

Industrial Solutions

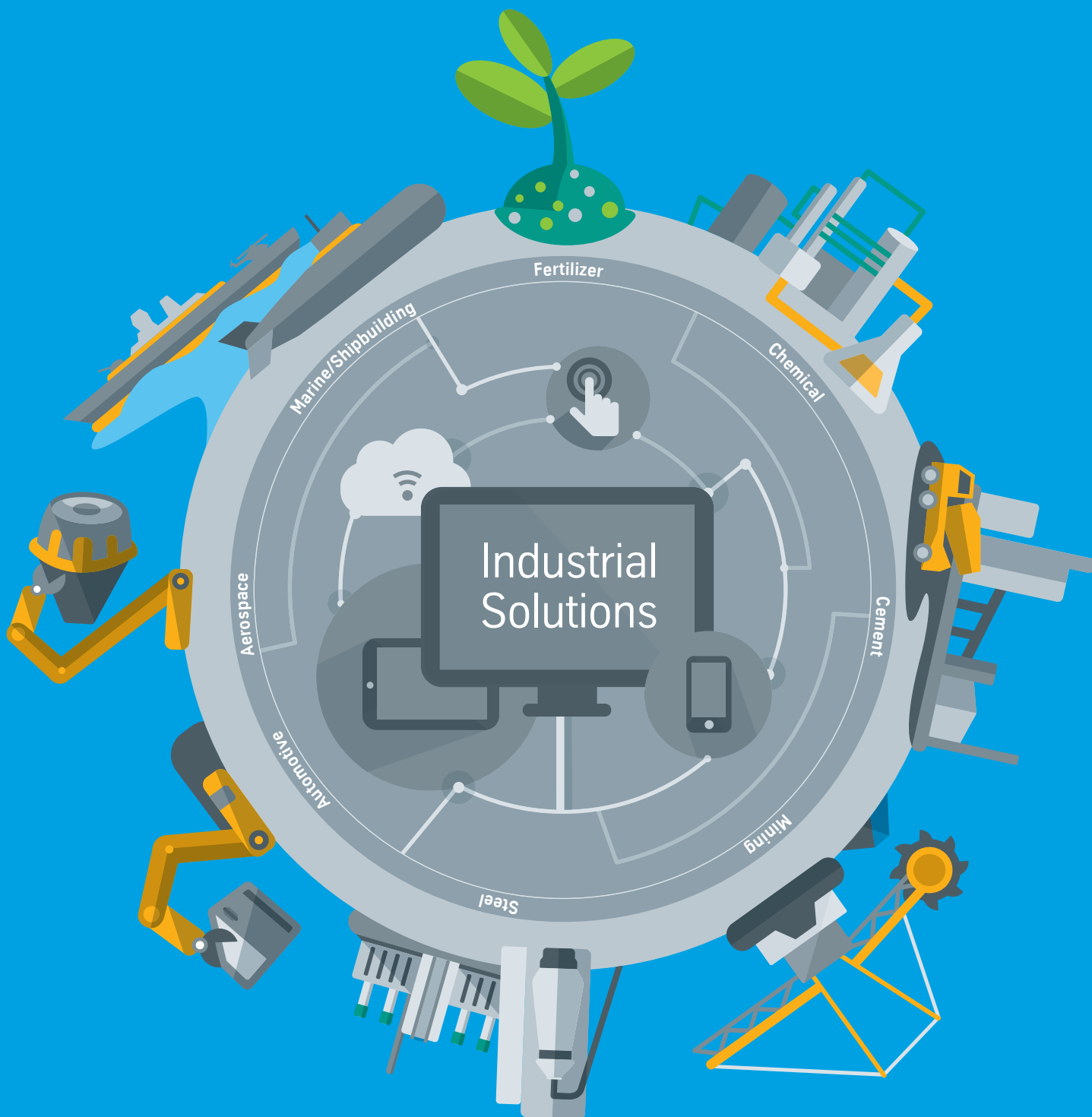
EnviNOx[®]

An environmental star



thyssenkrupp





The power of true efficiency

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.

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EnviNOx[®] – The N₂O/NO_x abatement process for nitric acid plants by Uhde

