filter (f) and compressed to 0.5 MPa in the compressor (g). About 86 % of the air is fed as primary air to the ammonia – air mixer (e). The mixed gas stream has a temperature of ca. 220 °C and contains ca. 10 vol % ammonia. It is transported through the gas-mixture filter (not illustrated) to the reactor (h). Here, ammonia reacts on the platinum – rhodium catalyst with atmospheric oxygen at 890 °C to produce a 96.5 % yield of nitrogen monoxide and water.

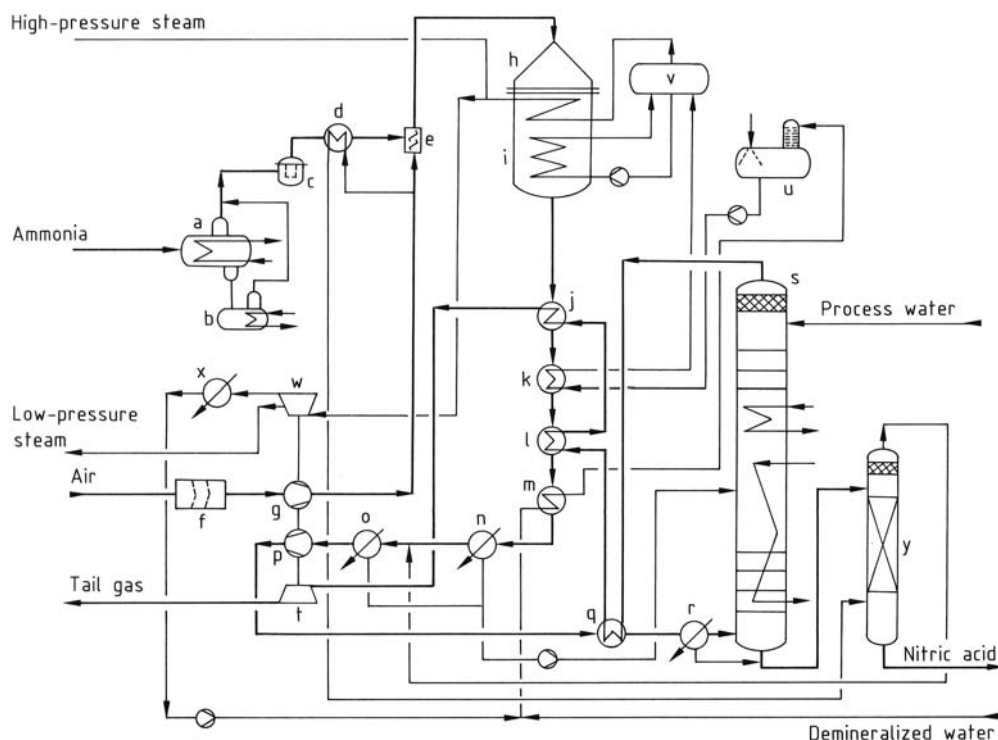


Figure 29. Simplified flow sheet of a dual-pressure process a) Ammonia evaporator; b) Ammonia stripper; c) Ammonia gas filter; d) Ammonia preheater; e) Ammonia – air mixer; f) Air filter; g) Air compressor; h) Reactor; i) Waste-heat boiler; j) Tail-gas preheater III; k) Economizer; l) Tail-gas preheater II; m) Feedwater preheater; n) Cooler – condenser I; o) Cooler – condenser II; p) Nitrous gas compressor; q) Tail-gas preheater I; r) Cooler – condenser III; s) Absorption tower; t) Tail-gas expansion turbine; u) Feedwater tank with deaerator; v) Steam drum; w) Steam turbine; x) Steam turbine condenser; y) Bleacher

The reaction gases next pass through the waste-heat boiler (i) and are cooled to 355 °C. The heat is used to raise high-pressure steam in the preevaporator, superheater, and reevaporator of the boiler.

The boiler system is fed with condensate from the steam turbine condenser (x) plus demineralized water from the battery limit. Both streams are led to a tank and then pass through the feedwater preheater (m) to the deaerator mounted on the feedwater tank (u). The tank serves as a suction vessel for the feedwater pumps, which deliver the water through the economizer (k) into the steam drum (v).

The water – steam mixture in the evaporator is circulated by the boiler circulation pump. Saturated steam and water are separated in the steam drum (v).

After exiting the waste-heat boiler and passing through a run of piping for oxidation, the nitrous gas is cooled from 390 to 280 °C in tail-gas preheater III (j). After further oxidation, it enters the economizer (k), where it is cooled from 310 to 200 °C. The nitrous gas gives up further useful heat to the tail gas in tail-gas preheater II (l) and its temperature falls to ca. 170 °C.

The gas passes through the feedwater preheater (m), mounted on the cooler – condenser inlet and thereby cools to ca. 100 °C. In the water-cooled cooler – condenser I (n), the gas is cooled to < 50 °C so that the water formed during ammonia oxidation condenses. A ca. 43 % acid results and is pumped to the appropriate tray of the absorption tower (s). The secondary air laden with NO_x and recycled from the bleacher (y) is now mixed with the nitrous gas stream. The mixed stream is then led into cooler – condenser II (o), where it is cooled to ca. 45 °C against chilled water. More water condenses and a ca. 52 % acid is formed, which is forwarded for absorption along with acid formed in cooler – condenser I. The gas is passed through a mist collector (not illustrated) upstream of the nitrous gas compressor (p).

The nitrous gas is compressed to 1.1 MPa in the compressor (p) and has an outlet temperature of ca. 130 °C. It passes to tail-gas preheater I (q), where it is cooled to ca. 75 °C. Downstream of the preheater is cooler – condenser III (r), which the nitrous gas leaves at 50 °C. The resulting acid condensate has a concentration of ca. 58 wt %

and is mixed with the raw acid from the absorption column.

From cooler – condenser III the nitrous gas, now at least 90 % oxidized, enters the absorption tower (s). The gas first passes through oxidation trays that receive only a slight flow of liquid, to attain the degree of oxidation needed for equilibrium with 68 % acid. In the absorption section, gas and liquid move countercurrently. Required process water is pumped to the tower head. The 68 % raw acid is withdrawn from the first absorption tray and then treated with secondary air in the bleacher (y). It is delivered to the battery limit with the aid of the system pressure.

Approximately 80 % of the heat generated by absorption is transferred to the cooling water and the remainder to the chilled water employed in the last part of the absorption step where very little heat of reaction is liberated.

The tail gas contains < 150 – 200 ppm NO_x and exits the absorber at 20 °C. It is heated to 110, 200, and finally 350 °C in the three downstream tail-gas preheaters (q, l, and j) before being expanded in the tail-gas turbine (t). The turbine supplies ca. 67 % of the power required by the air and the nitrous gas compressors. The expanded tail gas has a temperature of ca. 100 °C and is discharged through a stack.

The remaining power required to drive the rotating machinery can be obtained from a pass-out condensing steam turbine (w). Superheated steam is fed to the turbine or exported. Part of the steam supplied to the turbine may be withdrawn as low-pressure steam before it enters the condensing section. This low-pressure steam may be used in the plant or exported. The remainder of the steam fed to the turbine passes through the condensing section and is condensed in the steam turbine condenser (x).

Comparison of Medium- and High-Pressure Processes. [62]. Two trends can be seen in the worldwide development of weak acid processes. First, from the process-engineering standpoint, a progression occurs from low-through medium- to high-pressure processes [5]. Second, capacities continue to increase; single-train plants producing up to 2000 t of nitric acid per day are now being built. In Europe, the dual-pressure design is preferred for larger plants, whereas smaller ones employ the mono-

Table 5. Comparison of significant specific consumption figures for nitric acid plants (values are given per tonne of 100 % HNO_3 , the tail gas contains < 200 ppm of NO_x)

Parameter	Monopressure processes		Dual-pressure process
	Medium pressure	High pressure	
Operating pressure, MPa	0.55	1.080	0.45/1.1
Ammonia, kg	282*	283	279
Electric power, kW · h	8.5	8.0	9.0
Platinum, g	0.14	0.30	0.11
Cooling water, t ($\Delta t = 10\text{ }^\circ\text{C}$)**	120	125	130
Process water, t	0.3	0.3	0.3
Low-pressure heating steam, t	0.1	0.1	0.1
High-pressure excess steam, t (2.5 MPa, 400 $^\circ\text{C}$)	0.87	0.78	0.81

* Includes 1 kg NH_3 for NO_x reduction from 600 to < 200 ppm.

** Includes water for steam turbine compressor.

pressure design. Where feedstock and energy prices are low, monopressure operation offers special advantages; low investment costs ensure a quick payout, particularly in North America. If, on the other hand, feedstock and energy prices are very high (as in Europe), yield and energy efficiency must be maximized, so higher investment costs are acceptable. Table 5 compares consumption figures per unit product for monopressure and dual-pressure processes.

New pollution control regulations and the energy crisis of the mid-1970s have also led to the development of new processes or the improvement of existing ones. To avoid the need for catalytic tail-gas treatment in large-tonnage plants (and thus an increase in specific ammonia consumption), new facilities employ higher absorption pressures.

1.3.4.2. Concentrated Acid Processes

Industrially produced nitric acid contains 50 – 70 wt % HNO_3 . This is high enough for fertilizer production, but nitration processes in industrial organic chemistry call for concentrated acid (98 – 100 %). Distillation, the simplest way to concentrate dilute acid, fails because nitric acid and water form an azeotrope (68.4 % HNO_3 at atmospheric pressure).

Concentrated nitric acid is manufactured directly or indirectly [63]. In the *direct process*, the water generated in ammonia combustion is withdrawn by rapid cooling to give a nitrous gas mixture from which concentrated acid can be produced directly in one of two ways. First, the completely oxidized NO_x can be separated in liquid form by absorption in concentrated nitric

acid and then led to a reactor where it is reacted with oxygen and water (or weak acid) under pressure to yield concentrated acid. Second, nitrous gases can be reacted with azeotropic acid to form a concentrated acid that can be converted easily to concentrated and azeotropic acid by distillation. The latter product is either completely recycled or used in the production of ordinary weak acid.

In the *indirect processes*, concentration is based on extractive distillation and rectification with sulfuric acid or magnesium nitrate.

Direct Process. The essential feature of the classical direct process (Fig. 30) is that liquid dinitrogen tetroxide is produced and reacted under pressure with pure oxygen and a certain quantity of dilute nitric acid. A detailed account of concentrated acid production via azeotropic nitric acid is given in [61, pp. 99 – 130].

