Nitric acid
A true all-rounder!
The Business Area Industrial Solutions of thyssenkrupp is a world leader for planning, construction and service in the field of industrial plants and systems. Together with our customers we develop solutions at the highest level and deliver efficiency, reliability and sustainability throughout the entire life cycle. Our global network, with around 19,000 employees at 70 locations, enables us to provide turnkey solutions worldwide which set new benchmarks with their high productivity and particularly resource conserving technologies.

We are at home in many different industries. Along with chemical, fertilizer, coking, refinery, cement and other industrial plants, our portfolio also includes equipment for open-cast mining, ore processing and transshipment, as well as associated services. In the naval sector, we are a leading global system supplier for submarines and surface vessels. As an important system partner to our customers in the automotive, aerospace and battery industries, we optimize the value chain and improve performance.
The history of the Uhde nitric acid process / Market position

1905 young engineer Friedrich Uhde built the first nitric acid pilot plant
6 April 1921 foundation of Uhde Company
1926 first produced ammonia according to the Mont-Cenis-Uhde-Process
1928 full operation of the plant
1929 first design of a full scale commercial NA process
1932 first commercial scale NA plant in operation (for a customer in Russia)
The oxidation of ammonia over a platinum catalyst to nitrogen oxides, and their absorption in water to form nitric acid was first carried out in 1838 by C.F. Kuhlmann. However, this discovery was not then commercialised as ammonia was too expensive compared with the Chile saltpetre used to manufacture nitric acid in those days.

The history of the modern nitric acid process really begins in 1901 when W. Ostwald established the ammonia oxidation conditions necessary for high nitrogen oxide yields. The first plants using the Ostwald process were started up in the first decade of the 20th century.

With more than 55 plants built since 1980 thyssenkrupp Industrial Solutions (formerly known as Uhde) is nowadays the leading licensor for Nitric Acid Technology worldwide. As early as 1905, Dr. Friedrich Uhde, the founder of Uhde GmbH, designed and constructed, in cooperation with Prof. Wilhelm Ostwald, a pilot plant for the production of nitric acid by burning ammonia with air in the presence of a catalyst.

Since the company’s foundation in 1921, the number of plants for the production of weak and concentrated nitric acid as well as ammonia combustion units for nitrogen oxide production and absorption plants for nitrous waste gases, which have been designed, constructed and commissioned by thyssenkrupp Industrial Solutions under a variety of climatic conditions total some 200. The processes have been continually refined in order to meet ever more stringent requirements, particularly with regard to air pollution control and energy cost constraints.

The plants designed and constructed by thyssenkrupp Industrial Solutions are characterised by high reliability, profitability and on-stream time. Shutdown periods are now almost entirely limited to catalyst changes and equipment inspections.

The number of follow-up orders thyssenkrupp Industrial Solutions receives bears witness to the satisfaction of our customers.
Although the basic chemistry of the nitric acid process has not changed in the last hundred years, today’s highly efficient, compact and environmentally friendly plants have been developed by a process comparable with the advances made in automobile technology in the same period.

Today, nitric acid is produced exclusively from ammonia oxidised by combustion with air in the presence of a noble-metal catalyst.

The catalysts used in the process consist of a pack of platinum-rhodium gauzes, the number depending on the operating pressure and burner construction. The gauzes are produced nowadays by knitting thin wires, usually with a diameter of 60 or 76 µm.

A platinum recovery system made from palladium can easily be installed underneath the platinum catalyst. Combined catalyst and catchment systems are also available. Nowadays, it is possible to manufacture catalyst gauzes with a diameter of more than 5.5 m. More than 1,500 t/day of nitric acid can be produced from a single burner.

Even larger burners can be manufactured; the upper limit is dictated solely by transport restrictions and flange machining.

The production of nitric acid takes place in 3 process steps shown by the following main equations:

1. Ammonia combustion
   \[ 4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O} + 905 \text{kJ} \]

2. Oxidation of the nitric oxide
   \[ 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 + 113 \text{kJ} \]

3. Absorption of the nitrogen dioxide in water
   \[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO} + 116 \text{kJ} \]

In practice, these three process steps can be carried out in different ways, resulting in several different nitric acid processes. Modern nitric acid plants are designed according to the mono-pressure or the dual-pressure process.