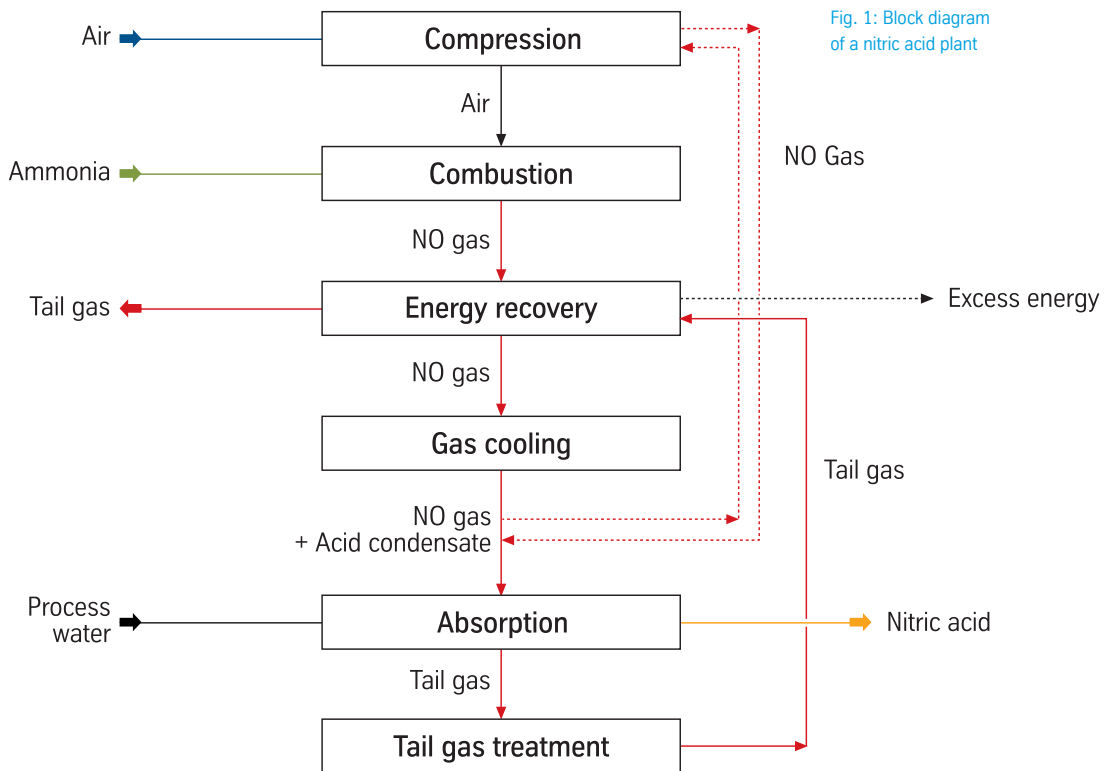


Fig. 1: Block diagram of a nitric acid plant

N₂O emissions in the production of nitric acid

The industrial production of nitric acid (HNO₃) involves oxidising ammonia (NH₃) with air over a platinum/rhodium gauze catalyst to produce nitrogen oxides. This process yields nitrogen monoxide (NO), which then reacts with oxygen and water to form nitric acid. However, it also produces nitrous oxide (N₂O) – a greenhouse gas and ozone killer – as an undesired by-product. Unlike NO, the nitrous oxide is not involved in the HNO₃ production process and would be emitted to the atmosphere if not appropriately treated.

The N₂O formation in nitric acid plants vary from about 3-4 kg of N₂O per metric ton of HNO₃ to as much as 20 kg of N₂O per metric ton of HNO₃ depending on the type of nitric acid plant. An estimated 400,000 metric tons of nitrous oxide are emitted each year by nitric acid plants worldwide. Due to its longevity in the earth's atmosphere and its special absorption properties for infrared radiation, N₂O is a potent greenhouse gas. One metric ton of N₂O emissions has the same effect on global warming as about 300 metric

tons of CO₂. Consequently, nitric acid plants are now the largest single source of greenhouse gas emissions among industrial manufacturing facilities. Whereas limits on NO_x emissions have long been in force (due to concerns about acid rain, smog, etc.), there have been no restrictions on N₂O emissions until recently. However, now that N₂O has been recognised as a major greenhouse gas (also designated as such in the Kyoto Protocol), some countries have introduced limits on emissions of N₂O from nitric acid plants.

Because the specific impact of N₂O on the greenhouse effect is many times greater than that of CO₂, the elimination of N₂O from nitric acid plants can make an important contribution to the protection of the earth's climate. An EnviNOx[®] system installed as a greenhouse gas emission reduction project under the Kyoto Protocol or under any similar emission trading scheme can offer process plant owners interesting opportunities for improving the environment and their balance sheet.