Ammonia Oxidation. As in weak acid processes, feed ammonia is evaporated, superheated, and filtered (see Section 1.3.4.1). Evaporation takes place with the aid of water heated with process heat. Because traces of water and oil accumulate in the ammonia evaporator the sump must be drained into the steam-heated stripper from time to time. Air for ammonia combustion is sucked through a filter (a) and mixed with purified ammonia in the mixer (b). The ammonia content of the mixture is held in the range 11.5–12.3 vol %, depending on the temperature. The optimal combustion temperature is 830 – 850 $^\circ\text{C}$. Ammonia oxidation takes place over conventional platinum – rhodium catalysts in the reactor (d). The heat of reaction is used to

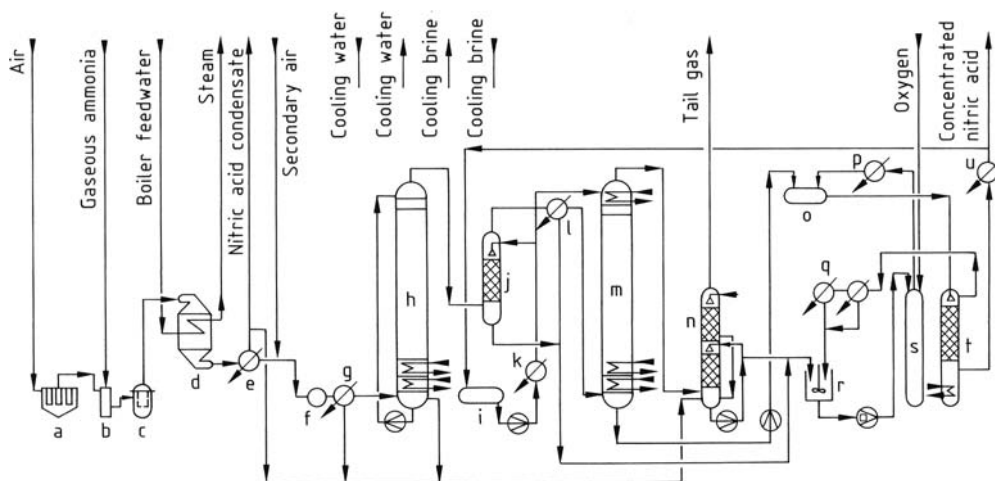


Figure 30. Simplified flow sheet of a process for direct production of strong nitric acid with oxygen a) Air Filter; b) Ammonia – air mixer; c) Gas mixture filter; d) Reactor; e) Cooler; f) Compressor; g) Cooler; h) Oxidation tower; i) Recirculating acid tank; j) Postoxidizer; k) Cooler; l) Cooler; m) Absorption tower; n) Final absorber; o) Raw acid tank; p) Cooler; q) Precondenser; r) Stirred tank; s) Reactor; t) Bleacher; u) Cooler

raise steam in a waste-heat boiler and an economizer. The process gas exits the economizer at ca. 170 °C and is then cooled to 25 °C in a cooler – condenser (e), giving an acid containing ca. 2 – 3 wt % nitric acid. The cooler – condenser is specially designed to condense as much water as possible without much NO_x absorption. Part of the process heat is also transferred to the warm water used for ammonia evaporation. The weak condensate generated in the cooler – condenser is used as scrub liquor for final absorption.

Oxidation of Nitrogen Monoxide. Secondary air is mixed with the cooled process gas to oxidize nitrogen monoxide to nitrogen dioxide. The amount of secondary air must be sufficient to ensure that the tail gas has a minimal oxygen content (2.5 – 3.5 vol %) before it is discharged to the atmosphere. The concentrated nitric acid venting system is connected to the secondary air intake in such a way that oxygen and nitrogen oxides liberated on venting are recycled to the process. The nitrogen monoxide gas and secondary air are compressed together to ca. 0.14 MPa (f). After further cooling (g) to remove the heat of compression, the mixture enters the oxidation tower (h), which is usually equipped with sieve trays. Tube coils on the trays remove the heat of oxidation. To maintain a liquid level on all trays,

acid from the tower bottom is pumped (recirculated) to the head.

Final Oxidation of Nitrogen Monoxide. The nitrous gases leaving the oxidation tower are approximately 95 % oxidized and are led to a final oxidizer (postoxidizer) (j) where they are completely oxidized by desorption of concentrated nitric acid. The acid moves countercurrently to the nitrous gases. Water produced in this reaction dilutes the concentrated acid; acid leaving the postoxidizer contains ca. 75 % HNO_3 . Flow control of the concentrated nitric acid feed into the postoxidizer is important because too high a rate lowers the output of concentrated acid, whereas too low a rate displaces final oxidation into the absorber, with the result that the concentrated nitric acid entering the absorption tower is too dilute. The product gas is saturated with nitric acid vapor. For the next step, absorption, the process gas is cooled to –10 °C against brine in a cooler (l). Virtually all the nitrogen dioxide is dimerized to dinitrogen tetroxide at this temperature.

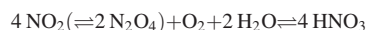
Absorption of Dinitrogen Tetroxide. The nitrous gases are completely dimerized to dinitrogen tetroxide and, in this condition, are fed into the absorber (m). The absorber consists of four sections, each packed with ceramic Raschig

rings. The dinitrogen tetroxide is absorbed in concentrated nitric acid that comes from the bleacher and is cooled to ca. -10°C (k, u). The acid leaving the absorption tower contains ca. 25 – 30 wt % dinitrogen tetroxide and is pumped to the raw acid tank (o).

Final Absorption. The gas exiting the absorption tower is practically free of nitrogen dioxide but saturated with nitric acid vapor. The vapor is removed by scrubbing in the final absorber (n), which consists of two sections. The scrub liquor (weak nitric acid from the cooler – condenser) is recirculated or used to make up the water balance in the stirred tank.

Dinitrogen Tetroxide Production. The laden concentrated nitric acid is sent from the raw acid tank (o) to the bleacher (t), which consists of a stripping section and a reboiler. The acid enters the head of the tower and flows downward countercurrently to the nitric acid vapor, which strips nitrogen dioxide from the concentrated nitric acid. The bleached concentrated acid goes to the reboiler section of the bleacher, where it is partially evaporated and partially withdrawn as product acid. The vapor exiting the bleacher contains ca. 95 % nitrogen dioxide and 5 % nitric acid. Most of the vapor condenses in a downstream precondenser (q). Dinitrogen tetroxide is liquefied in the liquefier and fed to a stirred tank (r).

Production of Concentrated Nitric Acid. The formation of concentrated nitric acid in the reactor (s) is described by the following equation:



This requires a $\text{N}_2\text{O}_4 - \text{H}_2\text{O}$ molar ratio of 1 : 1 and a weight ratio of 5.11 : 1. The reaction time can be considerably shortened if dinitrogen tetroxide is present in excess. On the other hand, an excess of dinitrogen tetroxide lowers the production rate of the reactor and increases the dinitrogen tetroxide recycle rate, resulting in higher steam consumption for bleaching and a greater cold requirement for dinitrogen tetroxide liquefaction.

The $\text{N}_2\text{O}_4 - \text{H}_2\text{O}$ ratio, denoted the R factor, is the most important criterion for monitoring reactor operation. In practice, it fluctuates between 6.5 and 7. A product concentration of

> 98 wt % nitric acid requires a higher R factor. The economically most favorable R factor can be found only by empirical means; the ratio can be varied to achieve optimal operating conditions. The makeup acid used to maintain the water balance of the raw acid mixture is taken from the bottom of the final absorber (n).

Concentrated nitric acid is formed in the reactor (s) at ca. 5.0 MPa and $60 - 80^{\circ}\text{C}$. High mechanical strength and corrosion resistance are needed, but these two requirements cannot be satisfied by any one material. The reactor thus has a carbon steel jacket to provide mechanical strength and a pure aluminum inner shell to provide corrosion resistance. Unreacted oxygen is supplied to the suction of the nitrous gas blower via the venting system. The concentrated nitric acid product is led to the raw acid tank (o) and then to the bleacher. The bleached concentrated acid is cooled to $+30^{\circ}\text{C}$ (u). Most of the concentrated nitric acid is returned to the absorption tower and final oxidation.

Indirect Processes. Two types of indirect process are used to produce concentrated nitric acid (i.e., product containing > 97 wt % HNO_3):

1. Sulfuric acid process
2. Magnesium nitrate process

Both concentration techniques are based on extractive distillation. Weak acid is first produced by a conventional process (Section 1.3.4.1), then a third component is added to extract the water so that up to ca. 99 % nitric acid can be distilled from the ternary mixture.

The starting product is ordinary commercial nitric acid (ca. 55 – 65 % HNO_3). Weaker acids can be preconcentrated in a single-stage or multistage process to give ca. 68 wt % nitric acid. Figure 31 illustrates a single-stage apparatus. Preconcentration takes place in a continuous countercurrent distillation tower (a), which can be of either the packed or the bubble-tray type. The system includes one or, if appropriate, two preheaters, a recirculating evaporator system for the tower bottom, a stripping and rectifying section for the tower, an overhead condenser, and a reflux separator (b).

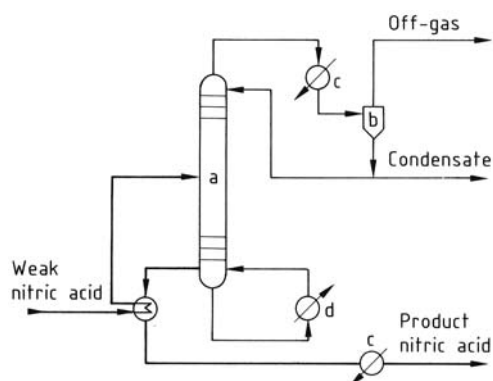


Figure 31. Simplified flow sheet of a process for preconcentration of nitric acid a) Preconcentrating tower; b) Separator; c) Recirculating evaporator system; d) Cooler

Sulfuric Acid Process. Sulfuric acid can be used as extracting agent (see also → Distillation, 1. Fundamentals). The concentrated nitric acid product is clear and colorless; it contains 98 – 99 wt % nitric acid and < 0.05 % nitrogen dioxide.

Consumption figures for the production of 1 t of 99 % nitric acid from dilute nitric acid are given in Table 6.

The nitric acid concentration step now operates with indirect heating, an advance over earlier technologies that reduces steam consumption by as much as 50 %.

The materials of construction are highly corrosion resistant. Towers are made of borosilicate glass, enameled steel, and steel – polytetrafluoroethylene. Heat exchangers are made of glass.

Table 6. Consumption figures for the production of 1 t of 99 % HNO₃ from dilute nitric acid by the sulfuric acid process*

Parameter	Starting HNO ₃ concentration, wt %		
	55	60	65
Heating steam (1.0 – 1.8 MPa), t	2.0	1.75	1.45
Cooling water, m ³	80	60	50
Electric energy, kW · h	17	14	11
Water evaporated, t	0.82	0.66	0.53

* Source: Plinke – NASAC plant data.

polytetrafluoroethylene, stainless steel, tantalum, titanium, high-purity aluminum, and special alloys.

Figure 32 is a flow sheet of a plant making concentrated nitric acid by the sulfuric acid process. The feed nitric acid, concentrated to about 68 wt %, is preheated (e) and then fed into the distillation tower (a). At least 80 wt % sulfuric acid is fed to the head of the tower. The part of the tower above the nitric acid inlet, which is irrigated with sulfuric acid, can be regarded as the rectifying section, with the sulfuric acid also functioning as reflux. The part of the tower below the nitric acid inlet is the stripping section.