Within the group of mono-pressure processes, a distinction is made between the medium-pressure process with a 4 - 6 bar abs. operating pressure and the high-pressure process which operates at 7 - 12 bar abs.

The dual-pressure process employs a medium pressure of approx 4 - 6 bar abs. for ammonia combustion and a high pressure of approx. 10 - 14 bar abs. for nitric acid absorption.

The optimum process is selected taking into account the costs of feedstocks and utilities, energy and capital investment as well as local conditions.
In compliance with stringent pollution abatement requirements, it is possible to achieve a NO\textsubscript{x} tail gas content of below 25 ppm. Furthermore, emissions of nitrous oxide, an unwanted by-product in the ammonia oxidation step, can be reduced to a minimum by the EnviNOx\textsuperscript{®} system by Uhde, which is the Best Available Technology (BAT) of today.

Nowadays 60 million t/year of nitric acid of various concentrations are produced worldwide. Approximately 85% of this is used as an intermediate in the production of nitrogenous mineral fertilizers, primarily ammonium nitrate and its derivatives such as calcium nitrate, calcium ammonium nitrate and urea ammonium nitrate solution. The remainder goes into the production of porous prilled ammonium nitrate for the mining industry, and as an intermediate for the production of special chemicals such as caprolactam or adipic acid. There is a growing demand for azeotropic nitric acid (approximately 68% concentration), which is used as a nitrating agent in the production of nitro-benzene, dinitrotoluene and other chemicals. These are further processed to TDI or MDI, and finally used for the production of polyurethane. thyssenkrupp Industrial Solutions covers many of the technologies mentioned.

Among the great variety of other applications, those most worthy of mention are its use as a chemical in metallurgy, for example as an etching and pickling agent for stainless steel, and its employment in the manufacture of dinitrogen tetroxide for rocket fuels.
The Uhde medium-pressure process

Nitric acid plant for SKW in Wittenberg, Germany

Capacity: 350 t/day HNO$_3$ (100%) (Mono medium-pressure)

The ammonia combustion unit was designed for a capacity equivalent to 500 t/day HNO$_3$ (100%). It supplies the existing plant for the production of highly concentrated nitric acid with nitrous gases.

Flowsheet of a medium-pressure nitric acid plant

1. Reactor
2. Process gas cooler
3. Tail gas heater 3
4. Economizer
5. Cooler condenser & feedwater preheater
6. Absorption
7. Bleacher
8. Tail gas heater 1 & 2
9. Tail gas reactor
10. Ammonia evaporation & superheating
11. Turbine steam condenser
In this process, the air required for burning the ammonia is supplied by an uncooled air compressor. The compressor set can be designed either as an inline train configuration or preferably as a bull gear type with an integrated tail gas turbine.

The operating pressure is governed by the maximum final pressure obtainable in an uncooled compressor, i.e. 4 - 5 bar abs. in the case of radial compressors and 5 - 6 bar abs. with axial flow compressors.

Plant capacities of up to 700 t/day of nitric acid (100%) can be realised using a single ammonia combustion unit and one absorption tower. Due to the process pressure, higher capacities of up to about 1,000 t/day are feasible if a second absorption tower is used. The medium pressure process is the process of choice when maximum recovery of energy is required. The air compressor is usually driven by a tail gas expansion turbine and a steam turbine, the steam being generated within the plant. If the credit for exported steam is high then the compressor train can be driven by a high voltage synchronous or asynchronous electric motor rather than a steam turbine so that all the steam generated can be exported.

With this plant type, it is possible to produce one type of nitric acid with a max. concentration of 65% or two types of acid with different concentrations, e.g. 60% nitric acid and 65% nitric acid.

The NO\textsubscript{X} content has to be reduced to the required value by selective catalytic reduction using a non-noble-metal catalyst and ammonia as the reducing agent.

The medium-pressure process is characterised by a high overall nitrogen yield of about 95.7% or 95.2% in conjunction with the tail gas treatment process, a low platinum consumption and a high steam export rate.