Development of the EnviNOx[®] process



thyssenkrupp Industrial Solutions mini-plant
installed at Borealis AG nitric acid plant, Austria

In light of the above, thyssenkrupp Industrial Solutions – a world leader in nitric acid technology – set about developing a technology for removing N_2O from the nitric acid production process. The goal was not only to achieve high rates of N_2O abatement but also to ensure that the technology itself could be safely and simply integrated into the HNO_3 production process without affecting it in any way. In particular, the aim was to find a suitable way of combining the N_2O removal process with the DeNOx stage, which is also necessary for tail gas treatment. Development therefore focussed on the catalytic removal of N_2O from the tail gas of HNO_3 plants (so-called tertiary measures). After preliminary tests, development concentrated on the use of special iron zeolite catalysts. Under laboratory conditions, these catalysts revealed a diverse reactivity towards N_2O : either by decomposing N_2O

into N_2 and O_2 – an effect increased significantly by the presence of NO_x in the tail gas (co-catalytic NO_x effect), or by reducing N_2O using various reducing agents, such as hydrocarbons. In addition, the iron zeolites also proved to be excellent DeNOx catalysts in an unusually wide temperature window, thus allowing N_2O abatement to be ideally combined with NO_x reduction. After optimising the catalysts, the positive laboratory results were verified under industrial conditions in a mini-plant installed in an HNO_3 production plant operated by Borealis AG in Linz, Austria.

The wealth of experimental results gained in the mini-plant enabled us to create N_2O and NO_x abatement solutions that are optimised for particular process conditions, such as the specific tail gas temperature or tail gas composition.

In particular, the following EnviNOx[®] process variants were developed:

- The DeNOx process by Uhde (catalytic reduction of NO_x)
- The EnviNOx[®] process variant 1 by Uhde (catalytic decomposition of N_2O and the catalytic reduction of NO_x)
- The EnviNOx[®] process variant 2 by Uhde (catalytic reduction of N_2O and NO_x)
- The De N_2O [®] process by Uhde (catalytic decomposition of N_2O)

Commercial scale implementation

Borealis AG, Linz, Austria (EnviNOx® process variant 1)



Borealis AG,
Linz, Austria

Process variant 1 has been in operation in the 1,000 mtpd Line E nitric acid plant of Borealis AG (formerly Agrolinz Melamine International) since 2003. The EnviNOx® reactor cleans a tail gas flow of 120,000 Nm³/h at 435°C and is the world's first commercial-scale facility for reducing N₂O and NO_x in the tail gas of a nitric acid plant.

Figure 6 shows that the EnviNOx® reactor consistently achieves very high abatement for N₂O (98%). The NO_x abatement obtained with this technology can be controlled by varying the amount of ammonia added and the NO_x emission level is currently set at 5-10 ppm.

Up to now, no significant deactivation of the initial catalyst charge has occurred since the first start-up.

Unlike other methods of selective catalytic reduction (SCR) of NO_x based on V₂O₅/TiO₂ catalysts, the EnviNOx® process, which uses an iron zeolite catalyst, has considerably reduced the risk of undesired NH₃ slip. Because excess NH₃ (within certain limits) is oxidised by the catalyst to N₂ and H₂O, the EnviNOx® process can, in principle, achieve higher rates of NO_x abatement than conventional SCR processes.

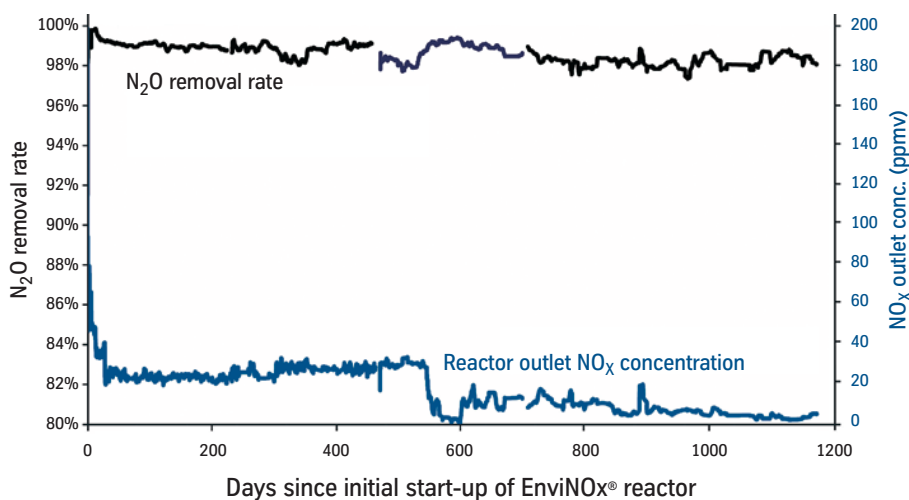
Overall, nitrous oxide emissions from this plant are reduced by some 2,400 t/year, equivalent to a reduction of around 750,000 t/year of CO₂.

Consequently, Borealis make a substantial contribution to climate protection in Austria. In fact, the Linz plant alone meets approximately 50% of Austria's greenhouse gas emissions reduction target for the industrial and manufacturing sectors as set by the Austrian government for the fulfilment of its Kyoto Protocol obligations. It is the largest single emissions reduction measure to be carried out in Austria. For this Borealis received the "Climate Pioneer" award from the Province of Upper Austria in 2003.