A circulating evaporator system takes care of bottom heating. The ca. 70 % sulfuric acid leaving the bottom of the tower goes to the concentrator (c), which operates under vacuum (8 kPa). The overhead vapor product from the tower is condensed to form 99 % nitric acid and then deaerated (b). The tail gases, which still contain

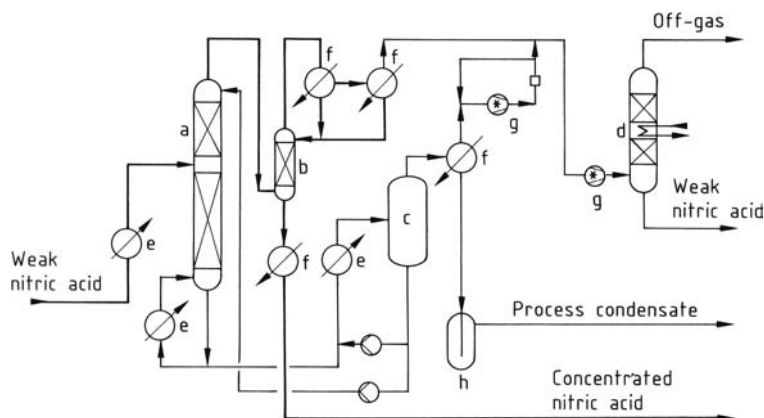


Figure 32. Simplified flow sheet of a process for concentrating nitric acid with sulfuric acid (Plinke – NACSAL process)
a) Concentrating tower; b) Condenser – deaerator; c) Sulfuric acid concentrating tower; d) Tail-gas treatment; e) Preheater;
f) Cooler; g) Blower; h) Separator

Table 7. Consumption figures for the production of 1 t of 99 % HNO_3 from dilute nitric acid by the magnesium nitrate process *

Parameter	Starting HNO_3 concentration, wt %		
	55	60	65
Heating steam (1.0 – 1.8 MPa), t	2.0	1.75	1.45
Cooling water, m^3	80	70	60
Electric energy, $\text{kW} \cdot \text{h}$	10	9	8
Water evaporated, t	0.82	0.66	0.53

* Source: Plinke – MAGNAC plant data.

nitric acid vapor, are scrubbed with dilute nitric acid (d).

Magnesium Nitrate Process. In this process a magnesium nitrate solution is used to extract water from the nitric acid. The resulting dilute magnesium nitrate solution is restored to the desired working concentration of about 72 % in a vacuum concentrator before being returned to the nitric acid concentration step.

Consumption figures for the production of 1 t of 99 % nitric acid from dilute nitric acid are given in Table 7.

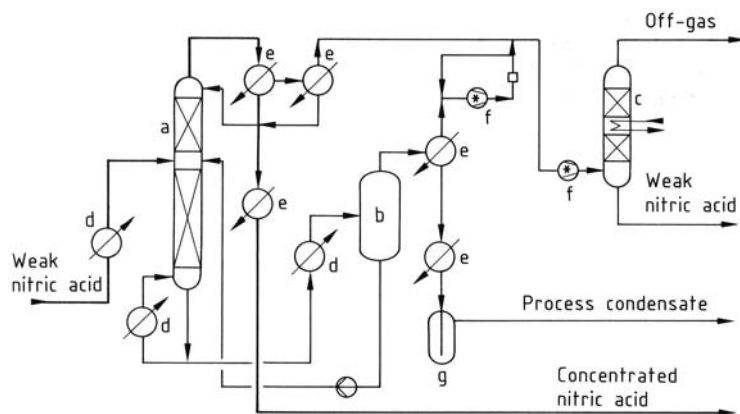
Figure 33 is the flow sheet of a plant making concentrated nitric acid by the magnesium nitrate process. Weak acid is fed to the dewatering tower (a). Extractive distillation with a concentrated (72 wt %) solution of magnesium nitrate at 140 °C gives an overhead product containing 99 % nitric acid. A small fraction of the condensed overhead product is refluxed to the

dewatering tower. The bottom of the tower is heated, and the dilute magnesium nitrate solution, containing < 0.1 % nitric acid, is led to the vacuum evaporator (b). Condensed weak acid is processed in the recovery tower (c) and recycled if appropriate. The tail gas still contains nitric acid vapor and can be scrubbed with dilute nitric acid (c).

Comparison of Indirect Processes. Which concentration process is better suited to a given task must be decided case by case. From a process-engineering standpoint, the magnesium nitrate process has the following advantages:

1. The installation is very compact. No holding tanks are needed, which reduces energy losses.
2. Because the reconcentration step for magnesium nitrate is carried out in stainless steel vessels, virtually no critical construction materials are required.
3. Magnesium nitrate can be transported in sacks, and is therefore much easier to handle than sulfuric acid.
4. The weak nitric acid condensate, which is produced when the magnesium nitrate solution is reconcentrated, is partly reused in NO_x absorption. Losses of nitric acid are very slight.

As in weak acid production, development of concentrated acid production has followed dif-

**Figure 33.** Simplified flow sheet of a process for concentrating nitric acid with magnesium nitrate (Plinke – MAGNAC process) a) Concentrating tower; b) Vacuum evaporator; c) Tail-gas treatment; d) Preheater; e) Cooler; f) Blower; g) Separator

ferent paths in the United States and the Federal Republic of Germany (and, in part, in Europe). In the United States estimated operating costs are significantly lower for concentration with magnesium nitrate than with sulfuric acid. The U.S. view is largely that, even after the change from autoclaves to continuous direct production, the equipment cost (i.e., investment cost) is too high for the latter process to be competitive.

1.4. Environmental Protection

In recent years, more stringent water pollution regulations have taken effect and legislative provisions for air pollution have been amended. New processes have been developed and introduced to significantly reduce pollutant emissions from nitric acid plants. The problem of nitrogen oxide pollution is treated in more detail in → Air, 2. Effects of Air Pollutants.

1.4.1. Wastewater

Wastewater problems can be overcome by appropriate design of the nitric acid plant. An especially simple form of wastewater treatment can be employed when the nitric acid is processed directly for the production of mineral fertilizers.

The solution from ammonia stripping contains up to 10 % ammonia; it can be neutralized with nitric acid and then subjected to absorption along with process water. The acid product then contains a small amount of ammonium nitrate, but this is not a problem when the acid is processed into mineral fertilizers.

Leaks from pumps, vessels, etc., are pumped into a separate acid drain tank, and then processed directly or indirectly. The apparatus used for this purpose is completely separate from the sewage system and thus prevents contamination of wastewater.

If heat is removed by recooling systems, cooling water blowdown is fed into the wastewater system to limit thickening of the cooling water. Fresh water must be supplied to compensate for the blowdown and evaporation losses. Corrosion inhibitors, hardness stabilizers, and in some cases, biocides are also carried out of the system by blowdown.

1.4.2. Stack Gas

Obsolescent nitric acid plants can be recognized by their strongly colored yellow to reddish brown plumes of stack gas. The coloration is due to nitrogen dioxide. Some stack gases contain up to 3000 ppm NO_x; very old plants may surpass these values [64].

The absorption of nitrous gases with water forms part of the nitric acid process. However, the laws of nature prevent complete absorption, and some residual emission cannot be avoided (see Section 1.3.2). These emissions can be minimized by optimizing process conditions, increasing the efficiency of absorption, or using special tail-gas treatment methods.

Crucial parameters for the absorption of nitrous gases in water are the following [65]:

1. Pressure
2. Temperature
3. Reaction volume
4. The efficiency of the absorption tower
5. The partial pressures of nitrogen oxides and oxygen

Emissions in the Federal Republic of Germany in 1986 totaled ca. 3×10^6 t NO_x [66]. Transportation, households, and small consumers accounted for ca. 66 % of this; power plants and district heating plants for ca. 25 %; and industry, including furnaces, for ca. 9 %. Nitrogen oxides from nitric acid production were responsible for < 1 % of the total emissions.

1.4.2.1. Emission Limits

Heightened sensitivity to environmental concerns, coupled with the need for larger and more efficient production systems, will lead to further reductions in NO_x emissions. Legislators are following this trend and modifying pollution limits in accordance with changing technical capabilities.

At the beginning of the 1980s the first general administrative regulation was issued in the Federal Republic of Germany under the Federal Pollution Control Act: the Technische Anleitung zur Reinhaltung der Luft (TA-Luft; Technical Instructions for Air Pollution Control) [67]. This regulation and the corresponding VDI guidelines [68] form the basis for

issuing operating permits. Regulations in many other countries are based on these guidelines.

The designation NO_x is commonly used to specify emission and concentration values because stack gases always include mixtures of nitrogen oxides. For the purpose of standardization, the oxides are calculated in terms of nitrogen dioxide. The acceptable concentrations from TA-Luft 1986 [67] are

1. Mass of substances emitted as mass concentration in units of g/m^3 or mg/m^3 , referred to the volume of stack gas at standard conditions (0°C , 101.3 kPa) after deducting the moisture content of water vapor, or to the volume of stack gas at standard conditions (0°C , 101.3 kPa) before deducting the moisture content of water vapor; and
2. Mass of substances emitted, referred to time, as mass velocity in units of kg/h , g/h , or mg/h ; and
3. Ratio of the mass of substances emitted to the mass of products generated or processed (emission factors), as mass ratio in units of kg/t or g/t .

The usual concentration unit ppm (mL/m^3) can be converted to the prescribed mass concentration (mg/m^3) with the following factor [69]: $1 \text{ ppm} = 1.88 \text{ mg}/\text{m}^3$ (based on monomeric NO_2 at 101.3 kPa and 298 K and ideal-gas behavior).

The TA-Luft [67] states that the emission of nitrogen monoxide and nitrogen dioxide in the stack gas of nitric acid plants must not exceed $0.45 \text{ g}/\text{m}^3$ as nitrogen dioxide. Furthermore, stack gases may be discharged only if colorless; as a rule, this is the case if the mass concentration of nitrogen dioxide in the stack gas does not exceed the value given by the following formula:

$$= \frac{\text{Mass concentration of nitrogen dioxide (mg}/\text{m}^3\text{)}}{1200} \times \text{Internal diameter of stack orifice (dm)}$$

The requirement of a colorless discharge sets a practical limit of $< 200 \text{ ppm NO}_x$. Older low- and medium-pressure plants should comply with these standards by March 1, 1996.

Plants whose emission of nitrogen monoxide and nitrogen dioxide (as nitrogen dioxide)

exceeds a rate of $30 \text{ kg}/\text{h}$ must be equipped with devices that continuously measure the mass concentration of nitrogen oxides. Quantitative relationships between emission and ground-level concentration are also described, thus setting guidelines for stack design.

If ground-level concentration limits are exceeded, the TA-Luft emission limits are further reduced by the relevant authorities. The ground-level concentration limits for gaseous pollutants in air are as follows [67]: nitrogen dioxide, long-term exposure (IW1), $0.08 \text{ mg}/\text{m}^3$; short-term exposure (IW2), $0.2 \text{ mg}/\text{m}^3$.

1.4.2.2. Analysis

The guidelines for the measurement and monitoring of NO_x emissions from nitric acid production are specified in [67], [70], [71].

Photometry without auxiliary chemical reaction and *chemiluminescence* [71c – e] are suitable for the continuous measurement of NO_x emissions [65].

Difficulties in gas sample preparation due to condensation are discussed in [71c – g]. Additional apparatus-related problems occur when chemiluminescence is used to measure emission of moist stack gases at higher NO_x levels. A chemiluminescence analyzer with a maximum range of $0 - 10\,000 \text{ ppm}$ has been developed [72].

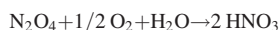
For stack gases containing traces of ammonia, precipitation of ammonium salts in the measuring cells has prevented continuous measurements. Two methods useful for the discontinuous measurement of nitrogen oxide emissions [65] are acidimetric titration and the photometric phenoldisulfonic acid technique [71a, b].