The catalyst gauzes only need to be changed once every 6 months due to the low burner load.
The Uhde high-pressure process

In the high-pressure process, a radial multi-stage compressor with an intercooler section is used to compress the process air to a final pressure of 7 - 12 bar abs. Preferably, the bull gear type with integrated tail gas turbine is selected but alternatively an inline machine can be used.

Due to the higher pressure, all equipment and piping can be of a smaller size and only one absorption tower is required.

The arrangement of all equipment is very compact so that the building for the machine set and the burner unit can be kept small, but this does not pose a problem for maintenance work.

This type of plant is always recommended when a quick capital return is desirable.

Plant capacities between 100 t/day (100%) and 1,000 t/day of nitric acid can be realised.

The achieved acid concentrations of up to 67% are slightly higher than with the medium-pressure process. Two or more product streams with different concentrations are likewise possible.

The compressor may be driven by a steam turbine or an electric motor.

The NO\textsubscript{X} concentration in the tail gas can be lowered to less than 25 ppm by an additional catalytic tail gas treatment unit. The nitrogen yield attained by the high-pressure process is in the order of 94.5%.

For capacities below 100 t/day, a low capital investment cost may be much more preferable to an optimum recovery of energy.

In such cases, thyssenkrupp Industrial Solutions can offer a greatly simplified process which does not include tail gas and steam turbines. The heating of the tail gas downstream of the absorption section is not necessary. Special design concepts for the process gas cooler unit, condenser and bleacher reduce the cost even further.

thyssenkrupp Industrial Solutions also provides a similar process without the ammonia evaporation and heat recovery units for recovering acid from the waste gas in, for example, adipic acid plants.
Two high-pressure nitric acid plants:

(left) Enaex S.A., Mejillones, Chile
Capacity: 925 t/day HNO₃ (100%)

(right) Thai Nitrate Company, Rayong, Thailand
Capacity: 210 t/day HNO₃ (100%)
The Uhde dual-pressure acid process

The dual-pressure process was developed to accommodate ever more stringent environmental pollution control requirements.

The process air is compressed to a final pressure of 4 - 6 bar abs.

The NO gas from the ammonia combustion unit is cooled in a heat exchanger train, producing steam and preheating tail gas, and then compressed to 10 - 14 bar abs in the NO\textsubscript{X} compressor. The final pressure is selected so as to ensure that the absorption section is optimised for the specified NO\textsubscript{X} content of the tail gas and that the compressors, driven by a steam turbine, can be operated using only the steam generated in the process gas cooler unit while ensuring that some excess steam will always be available in order to guarantee steady operating conditions at all times. Alternatively the compressor set can be driven by either a high voltage asynchronous or synchronous motor and the steam generated can be exported. The dual-pressure process combines in an economical way the advantages of the low pressure in the combustion section and the high pressure in the absorption section. Plant capacities of up to 1,600 t/day of nitric acid (100%) can be achieved in a single-train configuration. The machine set can be designed either as an inline-shaft set or optionally as a bull gear type unit with integrated air/NO\textsubscript{X} compression and tail gas expander stages. The inline machine concept is favourable in the case of higher plant capacities from 500 t/day up to 2,200 t/day or if an increased energy export is required.

The NO\textsubscript{X} is further reduced to less than 25 ppm by selective catalytic reduction using a non-noble-metal catalyst and ammonia as the reducing agent.

Due to the low burner load, the catalyst gauzes can remain in the burner for an operating period of 6 to 8 months or longer before being partially or completely replaced. Acid concentrations of more than 68% can be achieved. Two or more product streams with different concentrations are also possible. In addition, external streams of weak nitric acid (various concentrations) can be processed if required.
Two dual-pressure nitric acid plants:

(left) Abu Qir Fertilizers and Chemical Ind. Co., Abu Qir, Egypt
Capacity: 1,850 t/day HNO₃ (100%)
NOₓ in tail gas: less than 50 ppm as a result of a catalytic tail gas treatment process

(right) Borealis AG, Linz, Austria
Capacity: 1,000 t/day HNO₃ (100%)
NOₓ in tail gas: less than 10 ppm as a result of the N₂O/NOₓ abatement process by Uhde – EnviNOX®
The Uhde azeotropic nitric acid process

Azeotropic nitric acid with an elevated concentration of 68% by weight can replace concentrated nitric acid in some applications such as nitrations. Due to increased market demand, we have developed an enhanced process for the reliable production of azeotropic nitric acid without any further weak nitric acid co-production. The basic process design is mainly an extended dual-pressure process.