The Dutch company OCI Nitrogen (formerly DSM Agro) received the national Responsible Care prize 2008 of VNCI for the N₂O emission reduction in 4 nitric acid plants. The reduction to zero emission in 2 plants with an EnviNOx® reactor is considered a world record.

Further EnviNOx® process variant 1 systems are also in operation with similar very high N₂O abatement rates (99% and above). A reference list with more details is available on request.

Fig. 6: Borealis AG HNO₃ Plant
Line E - EnviNOx® Process
Variant 1 by Uhde



AFC, Abu Qir, Egypt (EnviNOx[®] process variant 2)

Process variant 2 has been in operation in the 1830 tpd nitric acid plant of Abu Qir Fertilizers and Chemicals in Egypt for over 2 years. This nitric acid plant is one of the largest in the world with a tail gas flow of 240,000 Nm³/h at a temperature of 415°C.

No deactivation of the initial catalyst charge has occurred since the first start-up in September 2006.

Figure 7 shows that the EnviNOx[®] reactor consistently achieves very high abatement for N₂O (99% and above), while NO_x emissions are reduced to effectively zero (< 1 ppm) making for an extremely clean tail gas.

The greenhouse gas emissions reduction is approximately 1.4 million metric tons of CO₂ equivalent per year. This is about the same as the greenhouse gas emissions from a 250 MW gas-fired electricity generation plant.

The reducing agents for N₂O and NO_x are natural gas and ammonia respectively.

Further EnviNOx[®] process variant 2 systems are also in operation with similar very high N₂O abatement rates (98% and above), e.g. in South Africa, Hungary and Korea. A reference list with more details is available on request.



Abu Qir Fertilizer Company
Abu Qir, Egypt

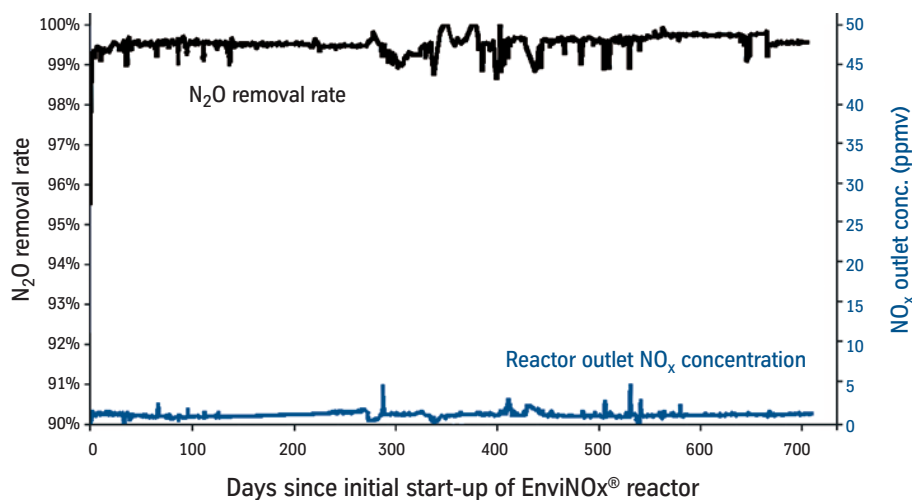


Fig. 7: Abu Qir HNO₃ Plant
EnviNOx[®] Process Variant 2 by Uhde

The DeNO_x process by Uhde

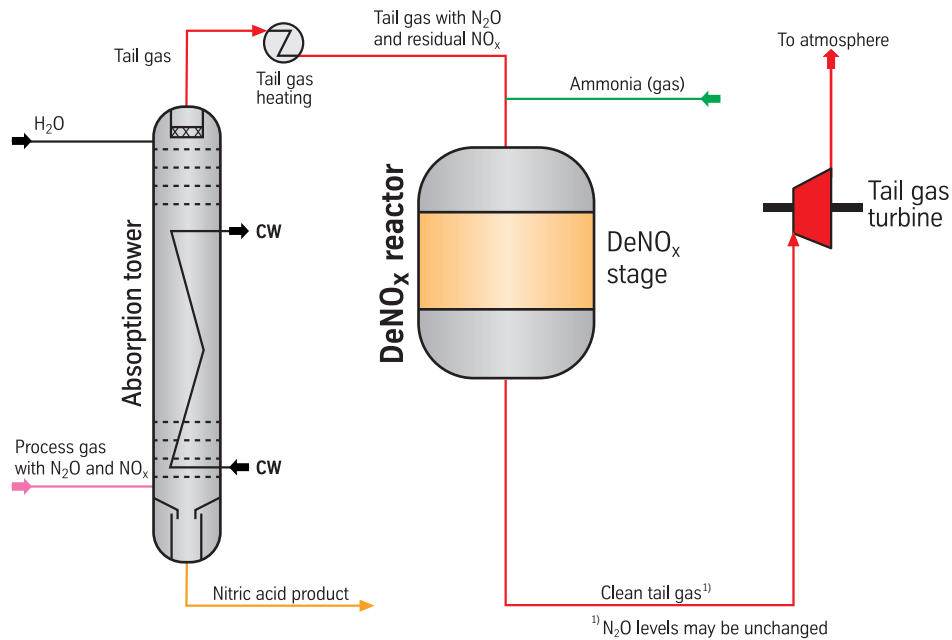


Fig. 2: DeNO_x process by Uhde:
catalytic NO_x reduction with ammonia over a zeolite catalyst