1.4.2.3. Control of NO_x Emissions

Four basic approaches are used to reduce tail-gas NO_x levels: improved absorption, chemical scrubbing, adsorption, and catalytic tail-gas reduction. Recent decades have seen intense research and development effort invested in these methods. More stringent environmental restrictions have lent special urgency to development in this area. The most important techniques are covered in this section.

Improved Absorption. Absorption efficiency depends chiefly on the absorption pressure, the number of stages, and the temperature. The temperature of the gas between stages is especially important because it governs the progress of oxidation, which is the limiting quantity for the entire absorption process (see Section 1.3.2). In an already existing nitric acid plant, the options are to expand the absorption volume and/or lower the absorption temperature. In the first approach, large additional volumes only result in small reductions of tail-gas NO_x levels because the oxidation of nitrogen monoxide to nitrogen dioxide proceeds very slowly when the NO_x concentration is low. The drawback to this method is that added absorption volume in stainless steel is very expensive. The advantage is that it does not require any new technology. The absorption volume is added in the form of a second tower; new absorption tower designs with very few stages have been devised [73].

The use of cold energy in the absorption process greatly accelerates oxidation of nitrogen monoxide to nitrogen dioxide. The disadvantage of this method is that the necessary refrigeration equipment and piping demand further investment. Another technique involving the use of cold to lower the NO_x level is to cool the nitrous gas so that more dinitrogen tetroxide than nitrogen dioxide is formed. The dinitrogen tetroxide is then scrubbed with nitric acid at ca. 0 °C; it can be stripped out, and converted to nitric acid by the reaction



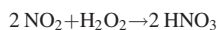
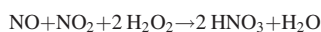
in an absorption reactor at ca. 60 – 80 °C. The technique is similar to that in concentrated nitric acid production. The method is, however, more suitable for investment in a plant being designed than for the expansion or upgrading of an existing plant.

Chemical Scrubbing. A number of patents and scientific publications deal with options for scrubbing NO_x out of tail gas. Problems related to the scrub liquor (cost, regeneration, quantity, and environmental impact) are encountered in all methods. These problems are always easier to manage if the nitric acid plant is part of an integrated chemical plant, which is usually the case. However, in some instances a nitric acid

plant or sections of a fertilizer complex must operate independently. The following scrub liquors have been proposed: aqueous suspension of magnesium carbonate and magnesium hydroxide [74]; solution of vanadium in nitric acid [75]; ammonium sulfide and bisulfide [76]; milk of lime [77]; ammonia [78]; hydrogen peroxide [79]; and urea [80].

Ammonia Scrubbing is used in the United States. Goodpasture (Texas) has developed a safe process based on scrubbing the tail gas with ammonium nitrate solution; nitrite formation is suppressed by aeration and the presence of free acid. The tail gas is then led through an ammoniacal scrub liquor, pH 7.5 – 8.5. The scrubbing product is a 30 – 50 % ammonium nitrate solution. The tail gas has a residual level of ca. 200 ppm NO_x .

Hydrogen Peroxide Scrubbing is based on the following overall reactions:



The reactions are carried on sieve trays or in packed towers with recirculation of the hydrogen peroxide solution. The advantage of this scrubbing process is that the reaction time is very fast; the disadvantage, that the hydrogen peroxide scrub liquor is expensive.

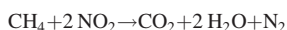
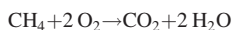
A solution containing 20 % urea and 10 % free nitric acid has also been suggested for scrubbing tail gas to remove NO_x . The process is carried at ca. 50 °C. Both nitrogen oxides are selectively reduced to nitrogen by urea, which decomposes to yield nitrogen and carbon dioxide. The process, developed by Norsk Hydro in Norway, has the advantage that urea is readily available and relatively cheap. The resulting stack gas plume is colorless but heavily laden with water vapor.

Adsorption Processes. The adsorption of NO_x by molecular sieves has long been known but has not yet been tested intensively in full-scale nitric acid plants.

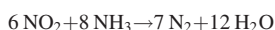
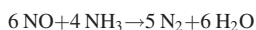
The Pura-Siv-N process (Union Carbide) is claimed to reduce stack gas levels below 50 ppm nitrogen dioxide [81], but high investment costs and other problems have prevented its adoption. A patent granted to Kernforschungsanlage Jülich GmbH has a similar object [82], but again indus-

trial experience is slight. A “wet” adsorption system has also been developed by Cofaz (France). A carbon-containing adsorbent is sprayed with water or dilute nitric acid and brought in contact with the tail gas. This process has been installed in three monopressure plants [83].

Catalytic Reduction. Catalytic reduction was the first method used to reduce NO_x emissions; as early as 1924, a patent for such a process was issued to FAUSER [84]. A fuel is added, at a level below the flash point, to the nitrogen oxides which then react on the catalyst surface to form nitrogen and water vapor. Most fuels (e.g., hydrocarbons and hydrogen), however, react preferentially with the free oxygen that is always present in tail gases from nitric acid production. As a result, the nitrogen oxides are not destroyed until free oxygen has been consumed. Under these conditions the reactions with methane can be described as



Ammonia can also be used as a reducing agent, preferentially reducing the nitrogen oxides:



Catalytic reduction processes are accordingly classified as nonselective or selective.

Catalysts for *nonselective reduction processes* are usually based on platinum, vanadium pentoxide, iron oxide, or titanium. The fuel requirement is the stoichiometric amount needed to reduce all the oxygen present (free and in nitrogen oxides) plus a small excess (ca. 0.5 vol % CH_4).

Unfortunately, the principal byproducts of this process are carbon monoxide (≤ 1000 ppm) and hydrogen cyanide. When hydrocarbon fuels are used, the tail gas must be preheated before the reaction on the catalyst proceeds at all. The

preheat temperature depends directly on the fuel selected:

Natural gas	450 – 480 °C
Propane	340 °C
Butane	340 °C
Naphtha	340 °C
Hydrogen	250 °C

The use of hydrogen allows the preheat temperature to be lowered to 150 – 200 °C but is generally too expensive.

If the quantity of fuel is not enough to reduce all the oxygen, nitrogen dioxide is reduced only to nitrogen monoxide. The stack gas is then decolorized; in some countries, this is sufficient. Complete NO_x removal generally requires preheating, multiple fixed-bed catalysts (with cooling between beds to prevent overheating), and careful heat recovery to offset part of the fuel cost.

Most nitric acid plants constructed or modified by Weatherly use nonselective catalytic NO_x abatement units with tail-gas exit temperatures of 650 – 675 °C. Some plants have gas exit temperatures > 815 °C, which is higher than the maximum for admission to the tail-gas expansion turbines. The tail gas must then be cooled, either against tail gas entering the catalytic unit or with the aid of waste-heat boilers.

In the process marketed by Du Pont the tail gas is dried, preheated, and then heated in two stages. The gas is subsequently divided into two streams. One substream is heated further, mixed with methane, and led over the first fixed-bed catalyst. The second substream is mixed with methane without further heating and led over the second fixed-bed catalyst, along with the first substream. Hot tail gases exit the bottom of the reactor and are led through the tail-gas expansion turbine, which recovers part of the work of compression.

Ammonia is the only economically relevant reducing agent for *selective catalytic processes*. The consumption of reducing agent in the selective treatment of NO_x is much smaller than in nonselective processes. Furthermore, the tail-gas temperature after reduction is significantly lower, allowing the use of simpler, cheaper construction materials. The optimal catalyst service temperature is 250 – 350 °C, but operation at up to 500 °C is possible. The costs due to the use

of expensive ammonia must, however, also be considered. To prevent formation of ammonium nitrate (a potential explosion hazard) in the expansion turbine or downstream, emissions must be monitored for ammonia (10 – 20 ppm).

When BASF, Ludwigshafen [85] began work on catalytic NO_x reduction in the early 1960s, existing patents indicated the use of ammonia together with noble-metal (Pt, Rh, Ru, Pd) and iron-group (Fe, Co, Ni) catalysts [86], [87]. Alternatives were found: vanadium pentoxide, tungsten oxide, and molybdenum oxide gave excellent results. Vanadium pentoxide on an alumina support proved to be most economical.

Selective processes also require oxygen, which oxidizes part of the nitrogen monoxide to nitrogen dioxide to ensure roughly equal levels of these two oxides (the best condition for reduction). Because the BASF process operates at 200 – 350 °C, side reactions between ammonia and oxygen can be neglected. The reaction is not affected by dinitrogen monoxide, carbon dioxide, or water vapor.

For a plant with a tail-gas stream of 37 000 m³/h (STP) operating at a pressure of 730 kPa with an inlet NO_x concentration of 500–1000 ppm, this process (270 °C) gives an exit concentration of 50 – 150 ppm NO_x . The treated tail gas contains < 20 ppm ammonia (usually ca. 5 ppm), and the nitrogen dioxide level is 30–50 ppm. The stack gas is generally colorless. Careful temperature monitoring at the tail-gas expansion turbine and measurement of the ammonia level can prevent the deposition of ammonium nitrate. To minimize the pressure drop, the reactor features an annular design with inward flow (Fig. 34).

Ammonia is uniformly mixed with the tail-gas stream in static mixers. The performance of the treatment process is monitored by measuring the temperature rise during reduction (ca. 10 °C/1000 ppm NO_x).

Uhde, Dortmund, as licensee, has retrofitted 14 plants with the BAVarphiSF process. The tail gas, usually containing 500 – 1000 ppm NO_x , is heated to about 260 °C. Ammonia gas is added to the tail-gas stream in a mixer and then led through the reactor. The pressure drop is ca. 25 kPa. The effluent meets the requirement of colorlessness.

The HGW – Didier process, developed jointly by Hamburger Gaswerke (HGW) and Didier,

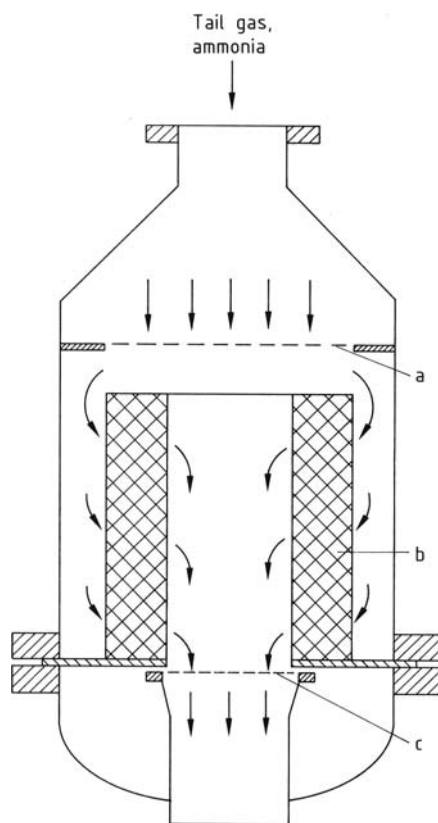


Figure 34. BASF tail-gas reactor for NO_x reduction a) Hole plate; b) Catalyst; c) Wire gauze

Essen uses a chromium oxide catalyst with a service temperature of 265 – 350 °C. The nitric acid plant planned for DSM Miststoffen (Geleen, Netherlands) is designed for a tail-gas stream of 76 000 m³/h (STP) with a maximum NO_x level of 2200 ppm. The exit concentration will not exceed 100 ppm NO_x . The tail gas is preheated before entering the reactor. To meet the strict emission limit of < 100 ppm, the catalyst is located in three beds. Ammonia can be admitted separately over each. The following distribution has proved most efficient: 70 % over the first bed, 20 % over the second, and 10 % over the third catalyst bed.