Important process features for the production of azeotropic acid are, in addition to sufficient absorption pressure and cooling, the overall water balance of the plant. Furthermore, the ratio of dinitrogen tetroxide to nitric oxide in the process gas at the absorption tower inlet has to be adjusted to a level that is in equilibrium with the acid concentration required.

To satisfy the overall water balance, it is mandatory at some locations to eliminate the water carried with the incoming air taken in by the air compressor. The necessary measures depend on climatic conditions, in particular air humidity and temperature. In the case of extreme conditions the installation of an additional air cooler/condenser operating partly with chilled water is recommended. Normally in the Uhde dual-pressure process, there is an extra chilled water circuit linked to the ammonia evaporation. This uses to a large extent the ammonia evaporation heat, especially in the absorption section, in order to establish the required acid strength and the $\text{NO}_x$ level at the absorption outlet. It is also possible to provide an external chilled water set. However, this solution is expensive and energy consuming and would only be considered by thyssenkrupp Industrial Solutions if all other measures prove insufficient.

The design of the absorption column is of particular importance especially for producing azeotropic acid. At thyssenkrupp Industrial Solutions a sophisticated computer program is used to predict the exact limits of acid concentration, heat loads, $\text{NO}_x$ in tail gas, etc.

Another important feature of the azeotropic nitric acid process by Uhde is the drying section for the secondary air.

Taking the above into consideration, thyssenkrupp Industrial Solutions is able to offer individual customers tailor-made solutions for azeotropic nitric acid plants.

The equipment shown as an example is fully integrated in thyssenkrupp Industrial Solutions’ compact bull gear concept, which is applicable for capacities up to 1,100 t/day. Above this capacity an inline machine set is employed as shown on page 13. The first pressure level delivered by the air compressor is advantageous for the ammonia combustion section, while the final pressure delivered by the $\text{NO}_x$ compressor promotes absorption and the formation of azeotropic acid.
Two azeotropic nitric acid plants:

(left) BP Köln, Cologne, Germany
Capacity: 1,500 t/day HNO₃ (100%)

(right) Namhae Chemical Corporation operated by HU-CHEMS, Yosu, Korea
Capacity: 1,150 t/day HNO₃ (100%)
Neglected for many years, nitrous oxide (N\textsubscript{2}O) – also known as “laughing gas” - is formed in the ammonia burner as an unwanted by-product. Depending on the performance of this burner around 1% to 2% of the ammonia feed is lost in this way, with a similar amount being lost due to the formation of nitrogen. The nitrous oxide passes through the rest of the nitric acid plant unchanged and is discharged to atmosphere with the tail gas. Emissions are now coming under scrutiny by regulators since nitrous oxide is a potent greenhouse gas some 300 times stronger than carbon dioxide and is implicated in the destruction of the ozone layer.

thyssenkrupp Industrial Solutions, having at an early stage recognised this trend, have developed a catalyst and a process for the lowering of nitrous oxide emissions from nitric acid plants. An added bonus is that emissions of nitrogen monoxide and dioxide (NO\textsubscript{X}) are also reduced.

The EnviNOx\textsuperscript{®} nitrogen oxide abatement process by Uhde features a tail gas reactor installed directly upstream of the tail gas turbine. thyssenkrupp Industrial Solutions has developed specific process variants to cater for the range of temperatures found in different nitric acid plants. The nitrous oxide decomposition (variant 1) is particularly suited to tail gas temperatures above 420°C. In this variant nitrous oxide is decomposed to oxygen and nitrogen in a first catalyst bed.

\[
\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2} \text{O}_2 + 82 \text{ kJ}
\]

The tail gas is then mixed with ammonia before entering the second bed in which NO\textsubscript{X} is catalytically reduced to water vapour and nitrogen:

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} + 1628 \text{ kJ}
\]
\[
3\text{NO}_2 + 4\text{NH}_3 \rightarrow \frac{7}{2}\text{N}_2 + 6\text{H}_2\text{O} + 1367 \text{ kJ}
\]

Further removal of nitrous oxide also takes place in this bed.