NO_x abatement by catalytic reduction

This NO_x abatement process is unusually flexible. Very high rates of NO_x reduction can be achieved over a wide range of tail gas temperatures from some 200°C to about 520°C.

The reactor contains a single catalyst bed filled with an iron zeolite catalyst EnviCat®-NO_x. The required reducing agent NH₃ is added via a mixing system upstream of the DeNO_x reactor.

DeNO_x reactions:



The EnviNOx[®] process variant 1 by Uhde

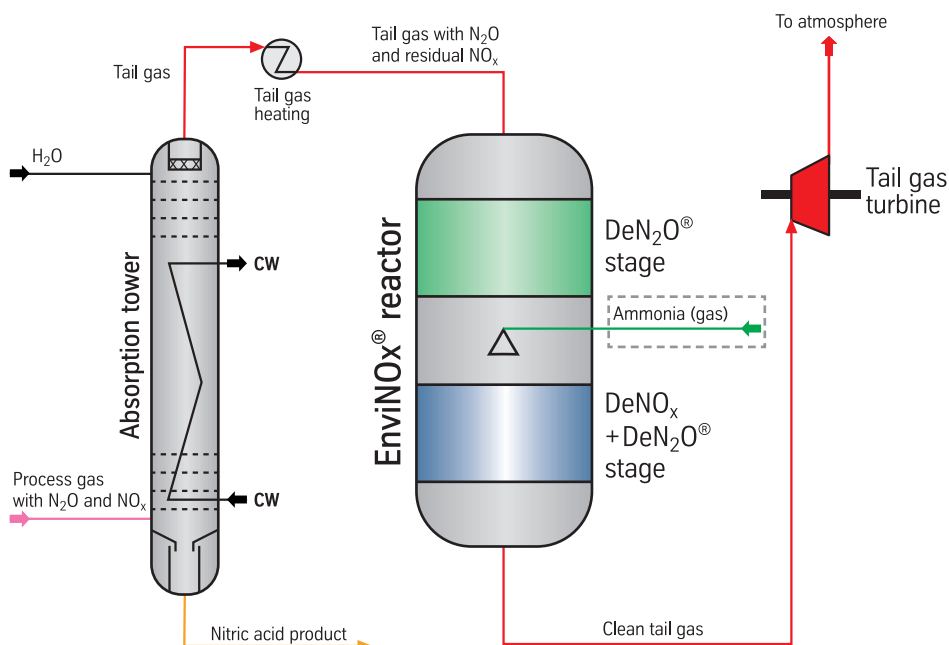


Fig. 3: EnviNOx[®] process variant 1:
catalytic decomposition of N₂O and catalytic NO_x reduction with ammonia over zeolite catalysts

N₂O abatement by catalytic decomposition with catalytic NO_x reduction

The EnviNOx[®] process variant 1 reactor is usually located between the final tail gas heater and the tail gas turbine and contains two catalyst beds filled with iron zeolite catalysts EnviCat[®]-NO_x and EnviCat[®]-N₂O-1 operating at the same pressure and temperature, and a device for the addition of NH₃ between the beds.

In the first DeN₂O[®] stage, the N₂O abatement is effected simply by the catalytic decomposition of N₂O into N₂ and O₂.

Since the NO_x content of the tail gas promotes the decomposition of N₂O, the

required DeNO_x stage is arranged downstream of the DeN₂O[®] stage (maximum exploitation of the NO_x effect).

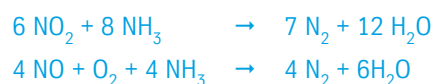
In the second stage, NO_x reduction is carried out using NH₃ as a reducing agent. At the same time the residual N₂O from the first stage is further destroyed by catalytic decomposition, thus maximising the overall rate of N₂O abatement.

This process variant is especially applicable for tail gas temperatures between about 425°C and 520°C.