Other companies also have selective catalytic reduction processes for nitric acid tail gases. For example, Mitsubishi Chemical has developed a process operating at 400 – 500 °C under pressure [88], [89]. The “DN-Cat” catalyst is installed between the heat exchanger and the tail-gas expansion turbine in the conventional flow sheet.

The Weatherly selective catalytic process operates at 250 – 310 °C. The noble-metal catalysts are the same ones employed in nonselective processes, except that the fuel is replaced by ammonia.

The Bergbauforschung – Uhde process [90] is chiefly employed for stack-gas cleanup at power plants but may later find use in emission abatement at nitric acid plants. The Bergbauforschung – Uhde process for simultaneous sulfur and NO_x removal from stack gases is utilized at the cold end of the power-plant boiler, i.e., downstream of the air preheater and electrostatic filter. It employs the adsorptive and catalytic properties of “activated coke” at 50 – 150 °C. The reducing agent is again gaseous ammonia. The technique combines a selective catalytic process for NO_x and an adsorptive one for sulfur dioxide. The catalyst is therefore installed in a moving-bed reactor.

1.5. Storage and Transportation

As a rule, nitric acid is stored in stainless steel tanks and transported in stainless steel containers.

The regulations for transport by rail [91], [92] and road [93], [94] differentiate among > 70 % nitric acid, 55 – 70 % nitric acid, and < 55 % nitric acid, and also between mixtures with sulfuric acid (“mixed acid”) containing > 30 % nitric acid and those containing < 30 % nitric acid. Similar regulations [95] apply to transport by ship. Important transport regulations for > 70 % nitric are as follows:

IMDG Code	Class 8, D 8261, E – F 8186
UN No.	2032
RID/ADR	Class 8, no. 2 a
CFR	49: 172.101, Cor. M

Regulations for < 70 % nitric acid are

IMDG Code	Class 8, D 8260, E – F 8185
UN No.	2031
RID/ADR	Class 8, no. 2 b
CFR	49: 172.101, Cor. M

Provisions range from details of technical equipment to labeling and give instructions in

case of accidents. Regulations for the road transport of nitric acid ($\leq 70\%$ HNO₃ emphasize the associated hazards (poisoning by inhalation of vapors, danger of chemical burns on contact with flammable substances, formation of nitrous gases). Protective equipment includes respiratory protection apparatus, goggles, and clothing affording complete coverage, as well as an eyewash bottle with pure water. In case of accident, the fire and police departments are to be notified immediately. Spilled nitric acid must not be absorbed with sawdust or other flammable material (because of the fire hazard); instead, its spread must be prevented by the construction of earth barriers.

1.6. Uses and Economic Aspects

The principal use of nitric acid is as a starting material in the manufacture of nitrogen fertilizers; large amounts are reacted with ammonia to yield ammonium nitrate (→ Ammonium Compounds, Section 1.2.1.). Weak acid (ca. 60 % HNO₃) is most suitable for this purpose. Smaller amounts of weak acid are used to digest crude phosphates. About 75 – 85 % of the nitric acid produced is used in the fertilizer sector. In addition, porous ammonium nitrate prills are still an important component of explosives (→ Explosives, Section 7.2.).

Nitric acid is used as a nitrating agent in the preparation of explosives (→ Explosives) and organic intermediates such as nitroalkanes (→ Nitro Compounds, Aliphatic) and nitroaromatics (→ Nitro Compounds, Aromatic). It is also used in the production of adipic acid (→ Adipic Acid, Section 4.1.).

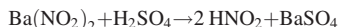
Other applications include use as a chemical in metallurgy (e.g., as an etchant and pickling agent for stainless steels) and in rocket fuel production.

Worldwide output of nitric acid in 1987 was 26.882×10^6 t, representing a slight increase of ca. 4 % over 1976. Production in industrialized countries has stagnated or even declined, but in 1976 – 1985 increases in capacity in less industrialized countries occurred [96]. Production figures for nitric acid in 1987 follow (10^6 t):

Europe, total	16.472
United States	6.553
Eastern Europe	4.289
Asia	1.544
Federal Republic of Germany	2.112
Poland	2.136
Belgium	1.470
Spain (1986)	1.249
Italy	1.195
Hungary	1.018

2. Nitrous Acid

Nitrous acid [7782-77-6], HNO_2 , M_r 47.01, is a moderately strong to weak acid. Its dissociation constant K in highly dilute solutions at 18 °C is 4.5×10^{-4} . The acid is stable only in cold dilute aqueous solution. It can be prepared as follows:



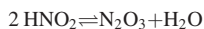
On heating in the presence of sand, glass splinters, or other sharp-edged objects, or even at low temperature, it disproportionates as



This disproportionation reaction influences the properties of nitrous acid solutions and is important in the production of nitric acid. Nitrous acid occurs as an intermediate product when NO_x gases are absorbed in water.

By virtue of the above reaction, nitrous acid can act as both a reducing and an oxidizing agent. Strong oxidizing agents such as potassium permanganate oxidize nitrous acid to nitric acid. It can be reduced to less oxygen-rich compounds (NO_2 , NO , $\text{H}_2\text{N}_2\text{O}_2$, NH_3) by alkali amalgams or by electrolytic means. Its salts (nitrites) are not stable in aqueous solution because of hydrolysis.

Nitrous acid in aqueous solutions is assumed to be in dynamic equilibrium with its anhydride:



Aqueous solutions of the acid appear colorless but take on an increasingly blue coloration at 5 % dinitrogen trioxide.

Figure 35 shows the phase diagram of the $\text{N}_2\text{O}_3 - \text{H}_2\text{O}$ system with its sizable miscibility gap. Mixtures break up into a lighter layer with a high water content and a heavy layer with a high dinitrogen trioxide content.

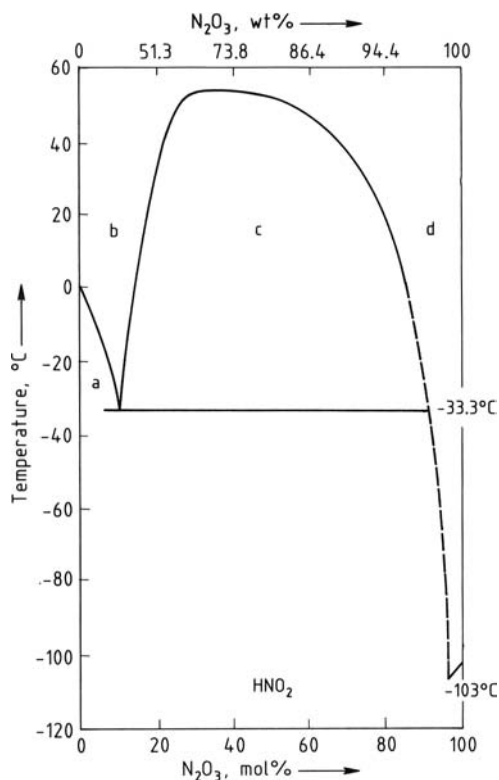
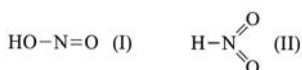
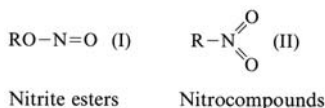


Figure 35. The system $\text{N}_2\text{O}_3 - \text{H}_2\text{O}$ a) Ice; b) Homogeneous liquid, water + dinitrogen trioxide; c) Liquid phase, two layers; d) Homogeneous liquid, dinitrogen trioxide + water

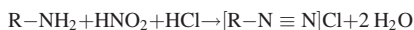
Nitrous acid exists in two isomeric forms:



These structures lead to two series of industrially important organic derivatives:

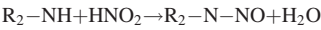


An especially important property of nitrous acid is its ability to diazotize organic amines. With primary amines, the acid forms diazonium salts:

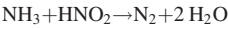


These salts are used widely in the manufacture of azo dyes (\rightarrow Azo Dyes, 1. General).

With secondary amines, nitrosamines are formed:



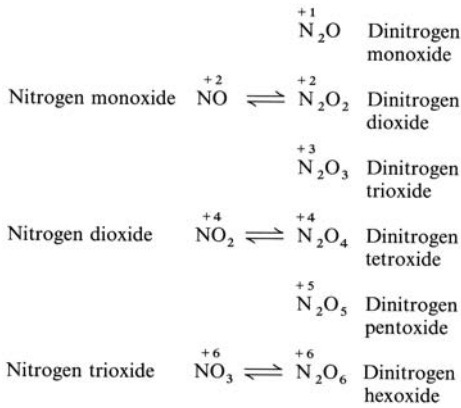
Ammonia and urea react with nitrous acid to yield nitrogen:



3. Nitrogen Oxides

Compounds of oxygen with nitrogen are considered as a class and called nitrogen oxides (often denoted as NO_x).

The known oxides and their equilibrium reactions are as follows:

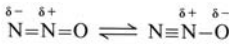


Very little is known about nitrogen trioxide (NO₃) or its dimeric form (N₂O₆).

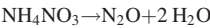
The compounds listed above are described in more detail in order of their oxidation state. Table 8 lists their most important physical properties.

3.1. Dinitrogen Monoxide

Properties (see Table 8). Under normal conditions (i.e., room temperature and atmospheric pressure), dinitrogen monoxide [10024-97-2], also called nitrous oxide, N₂O, *M_r* 44.01, is a colorless gas with a weak, pleasant odor and a sweetish taste. If inhaled, it can bring about a spasmodic inclination to laugh and a condition resembling drunkenness—hence, its historic name, laughing gas [97]. Two mesomeric forms in resonance with each other describe the electron distribution in the molecule [7]:



Production. Dinitrogen monoxide occurs as a byproduct of denitrification (especially in the heavy use of nitrogen fertilizers) and, to some extent, in the nitrification of nitration waste acids. The compound was first prepared by PRIESTLEY, who carefully heated ammonium nitrate:



This is still a common route for industrial production.

Table 8. Physical properties of nitrogen oxides

Compound	N ₂ O	NO	NO ₂ /N ₂ O ₄	N ₂ O ₃	N ₂ O ₅
Oxidation state	+ 1	+ 2	+ 4/ + 4	+ 3	+ 5
<i>T</i> _C , °C	36.41	−93	157.85		
<i>p</i> _C , MPa	7.245	6.485	10.132		
<i>ρ</i> _C , kg/m ³	452	520	550		
<i>m</i> <i>p</i> , °C	−90.86	−163.65	−11.2	−100.7	32.4 *
<i>b</i> <i>p</i> , °C	−88.48	−151.77	21.15	−40 to + 3	
Specific heat <i>c_p</i> , kJ kg ^{−1} K ^{−1}	0.879	0.996	1.326	0.862	0.778
Standard enthalpy of formation Δ <i>H</i> _f ⁰ , kJ/kg	1864.190	3007.684	721.199	1101.435	104.589
Heat of vaporization at <i>b</i> <i>p</i> , kJ/kg	376.07	459.031	414.257	517.416	
Density, kg/m ³					
Gas (0 °C, 101.3 kPa)	1.9775	1.3402	3.4 (20 °C)	1.447(2 °C)	2.05
Liquid (20 °C, 101.3 kPa)	793		1446.8		(solid)
Dynamic viscosity, mPa · s					
Gas (25 °C, 101.3 kPa)	14.874	19.184	12.838		
Thermal conductivity, W m ^{−1} K ^{−1}					
Gas (25 °C, 101.3 kPa)	0.01718	0.02573	0.1124		
Liquid (20 °C, 101.3 kPa)			0.1336		

* Sublimation point.