For lower temperatures thyssenkrupp Industrial Solutions’ solution is based on the catalytic reduction of nitrous oxide with hydrocarbons, such as natural gas, combined with the reduction of NO\textsubscript{X} by ammonia (variant 2). In most situations the removal of both N\textsubscript{2}O and NO\textsubscript{X} can take place in parallel in a single catalyst bed. The quantity of the greenhouse gas carbon dioxide, that is produced due to the use of hydrocarbons is insignificant in comparison to the amount of greenhouse gas emission reduction that the EnviNOx\textsuperscript{®} process achieves by the removal of nitrous oxide.

In both EnviNOx\textsuperscript{®} process variants the tail gas leaving the reactor has reduced concentration of N\textsubscript{2}O of 30 ppm. The low outlet NO\textsubscript{X} concentration is significantly smaller than that commonly attained in conventional DeNO\textsubscript{X} units, and results in an invisible stack plume. The NO\textsubscript{X} reduction component is also available without the N\textsubscript{2}O removal component and is applicable to temperatures between about 200°C and 500°C.

EnviNOx\textsuperscript{®} technology by Uhde is suited equally well to retrofits or to new plants. As it is an end-of-pipe process there is no contact with the product nitric acid or intermediate NO gas, thus eliminating any possibility of product loss or contamination.

For more details, please refer to our brochure: An environmental star: EnviNOx\textsuperscript{®}
Flowsheet of tail gas section of a nitric acid plant with EnviNOx® reactor (variant 1)

1. Absorption
2. Tail gas heating
3. EnviNOx® combining DeN₂O and DeNOₓ functions

Flowsheet of tail gas section of a nitric acid plant with EnviNOx® reactor (variant 2)

1. Absorption
2. Tail gas heating
3. EnviNOx® combining DeN₂O and DeNOₓ functions

(for lower temperature applications)
The dual-pressure nitric acid plant in Donaldsonville, Louisiana, USA. Capacity: 870 t/day HNO₃ (100%)
## Typical consumption figures

<table>
<thead>
<tr>
<th>Plant type</th>
<th>Medium-pressure process</th>
<th>High-pressure process</th>
<th>Dual-pressure process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure $p_{\text{abs}}$</td>
<td>5.8 bar</td>
<td>10.0 bar</td>
<td>4.6/12.0 bar</td>
</tr>
<tr>
<td>Ammonia</td>
<td>284.0 kg</td>
<td>286.0 kg</td>
<td>282.0 kg</td>
</tr>
<tr>
<td>Electric power</td>
<td>9.0 kWh</td>
<td>13.0 kWh</td>
<td>8.5 kWh</td>
</tr>
<tr>
<td>Platinum, primary losses</td>
<td>0.15 g</td>
<td>0.26 g</td>
<td>0.13 g</td>
</tr>
<tr>
<td>with recovery</td>
<td>0.04 g</td>
<td>0.08 g</td>
<td>0.03 g</td>
</tr>
<tr>
<td>Cooling water (Δt = 10 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>including water for steam turbine condenser</td>
<td>100 t</td>
<td>130 t</td>
<td>105 t</td>
</tr>
<tr>
<td>Process water</td>
<td>0.3 t</td>
<td>0.3 t</td>
<td>0.3 t</td>
</tr>
<tr>
<td>LP heating steam, 8 bar, saturated</td>
<td>0.05 t</td>
<td>0.20 t</td>
<td>0.05 t</td>
</tr>
<tr>
<td>HP excess steam, 40 bar, 450 °C</td>
<td>0.76 t</td>
<td>0.55 t</td>
<td>0.65 t</td>
</tr>
</tbody>
</table>

Note: Comparison of typical consumption figures for steam turbine-driven and inline compressor set nitric acid plants, per tonne of nitric acid (100%).