DeN₂O[®] reactions:



DeNO_x reactions:



The EnviNOx[®] process variant 2 by Uhde

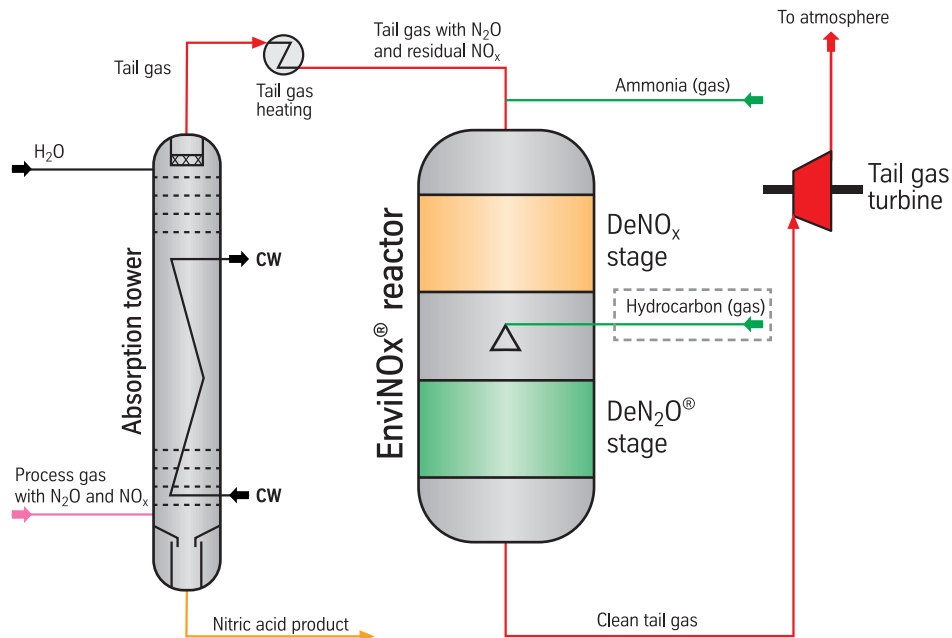


Fig. 4: EnviNOx[®] process variant 2:
catalytic reduction of NO_x with ammonia and N₂O with hydrocarbons over zeolite catalysts

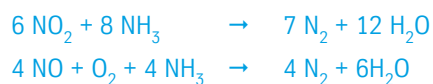
N₂O abatement by catalytic reduction with catalytic NO_x reduction

In this variant, N₂O is removed by catalytic reduction with a hydrocarbon such as natural gas or propane. Unlike with N₂O decomposition, the NO_x content of the tail gas inhibits the N₂O reduction reaction. It is therefore necessary to completely eliminate the NO_x in the tail gas. Depending on the tail gas composition and the particular operating conditions, this can be accomplished in a DeNO_x unit located upstream of the DeN₂O[®] equipped with EnviCat[®]-N₂O-2 stage or, preferably, simultaneously with the N₂O reduction in a single common stage.

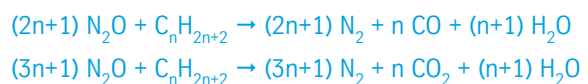
In the latter case, a separate upstream DeNO_x unit is not required.

Either the common stage process or the two-stage process with its hydrocarbon reducing agent feed mixer can be accommodated in a single reactor vessel. EnviNOx[®] process variant 2 is suitable for temperatures between about 340°C and 520°C depending on the specific conditions in the nitric acid plant. This temperature range can be extended by the implementation of a recuperative heat exchanger.

DeNO_x reactions:



DeN₂O[®] reactions:



The DeN₂O[®] process by Uhde

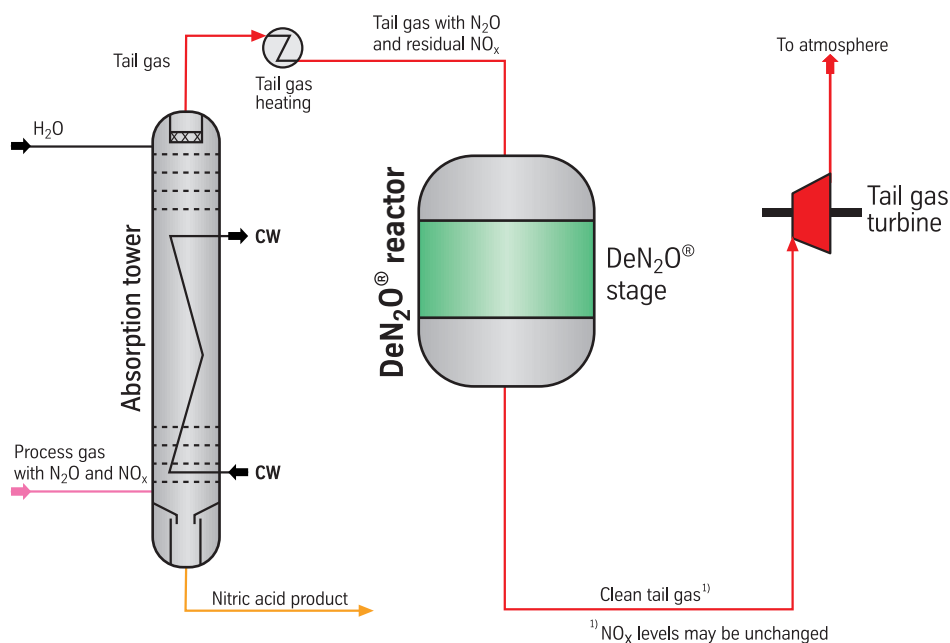


Fig. 5: DeN₂O[®] process by Uhde:
catalytic N₂O decomposition process (without reducing agents)