In earlier processes [98], high-purity ammonium nitrate was used (contamination by organic material and chlorides had to be avoided), and temperatures up to 260 °C were reached. Today, in contrast, ammonium nitrate can be decomposed in aqueous solution containing chlorides and nitric acid at temperatures as low as 100 – 160 °C. This synthesis was introduced in 1970 by Hoechst [99] (Fig. 36)

The decomposition flask (a) is supplied with gaseous ammonia and nitric acid (30 – 100 %). Ammonia gas forms the atmosphere for the entire system, including the tower (b). A small amount of chloride ion (> 0.2 %) is maintained in the aqueous nitric acid solution in the decomposition flask (a) to accelerate the reaction. If appropriate, catalytically useful amounts of metal ions (manganese, copper, cerium, lead, bismuth, cobalt, or nickel) may also be added. Heat liberated during the reaction raises the temperature to 100 – 160 °C. The solution contains 15 – 35 % nitric acid, 30 – 50 % ammonium nitrate, 15 – 55 %

water, and 0.01 – 0.1 % chloride ion. The impure product dinitrogen monoxide ascends from the decomposition flask (a) into the tower (b). Ammonia in the gas space neutralizes any entrained acidic constituents, and this reaction heats the lower part of the tower (b). The hot gas is cooled and scrubbed by an aqueous ammonium nitrate solution fed through a distributor (c). The solution collected in the bottom of the tower (b) has a temperature of 50 – 110 °C; most of it is recycled through the heat exchanger (d). The thermal energy recovered serves to heat the evaporator (e), which concentrates a small part of the solution stream for recycling to the decomposition flask (a). If the temperature profile in the system is not too low, the process does not need a heat supply.

This process has two main advantages over earlier ones: it offers a substantial energy saving and produces dinitrogen monoxide free of harmful byproducts.

The dinitrogen monoxide can easily be liquefied under pressure and is available in steel cylinders. Transport regulations for dinitrogen monoxide (compressed) are as follows:

IMDG Code	Class 2.2
UN No.	1070
RID/ADR	Class 2, no. 5 a
CFR	49: 172.102 Nonfla. G

Uses. The principal uses of dinitrogen monoxide are as follows:

1. In medicine, as an anesthetic
2. In the munitions – explosives industry, as a propellant
3. In the food industry, as a foaming agent (whipped cream)

Production data for dinitrogen monoxide are given in [100].

3.2. Nitrogen Monoxide

Nitrogen monoxide [10102-43-9], also called nitric oxide, NO, *M_r* 30.01, is a colorless, toxic, nonflammable gas at room temperature. As soon as it comes in contact with atmospheric oxygen, it is oxidized to nitrogen dioxide, a brown vapor. For physical properties, see Table 8.

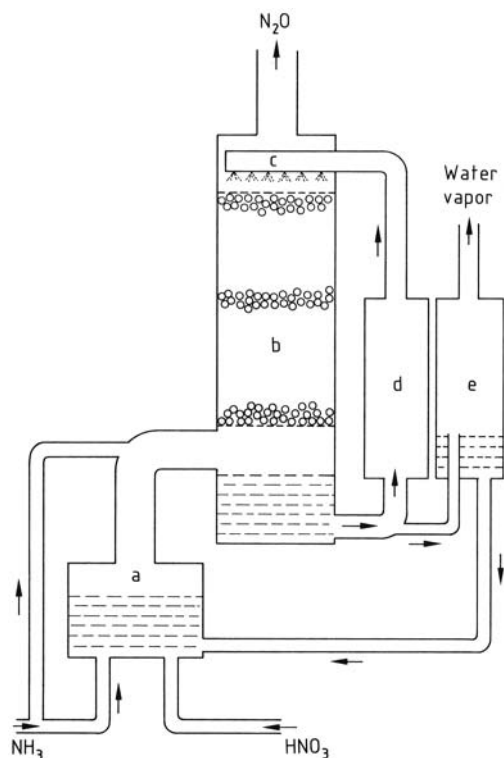


Figure 36. Industrial production of dinitrogen monoxide [99] a) Decomposition flask; b) Scrubbing tower; c) Ammonium nitrate distributor; d) Heat exchanger; e) Evaporator

Nitrogen monoxide is at dynamic equilibrium with its dimer:



At high temperature, however, the equilibrium is shifted all the way toward nitrogen monoxide. Liquid nitrogen monoxide is completely dimerized, probably as angular ONNO molecules. The nitrogen monoxide molecule contains a double bond and a three-electron bond [101]

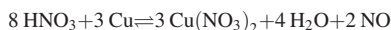


This makes the molecule more stable than the resonant structure



so that the heat of dimerization is slight; the reaction therefore does not occur in the gas phase. The nitrogen monoxide molecule contains 11 valence electrons and thus, like all gases with an odd number of electrons, is paramagnetic.

Laboratory preparation usually involves the reaction of moderately concentrated nitric acid with copper:



Nitrogen monoxide is very reactive and can, as a strongly endothermic compound, be prepared from nitrogen and oxygen in an electric flame arc:



In acidic solution (e.g., chromic acid, acidified permanganate solution, hydrochloric acid), nitrogen monoxide is oxidized to nitric acid. The combustion of nitrogen (Birkeland – Eyde, Schönherr, Pauling processes) was formerly an important method of industrial nitric acid production; however, these processes are no longer used due to the high energy cost of the arc. Nitric acid production is now based on the combustion of ammonia; nitrogen monoxide is the first reaction product and has thus gained some importance as an intermediate.

Another use of nitrogen monoxide is in nitrosation, where chlorine or bromine reacts with it to yield nitrosyl halides. In the lead-chamber process for sulfuric acid production, nitrosyl hydrogen sulfate is treated with sulfu-

rous acid in the Glover tower, to yield nitrogen monoxide and sulfuric acid.

With aqueous iron sulfate solutions, nitrogen monoxide forms dark brown nitroso iron (II) sulfate $[(\text{FeNO})\text{SO}_4]$, thus affording a detection method for nitric acid and nitrates. Transport regulation are as follows:

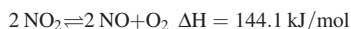
IMDG Code	Class 2, D, E – F 2095
UN No.	1660
RID/ADR	Class 2, no. 1 ct
CFR	49: 172.101 Nonfla. G

3.3. Nitrogen Dioxide and Dinitrogen Tetroxide

Nitrogen dioxide [10102-44-0], NO_2 , M_r 46.01, is a brownish red, toxic gas with a pungent odor; for physical properties, see Table 8. It is in equilibrium with its dimer, dinitrogen tetroxide [10544-72-6], also called nitrogen peroxide, N_2O_4 , M_r 92.01. The equilibrium is strongly temperature dependent; at higher temperature (ca. 100 °C), it is shifted almost all the way toward nitrogen dioxide.



Above 150 °C, nitrogen dioxide begins to dissociate:

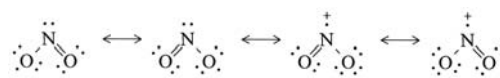


This reaction goes to completion at 650 °C. Figure 37 illustrates the dissociation of dinitrogen tetroxide and nitrogen dioxide as a function of temperature.

The following values for the equilibrium constant of the bidirectional reaction are given in [102]:

Temperature, K	273.2	298.5	323.5	359.7
K_p , (101.3 kPa)	0.017513	0.1458	0.8492	7.247

According to PAULING, the nitrogen dioxide molecule probably exists in two mesomeric forms with two ionic structures:



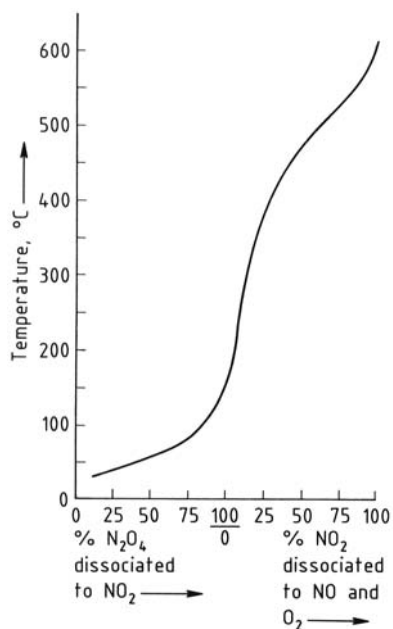
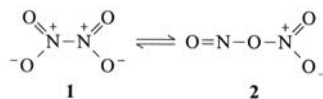


Figure 37. Dissociation of dinitrogen tetroxide and nitrogen dioxide

Dinitrogen tetroxide can be prepared in two structures, **1** exists at room temperature and is in equilibrium with **2** at low temperature:



Nitrogen dioxide, like nitrogen monoxide, is an odd-electron compound and therefore paramagnetic; dinitrogen tetroxide is diamagnetic. To reach an even electron number, nitrogen dioxide can give up an electron (NO_2^+ , nitronium ion) or gain one (NO_2^- , nitrite anion).

Industrial production of $\text{NO}_2 - \text{N}_2\text{O}_4$ employs the Ostwald process (catalytic combustion of ammonia) and constitutes the initial step in the production of nitric acid (see Section 1.3).

Other commercial processes for producing $\text{NO}_2 - \text{N}_2\text{O}_4$ are the oxidation of nitrosyl chloride yielding chlorine, and the treatment of sodium nitrite with nitric acid and oxidation of the liberated nitrogen monoxide to nitrogen dioxide.

High-purity $\text{NO}_2 - \text{N}_2\text{O}_4$ is obtained in the production of sodium nitrate from sodium chloride and nitric acid. The dioxide and tetroxide (oxidation state 4) are strong oxidizing agents,

comparable in strength to elemental bromine. They form explosive mixtures with hydrogen; mixtures with ammonia explode even at low temperature.

Transport regulations for liquefied nitrogen dioxide are as follows:

IMDG Code	Class 2, D 2213, E – F 2099
UN No.	1067
RID/ADR	Class 2, no. 3 at
CFR A	49

Nitrogen dioxide is involved in the production of “photochemical smog” and is a major air pollutant because it is produced in all combustion processes. It is therefore subject to strict emission limits (see Section 1.4.2.1) [67].

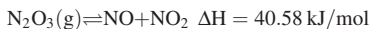
Dinitrogen tetroxide has many applications because of its strong oxidizing action. For example, it is employed as a catalyst in oxidation reactions and as an inhibitor in the distillation of acrylates. It is also used in the manufacture of explosives, as a rocket propellant, and as a bleach.

For details on the chemistry of liquid dinitrogen tetroxide, see [103].