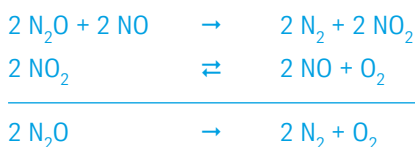
N₂O abatement by catalytic decomposition

The DeN₂O[®] process by Uhde consists of the first DeN₂O[®] stage of the EnviNOx[®] variant 1 as a single catalyst bed reactor.

The DeN₂O[®] process requires a tail gas temperature between about 425°C and 600°C. For high temperature applications the EnviNOx[®] technology in general is limited by the thermal and mechanical durability of the EnviCat[®] material (iron loaded zeolite). Corresponding laboratory investigations together with long-term large scale experiences are available from the realized installation for

operating temperatures up to 510°C allowing prediction of possible degradation of the catalyst. For applications exceeding this temperature the process concept of using a recuperator is considered a viable solution as well. In this case, the recuperator will reduce the temperature of the tail gas upstream the EnviNOx[®] reactor and reheat the tail gas after the treatment before entering the turbine. Furthermore it is also possible to use a new, modified type of iron zeolite catalyst, which is stable up to an operating temperature of 600°C.

DeN₂O[®] reactions:



The EnviNOx[®] process variant 2 by Uhde for extended temperature range

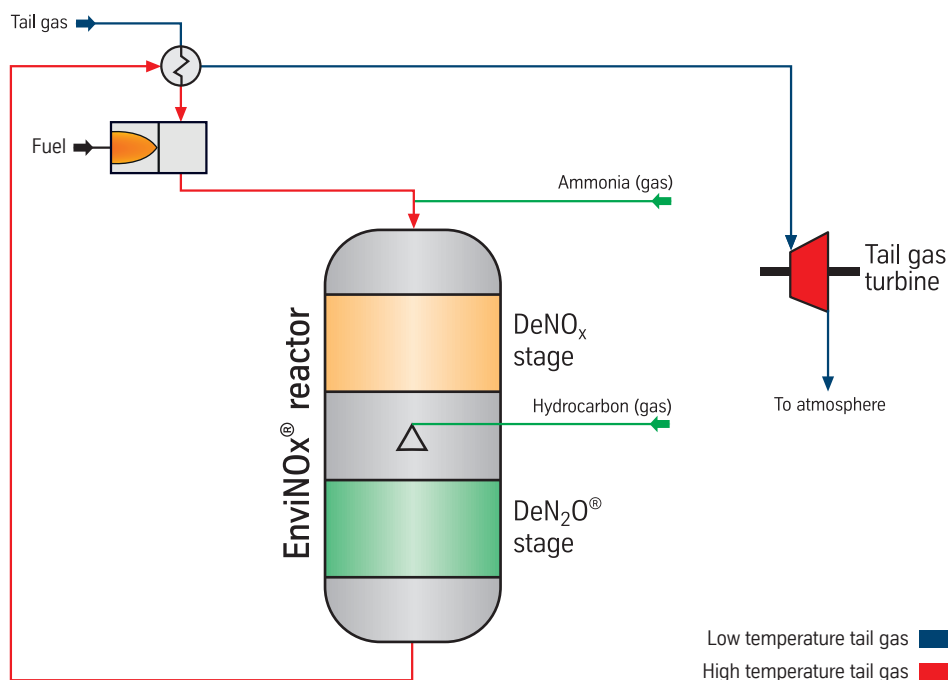


Fig. 6: EnviNOx[®] process variant 2 for low temperature application

Process Scheme of EnviNOx[®] with recuperator

A number of existing HNO₃ plants, optionally to be retrofitted with an EnviNOx[®] unit, do not provide the minimum tail gas temperature needed and may be limited in temperature by the mechanical design constraints of the plant equipment, too.

For these cases a practical solution has been developed in which the EnviNOx[®] unit is integrated in a heat exchange cycle. Introducing a recuperative heat exchanger enables the tail gas to be heated up to the required optimum temperature range and the desired abatement performance to be achieved. The heat exchanger uses the heat content of the cleaned tail gas including the enthalpy released by the N₂O and NO_x reduction to heat up the incoming, untreated gas. Thus the higher temperature zone is kept within the boundaries of the EnviNOx[®] system and does not affect the existing plant components.

During start-up an additional tail gas heater (inline burner) brings the EnviNOx[®] system up to the operating temperature. While in steady state operation, the recuperator recovers the gas temperature taking advantage of the additional heat released in the exothermic reactions taking place in the EnviNOx[®] reactor. Only little support by the inline burner is required to maintain the system temperature stable during continuous operation.

A corresponding technical system has first been implemented in a nitric acid plant of Radici Chimica SpA in Novara /Italy, in which the tail gas temperature comes to only 290°C and is limited by mechanical design of the tail gas turbine to about 310°C further limited by a safety trip at 300°C. By installation of the integrated heat exchange cycle temperature at the inlet of the EnviNOx[®] reactor is raised to 380°C resulting in a 98% N₂O removal and a NO_x reduction from about 800 ppm to virtual 0 ppm.

Advantages that speak for themselves

Starting from initial laboratory experiments, thyssenkrupp Industrial Solutions developed the EnviNOx® process to commercial-scale implementation in just three years, and it is now available to clients (i.e. owners of nitric acid plants) worldwide as a proven technology (please see enclosed Reference List). The extremely high rates of N₂O (99% and above) and NO_x (down to nearly zero ppm) abatement that can be achieved in a single reactor vessel mean that current and future N₂O and NO_x emission standards (e.g. best available technique (BAT) for nitric acid, please see Fig. 8) can be easily met. As a result, operating licences for nitric acid plants can be retained and an effective contribution made to lowering site emissions.

The EnviNOx® process has all the advantages of an "end-of-pipe technology". There is no risk of either product contamination or a loss of nitric acid plant capacity, because

there is no direct contact between the feedstock and the EnviNOx® technology, the intermediate products or the nitric acid product. EnviNOx® technology is based on highly active zeolite catalysts which contain no toxic components and have a long service life. A significant advantage of EnviNOx® technology is the fact that the inlet and outlet concentrations of N₂O at the EnviNOx® reactor can be measured continuously online. This permits the instantaneous N₂O abatement efficiency of the EnviNOx® reactor to be determined precisely at any moment. EnviNOx® technology enables numerous clients to trade greenhouse gas emissions rights in accordance with the flexible mechanisms (CDM, JI & ET) of the Kyoto Protocol or other emission trading schemes.

For more information, please contact one of our offices in your area or visit www.thyssenkrupp-industrial-solutions.com.



The EnviNOx® process by Uhde for the combined reduction of N₂O and NO_x emissions from nitric acid plants has received two awards: First Prize in the 2005 thyssenkrupp Innovation Contest and the 2004 Silver Award for "Environmental Innovation for Europe" from the European Environmental Press (EEP).

		N ₂ O emission level*	
		kg/tonne 100% HNO ₃	ppmv
M/M, M/H and H/H	New plants	0.12-0.6	20-100
	Existing plants	0.12-1.85	20-300
L/M plants		No conclusion drawn	

*the levels relate to the average emission levels achieved in a campaign of the oxidation catalyst

N₂O emission levels associated with the application of BAT for the production of HNO₃

Plant type: L/M - Dual Low/Medium, M/M - Mono Medium/Medium, M/H - Dual Medium/High, H/H - Mono High/High

NO _x emission level as NO ₂		
	kg/tonne 100% HNO ₃	ppmv
New plants	—	5-75
Existing plants	—	5-90*
NH ₃ slip from SCR	—	< 5

*up to 150 ppm, where safety aspects due to deposits of AN restrict the effect of SCR or with addition of H₂O₂ instead of applying SCR

NO_x emission levels associated with the application of BAT for the production of HNO₃

N₂O and NO_x emission level associated with BAT

Source: European Commission Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilizers, August 2007



EnviNOx features

- High N₂O removal rates (up to 99% and above)
- Availability of CDM approved methodology AM 0028
- Online measurement of N₂O inlet and outlet concentration (ensuring maximum carbon credits)
- N₂O and NO_x emissions reduction can be combined in a single reactor vessel
- High NO_x removal rates (down to nearly zero ppm NO_x)
- Proven on an industrial scale
- End-of-pipe technology:
 - no risk of product contamination
 - no risk of nitric acid production loss
 - no risk of fouling (e.g. waste heat boiler)
- Low consumption of N₂O reducing agents
- Non-toxic catalyst – easy handling and disposal
- Long catalyst service life
- Moderate pressure drop
- Wide temperature range:
 - DeNO_x process by Uhde: 200-520°C
 - DeN₂O[®] by Uhde: 425-600°C
 - EnviNO_x[®] process variant 1 by Uhde: 425-520°C
 - EnviNO_x[®] process variant 2 by Uhde: 330-520°C

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