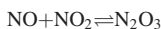
3.4. Dinitrogen Trioxide

Dinitrogen trioxide [10544-73-7], also called nitrous anhydride, N_2O_3 , M_r 76.01, is stable only below 0 °C, taking the form of a deep-blue liquid. When cooled further, it solidifies as pale blue crystals. For physical properties, see Table 8.

Even below 0 °C, dinitrogen trioxide dissociates to a considerable extent:



At 10 °C and ambient pressure, only 10 % of the molecules are in the form of undissociated dinitrogen trioxide (as $\text{ON}-\text{NO}_2$ [104]). This dissociation means that a well-defined boiling point cannot be given for dinitrogen trioxide (*bp* range –40 to +3 °C). The compound is prepared by saturating liquid nitrogen dioxide with nitrogen monoxide:



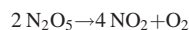
However, because nitrogen dioxide is present mainly as the dimer, a eutectic of nitrogen monoxide and nitrogen dioxide can be postulated [105] with the empirical composition $\text{NO}_{1.56}$. The equilibrium constant for the reaction has been measured at various temperatures [106]. Because the equilibrium is easily shifted, a mixture of nitrogen monoxide and nitrogen dioxide behaves chemically like dinitrogen trioxide.

Dinitrogen trioxide occurs chiefly in nitric acid production. As much as 4 vol % of the NO_x may be present as dinitrogen trioxide. The trioxide is used in preparing high-purity alkali nitrites from alkali. It also finds use as an oxidizing agent in special fuel systems.

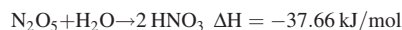
3.5. Dinitrogen Pentoxide

Dinitrogen pentoxide [10102-03-1], also called nitrogen pentoxide, N_2O_5 , M_r 108.01, is the anhydride of nitric acid. It is a colorless crystalline substance that melts under pressure but sublimates at atmospheric pressure. For physical properties, see Table 8.

In the solid state, dinitrogen pentoxide has a salt-like structure $[\text{NO}_2]^+[\text{NO}_3]^-$. It is not very stable and can undergo spontaneous explosive decomposition [107]:



Dinitrogen pentoxide can be prepared by treating nitric acid with phosphorus pentoxide. It has strong oxidizing properties and reacts vigorously with organic substances. With water, the hygroscopic crystals form nitric acid:



With boron trifluoride, it forms a binary compound $\text{N}_2\text{O}_5 - \text{BF}_3$ that is stable at room temperature. This compound is a good nitrifying agent. Nitrogen pentoxide has not become important in industry.

4. Toxicology and Occupational Health

Nitric Acid. Nitric acid has a caustic effect on the skin and mucous membranes. Industrial safety regulations stipulate the following work-

place concentrations [108], [109]: MAK value 10 ppm (25 mg/m^3); TLV-TWA 2 ppm (5.2 mg/m^3); TLV-STEL 4 ppm (10 mg/m^3). Nitric acid reacts with and causes spontaneous ignition of organic substances such as wood shavings, saw dust, cotton, and cellulose. Spill acid should therefore never be absorbed with such substances.

Nitric acid is classified as a hazardous substance [109], [110]. Indications of special hazards (R warnings) and safety advisories (S warnings) are given in [109].

Nitric acid > 70 %	
R 8:	Danger of fire when in contact with flammable substances
R 35:	Causes severe burns
S 23:	Do not inhale vapor
S 26:	In case of contact with eyes, flush eyes thoroughly with water and call physician
S 36:	Wear appropriate protective clothing when working
Nitric acid 20 – 70 %	
R 35:	Same as above
S 2:	Must be kept away from children
S 23, S 26:	Same as above
S 27:	Immediately remove contaminated or saturated clothing
Mixtures of nitric acid (> 30 % HNO_3) and sulfuric acid (nitrating acid)	
R 8, R 35:	Same as above
S 23, S 26, S 36:	Same as above
S 30:	Never add water to acid

Protective clothing should be worn to prevent contact with the skin. The acid must be kept away from children. In case of burns, the affected area should be washed with copious amounts of water and a doctor should be consulted. Skin burns itch and become yellow due to the formation of xanthoproteins.

Death may occur if large areas of skin are burned. Since regulation of the body temperature is disturbed, the patient must be kept warm. Protein enters the bloodstream and the patient may suffer from shock, appropriate preventive measures must therefore be taken. In case of contact with the eye, the eyelids must be opened and the eye washed with copious amounts of water. A doctor must be consulted.

Nitrous gases are released from nitric acid at room temperature, a fume cupboard should therefore be used when working with the acid. Use of respiratory protection equipment with a B, E, or NO filter is recommended.

Oral consumption of nitric acid leads to attack of the mucous membranes of the mouth, the esophagus, and the stomach. Shock may result. If conscious, the patient should drink lukewarm water to dilute the acid.

Nitrous Acid. Nitrous acid is toxic because it decomposes to form nitric acid and nitrogen monoxide.

Nitrogen Monoxide. Pure nitrogen monoxide does not have any irritating effects. It reacts, however, with hemoglobin to form methemoglobin, resulting in cyanosis and possibly death. The TLV-TWA value is 25 ppm (31 mg/m³).

Nitrogen Dioxide. Nitrogen dioxide is an irritant gas. Its MAK value is 5 ppm (9 mg/m³), TLV-TWA 3 ppm (5.6 mg/m³), TLV-STEL 5 ppm (9.4 mg/m³). Inhalation of nitrogen dioxide causes pulmonary edema which may result in death (lethal dose 200 ppm). The substance is only slightly water-soluble but highly lipid-soluble. It therefore penetrates the alveoli where it damages the capillary walls resulting in exudative inflammation. The respiratory tract is obstructed due to formation of foam. Concentrations exceeding 60 – 150 ppm produce coughing and a burning sensation in the chest. Pulmonary edema becomes apparent after 2 – 24 h. The patient suffers respiratory distress and insomnia. Chronic exposure to low doses results in coughing, headache, loss of appetite, and gastrointestinal disorders. Patients should be kept under clinical observation. Inhalation of ammonia from ammonium hydrogen carbonate is recommended.

If the presence of nitrous gas is to be expected a gas mask should be worn (NO filter).

Dinitrogen Monoxide. Dinitrogen monoxide (laughing gas) does not irritate the mucous membranes. It has a powerful analgesic action but is only weakly narcotic. The gas displaces nitrogen from air-filled body cavities (middle ear, sinuses, intestines, brain ventricles) resulting in an increase in pressure. After chronic exposure, polyneuropathy and myelopathy have been observed. TLV-TWA value is 50 ppm (90 mg/m³).

References

- 1 J. Brunborg, P. B. Holmesland in C. Keleti (ed.): *Nitric Acid and Fertilizer Nitrates*, Marcel Dekker, New York-Basel 1985, pp. 1 – 164.
- 2 H. Chilton: *Strong Water*, The M.I.T. Press, Cambridge, Mass. 1968.
- 3 Ullmann, 3rd ed., **15**, 3 – 67
- 4 E. M. Horn, H. Keiser, K. Schoeller, *Monatsh. Chemie* **118** (1987) 1205 – 1218.
- 5 Ullmann, 4th ed., **20**, 305 – 332.
- 6 S. A. Stern, J. T. Mullhaupt, W. B. Kay: "The Physicochemical Properties of Pure Nitric Acid," *Chem. Rev.* **60** (1960) no. 2, 186 – 207.
- 7 A. F. Hollemann, E. Wiberg: *Lehrbuch der anorganischen Chemie*, 81st – 90th ed., De Gruyter, Berlin 1976.
- 8 Y. Fogel *et al.*, *Kinet. Katal.* **5** (1964) 496 – 504.
- 9 E. J. Nowak, *Chem. Eng. Sci.* **21** (1966) 19 – 27.
- 10 T. Pignet, L. D. Schmidt, *J. Catal.* **40** (1975) 212–225.
- 11 G. Nettesheim, *Chem. Ing. Tech.* **41** (1969) 773 – 775.
- 12 *Nitrogen* **183** (1990) 27 – 32.
- 13 S. P. S. Andrew in C. Keleti (ed.): *Nitric Acid and Fertilizer Nitrates*, Marcel Dekker, New York-Basel 1985, pp. 31 – 40.
- 14 Johnson Matthey, DE 3 042 362, 1988 (D. J. Stephanson, A. E. Heywood, G. L. Selman).
- 15 Johnson Matthey, DE 3 039 286, 1981 (A. G. Knapton, G. L. Selman).
- 16 Johnson Matthey, EP 0 275 681, 1988 (J. R. Handley).
- 17 A. R. McCabe, G. D. W. Smith, *Platinum Met. Rev.* **27** (1983) no. 1, 19 – 25.
- 18 J. K. Bradley, G. Drake: "Nitric Acid Technology," Paper read before the Fertiliser Society of London, 15th October 1981.
- 19 R. M. Heck, J. C. Bonacci, W. R. Hatfield, T. H. Hsiung, *Ind. Eng. Chem. Process Des. Dev.* **21** (1982) 73 – 79.
- 20 A. J. Fischer, M. A. Lang: "Engelhard's Role in Advancing Nitric Acid Catalyst Technology," Paper read before The British Sulphur Society, 14th Int. Conference, Caracas, 9th – 12th April 1989. Engelhard Corporation, EP 0 259 966, 1988 (H. C. Lee, R. J. Farrauto, R. W. Hatfield).
- 21 H. C. Lee, R. J. Farrauto, *Ind. Eng. Chem. Res.* **28** (1989) 1 – 5.
- 22 A. E. Heywood, *Platinum Met. Rev.* **17** (1973) no. 4, 118 – 129.
- 23 *Nitrogen* **66** (1970) 40 – 42.
- 24 Engelhard Corporation, EP 0 077 121, 1983 (R. W. Hatfield *et al.*).
- 25 *Nitrogen* **159** (1986) 28 – 32.
- 26 M. Bodenstein, *Z. Phys. Chem.* **100** (1922) 68 – 123.
- 27 W. T. Richards, J. A. Reid, *J. Am. Chem. Soc.* **54** (1932) 3014 – 3015.
- 28 P. J. Hoftyzer, F. J. G. Kwanten in G. Nonhebel (ed.): *Gas Purification Processes for Air Pollution Control*, Butterworths, London 1972.

- 29 S. P. S. Andrew, D. Hanson, *Chem. Eng. Sci.* **28** (1961) 105 – 114.
- 30 E. Abel, H. Schmid, *Z. Phys. Chem.* **132** (1928) 55–63; **134** (1928) 279 – 301.
- 31 U. Hoffmann, G. Emig, *Chem. Ing. Tech.* **51** (1979) no. 5, 516 – 517.
- 32 M. M. Wendel, R. L. Pigford, *AIChE J.* **4** (1958) no. 3, 249 – 256.
- 33 W. Weisweiler, *Chem. Eng. Tech.* **13** (1990) no. 2, 97–101.
- 34 M. Baerns, H. Hofmann, A. Renken: *Chemische Reaktionstechnik*, Thieme Verlag, Stuttgart-New York 1987.
- 35 D. N. Miller, *AIChE J.* **33** (1987) no. 8, 1351 – 1358.
- 36 J. B. Lefers, P. J. v.d. Berg, *Chem. Eng. J.* **23** (1982) 211 – 221.
- 37 J. J. Carberry: *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, New York 1976, pp. 289–293.
- 38 W. Brötz, F. Schnur: “Chemische Reaktionstechnik,” *Chem. React. Eng. Eur. Symp.* 1ct 1957, Amsterdam 1957, p. 1.
- 39 C. Toniolo, G. Giammarco: *C. R. Congr. Int. Chim. Ind.* **4** (1932) 829 – 859.
- 40 Gmelin **4**, “Stickstoff”, 953.
- 41 L. Hellmer, *Chem. Ing. Tech.* **55** (1972) no. 6, 420–424.
- 42 R. W. King, J. C. Fielding, *Trans. Inst. Chem. Engr.* **38** (1960) 71 – 83.
- 43 M. Koukolik, J. Markek: *Chem. React. Eng. Proc. Eur. Symp.* 4th 1986, Brüssel Sept. 1968, pp. 347–359.
- 44 G. Boy, B. Koehret, A. Piquereau: *Routine Programs and Use of Computers in Chemical Engineering*, International Congress, Paris March 1978, C 18, 81 – 85.
- 45 V. I. Glushchenko, E. D. Kirichuk, *Int. Chem. Eng.* **22** (1982) no. 1, 181 – 186.
- 46 H. Hesky, *Chem. Ing. Tech.* **33** (1961) no. 1, 27 – 31.
- 47 T. H. Chilton, *Chem. Eng. Prog. Monogr. Ser.* **56** (1960) no. 3, 1 – 22.
- 48 K. Asperger, *Chem. Tech. (Leipzig)* **14** (1962) no. 10, 582 – 589.
- 49 L. R. Roudier *et al.*, *Inf. Chim.* **88** (1970) 63 – 70.
- 50 R. M. Counce, J. J. Perona, *Ind. Eng. Chem. Process Des. Dev.* **19** (1980) 426 – 431.
- 51 H. Holma, J. Sohlo, *Comput. Chem. Eng.* **3** (1979) 135 – 141.
- 52 K. W. Wiegand, E. Scheibler, M. Thiemann, *Chem. Eng. Tech.* **13** (1990) no. 5, 289 – 297.
- 53 J. J. Carberry: *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, New York 1976, pp. 286–293.
- 54 R. Wetter, *Chem. Tech. (Heidelberg)* **13** (1984) no. 3, 59 – 60.
- 55 W. Hänggeli: “Steam Washing of Nitrous Gas Compressors”. *Techn. Inf. Nr. T8/8*, Sulzer, Zürich.
- 56 R. Staudé, *Chem. Prod.* **4** (1980) 32 – 41.
- 57 *Kältetechnik* **10** (1958) no. 8; DKV-Arbeitsblatt 2 – 26.
- 58 J. Eimers in C. Keleti (ed.): *Nitric Acid and Fertilizer Nitrates*, Marcel Dekker, New York-Basel 1985.
- 59 ASTM A 262–85a Practice C: Nitric Acid Test for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels.
- 60 G. Berglund, *Chem. Ind. (Düsseldorf)* **34** (1982) 669 – 673.
- 61 G. H. Honti in C. Keleti (ed.): “Various Processes for the Production of Commercial – Grade Nitric Acid,” pp. 61 – 98, and “Various Processes for the Production of Concentrated Nitric Acid,” pp. 99 – 130 in *Nitric Acid and Fertilizer Nitrates*, Marcel Dekker, New York-Basel 1985.
- 62 *Nitrogen* **154** (1985) 28 – 37.
- 63 *Nitrogen* **129** (1981) 32 – 39.
- 64 W. Freitag, M. W. Packbier: “Solving Nitric Acid Plant Pollution Problems,” *Ammonia Plant Saf.* **20** (1978) 11 – 16.
- 65 VDI-Richtlinie 2295, VDI-Verlag, Düsseldorf.
- 66 Umweltbundesamt, *Statistisches Jahrbuch*, StBA, Berlin 1988, Tab. 25.
- 67 Erste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft- TA Luft) 1986.
- 68 *VDI-Handbuch Reinhaltung der Luft*, VDI-Verlag, Düsseldorf 1974.
- 69 VDI-Richtlinie 2310, Blatt 12, VDI-Verlag, Düsseldorf 1985.
- 70 VDI-Richtlinie 2066, Blatt 1, VDI-Verlag, Düsseldorf 1975.
- 71 VDI-Richtlinie 2456, VDI-Verlag Düsseldorf: a) Blatt 1, 1973; b) Blatt 2, 1973; c) Blatt 3, 1975; d) Blatt 4, 1976; e) Blatt 5, 1978; f) Blatt 6, 1978; g) Blatt 7, 1981; h) Blatt 8, 1986; i) Blatt 9, 1989; j) Blatt 10 (Entwurf) 1989.
- 72 G. A. Heymann, G. S. Turner, *ISA Trans.* **3** (1976) 209 – 213.
- 73 “Additional Absorption Capacity Stems Nitric Acid Plant NO_x Pollution,” *Nitrogen* **91** (1974) 36.
- 74 Österreichische Stickstoffwerke, US 3 034 853, 1962 (A. Schmidt, F. Weinrotter).
- 75 “Oxidative Tailgas Scrubbing Technique,” *Nitrogen* **94** (1975) 471.
- 76 Office National Industriel de Lazote, US 3 329 478, 1967 (R. Garlet).
- 77 Potasse et Engrais Chimiques, US 3 348 914, 1967 (B. Quanquin, H. Trimbach).
- 78 “Pollution Control,” *Nitrogen* **95** (1975) 44.
- 79 J. C. Adrian, J. Verilhac: A Process for Reduction of NO_x Content in Flue Gas, *2nd International Conference on Control of Gaseous Sulphur and Nitrogen Compound Emissions*, University Salford, April 1976.
- 80 “Urea as a Pollution Control Agent,” *Nitrogen* **95** (1975) 32.
- 81 B. J. Buck, W. G. Matthews, *Proc Environ. Symp.* 1976, 157 – 168.
- 82 Kernforschungsanlage Jülich, DE 3 226 840 A1, 1984 (H. Ringel).
- 83 L. Rodier, N. Durand, B. Mouille: “Nitric Acid Recovery from Waste Nitrous Gases by the COFAZ Process,” *Fert. Nitrogen: Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol.* 4th 1981, **2** (1982) 561 – 569.

- 84 *Nitrogen* **171** (1988) 25 – 34.
- 85 H. Dittmar: “Katalytische Reduktion von nitrosen Gasen bei der Salpetersäurefabrikation”, *VDI-Bericht* 525, VDI-Verlag, Düsseldorf 1985.
- 86 W. Weisweiler, B. Retzlaff, B. Hochstein, *Staub Reinhalt. Luft* **48** (1988) 119 – 126.
- 87 W. Weisweiler, B. Hochstein, *Staub Reinhalt. Luft* **49** (1988) 37 – 43.
- 88 A. More: “The Mitsubishi Process,” *Fert. Acids Proc. Br. Sulphur Corp. Int. Conf. Fert. 3rd* (1979) Paper VI, p. 536.
- 89 M. Yamaguchi, K. Matsushita, K. Takami: “New Catalytic Process for Removing Nitrogen Oxides from Nitric Acid Tail Gas,” *Fert. Acids Proc. Br. Sulphur Corp. Int. Conf. Fert. 3rd* **1** (1979) no. 6, 20.
- 90 R. Erath: “Das Bergbau-Forschung/UHDE-Verfahren”, *Brennstoff-Wärme-Kraft* (1985) no. 9; *Staub Reinhalt. Luft* (1985) no. 9; *Umwelt* (1985) no. 4.
- 91 “Gefahrgutverordnung Eisenbahn GGVE”, *Bundesgesetzblatt I*, 23.8. 1979, p. 1502.
- 92 “Règlement international concernant le transport des marchandises dangereuses par chemins de fer –RID”, *Bundesgesetzblatt II*, 26.10. 1978, p. 1285.
- 93 “Gefahrgutverordnung Straße – GGVS”, *Bundesgesetzblatt I*, 23.8.1979, p. 1509.
- 94 “Gesetz zu dem europäischen übereinkommen über die internationale Beförderung gefährlicher Güter auf der Straße (ADR),” ADR Rn. 2801, *Bundesgesetzblatt II*, 1969, p. 1489.
- 95 “Verordnung über die Beförderung gefährlicher Güter auf dem Rhein (ADNR),” ADNR. Rn. 6500/6501.
- 96 *Industrial Statistic Yearbook*, vol. 2, Commodity Production Statistics, United Nations, 1989.
- 97 J. S. Lundsgaard *et al.*, *Acta Anaesthesiol. Scand.* **21** (1977) no. 4, 308 – 313.
- 98 *Ullmann*, 3rd ed., **15**, 44.
- 99 Hoechst AG, DE 1 921 1815 1970 (H. T. Baechle, R. Kohlhaas).
- 100 N. M. Levenson: “Nitrous Oxide – U.S. Salient Statistics” in *Chemical Economic Handbook*, SRI International, 1983, pp. 7436000A–7436000E.
- 101 L. Pauling: *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, Verlag Chemie, Weinheim, Germany 1976.
- 102 F. H. Verhoek, F. Daniels, *J. Am. Chem. Soc.* **53** (1931) 1254 – 1259.
- 103 C. C. Addison: *Chemie der nichtwäßrigen ionischen Lösungsmechanismen*, Vieweg Verlag, Braunschweig 1967, pp. 1 – 78.
- 104 A. H. Brittain *et al.*, *Trans. Faraday Soc.* **65** (1969) 1963.
- 105 I. R. Beattie, *Prog. Inorg. Chem.* **5** (1963) 1 – 26.
- 106 I. C. Tracy, F. Daniels, *J. Am. Chem. Soc.* **77** (1955) 2033.
- 107 R. A. Ogg, *J. Chem. Phys.* **15** (1947) 337 – 338.
- 108 G. Sorbe: *Sicherheitstechnische Kenndaten chemischer Stoffe*, 15. Erg.-Lfg, ecomed Verlagsgesellschaft, Landsberg 1989.
- 109 “Verordnung über gefährliche Stoffe (Gefahrstoffverordnung – GefStoffV)”, *Bundesgesetzblatt I*, 1986, p. 1470; *Bundesgesetzblatt I*, 1987, p. 2721.
- 110 *GefStoffV: Gefahrstoffverordnung*, 3rd ed., ecomed Verlagsgesellschaft, Landsberg 1988. *Erste Verordnung zur Änderung der Gefahrstoffverordnung vom 16. Dezember 1987*, Deutscher Bundes-Verlag GmbH, 5300 Bonn 1.

Further Reading

- H. Bothe, S. Ferguson, W. E. Newton (eds.): *Biology of the Nitrogen Cycle*, 1st. ed., Elsevier, Amsterdam 2007.
- M. S. Clark, A. L. Brunick: *Handbook of nitrous oxide and oxygen sedation*, 3rd ed., Mosby/Elsevier, St. Louis Mo. 2008.
- S. I. Clarke, W. J. Mazzafrro: *Nitric Acid*, “Kirk Othmer Encyclopedia of Chemical Technology”, 5th edition, vol. 17, p. 170–195, John Wiley & Sons, Hoboken, NJ, 2006, online: DOI: 10.1002/0471238961.1409201803120118.a01.pub2.
- J. S. Schepers: *Nitrogen in agricultural systems*, American Society of Agronomy [u.a.], Madison, WI 2008.

