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1. Company profile

With its highly specialised workforce of more than 5,600 employees and its international network of subsidiaries and branch offices, Uhde, a Dortmund-based engineering contractor, has to date successfully completed over 2,000 projects throughout the world.

Uhde’s international reputation has been built on the successful application of its motto *Engineering with ideas* to yield cost-effective high-tech solutions for its customers. The ever-increasing demands placed upon process and application technology in the fields of chemical processing, energy and environmental protection are met through a combination of specialist know-how, comprehensive service packages, top-quality engineering and impeccable punctuality.
EnviNOx® – The Uhde N₂O/NOₓ abatement process for nitric acid plants

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 is emitted into the atmosphere with the tail gas.

The N₂O emissions 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 NOₓ 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. These facts make nitric acid plants an ideal object for the implementation of a carbon trading project under the flexible mechanisms of the Kyoto Protocol or other Emission Trading Schemes (e.g. EU-ETS).
Kyoto Protocol, its flexible mechanisms and other Emission Trading Schemes

The 1997 Kyoto Protocol, which came into force on February 16, 2005, commits participating industrialised countries, the Annex I countries, to individual, legally-binding targets to limit or reduce their greenhouse gas emissions. Many of these Annex I countries will be unable to fulfill their obligations under the Kyoto Protocol within their own borders. The Kyoto Protocol therefore provides three flexible mechanisms (Emissions Trading (ET), Joint Implementation (JI) and Clean Development Mechanism (CDM)), which allow an Annex I country to be credited with emission reductions made outside its borders.

In view of the fact that, since February 16, 2005, it has become possible to obtain Certified Emission Reductions (CERs) from CDM projects, the interest in greenhouse gas emission reduction technologies has increased rapidly and, within the 2nd phase (2008 – 2012) under the Kyoto Protocol, it will increase further still.

Emissions Trading (ET) allows companies within Annex I countries to trade emission rights with each other both nationally and across borders. The European Union Emissions Trading Scheme (ETS) became effective in 2005, but included only carbon dioxide in its cap and trade system. The next ETS round will start in 2013 and will include N₂O. The installation of an N₂O abatement unit is obligatory for nitric acid plant owners in the European Union due to regulations that will come into force in 2013 (auctioning or cap and trade system most probable).

Similar emission trading schemes are currently under discussion (e.g. in Australia, North America).

During the period 2008 to 2012, a further kind of emission reduction project – the “Opt-In” – was developed in some EU countries.

With Joint Implementation (JI), the emission reductions of a project in a host Annex I country are transferred to a second Annex I country. Suitable host countries include those of Eastern Europe and Russia, which have already fulfilled their Kyoto obligations due to the reduction in industrial activity since the baseline year of 1990. Emission reductions obtained under JI count from the beginning of 2008.

The Clean Development Mechanism (CDM) is similar to JI except that the host country is a developing country without any Kyoto obligation. Thanks to the EU linking directive, emission reductions under CDM and JI can be acquired by organisations participating in the ETS in the same way as other emission rights within the ETS. CDM and JI are subject to very strict rules aimed at preventing CDM/JI projects from being unfairly credited with emission reductions. These rules are laid down in the approved methodologies which are subjected to intense scrutiny by the public and by experts before being passed by the CDM Executive Board.

A CDM project without an approved methodology cannot generate saleable greenhouse gas emission reductions. The very first CDM approved methodology for N₂O abatement in nitric acid plants (AM 0028) was submitted for the Abu Qir project and is generally applicable to all EnviNOx® process variants.

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.
In light of the above, Uhde – a world leader in nitric acid technology – set about developing a technology for removing N\textsubscript{2}O from the nitric acid production process. The goal was not only to achieve high rates of N\textsubscript{2}O abatement but also to ensure that the technology itself could be safely and simply integrated into the HNO\textsubscript{3} production process without affecting it in any way. In particular, the aim was to find a suitable way of combining the N\textsubscript{2}O removal process with the DeNO\textsubscript{X} stage, which is also necessary for tail gas treatment. Development therefore focussed on the catalytic removal of N\textsubscript{2}O from the tail gas of HNO\textsubscript{3} plants (so-called tertiary measures). After preliminary tests, development concentrated on the use of special iron zeolite catalysts, which were supplied by Süd-Chemie AG. Under laboratory conditions, these catalysts revealed a diverse reactivity towards N\textsubscript{2}O: either by decomposing N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{2} - an effect increased significantly by the presence of NO\textsubscript{X} in the tail gas (co-catalytic NO\textsubscript{X} effect), or by reducing N\textsubscript{2}O using various reducing agents, such as hydrocarbons. In addition, the iron zeolites also proved to be excellent DeNO\textsubscript{X} catalysts in an unusually wide temperature window, thus allowing N\textsubscript{2}O abatement to be ideally combined with NO\textsubscript{X} reduction. After optimising the catalysts, the positive laboratory results were verified under industrial conditions in a mini-plant installed in an HNO\textsubscript{3} production plant operated by Borealis AG in Linz, Austria.

The wealth of experimental results gained in the mini-plant enabled Uhde to create N\textsubscript{2}O and NO\textsubscript{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 EnviNO\textsubscript{X}® process variants were developed:

- The Uhde DeNO\textsubscript{X} process (catalytic reduction of NO\textsubscript{X})
- The Uhde EnviNO\textsubscript{X}® process variant 1 (catalytic decomposition of N\textsubscript{2}O and the catalytic reduction of NO\textsubscript{X})
- The Uhde EnviNO\textsubscript{X}® process variant 2 (catalytic reduction of N\textsubscript{2}O and NO\textsubscript{X})
- The Uhde DeN\textsubscript{2}O\textsuperscript{®} process (catalytic decomposition of N\textsubscript{2}O)
This NOX abatement process is unusually flexible. Very high rates of NOX 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. The required reducing agent NH₃ is added via a mixing system upstream of the DeNOₓ reactor.

**DeNOₓ reactions:**

- \[6 \text{ NO}_2 + 8 \text{ NH}_3 \rightarrow 7 \text{ N}_2 + 12 \text{ H}_2\text{O}\]
- \[4 \text{ NO} + \text{ O}_2 + 4 \text{ NH}_3 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}\]
The Uhde EnviNOx® process variant 1

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 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 NOx content of the tail gas promotes the decomposition of N₂O, the required DeNOx stage is arranged downstream of the DeN₂O® stage (maximum exploitation of the NOx effect).

In the second stage, NOx 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:**

\[
\begin{align*}
2 \text{N}_2\text{O} + 2 \text{NO} & \rightarrow 2 \text{N}_2 + 2 \text{NO}_2 \\
2 \text{NO}_2 & \rightarrow 2 \text{NO} + \text{O}_2 \\
2 \text{N}_2\text{O} & \rightarrow 2 \text{N}_2 + \text{O}_2
\end{align*}
\]

**DeNOx reactions:**

\[
\begin{align*}
6 \text{NO}_2 + 8 \text{NH}_3 & \rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \\
4 \text{NO} + 2 \text{O}_2 + 4 \text{NH}_3 & \rightarrow 4 \text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\]
The Uhde EnviNOx® process variant 2

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

**N₂O abatement by catalytic reduction with catalytic NOx reduction**

In this variant, N₂O is removed by catalytic reduction with a hydrocarbon such as natural gas or propane. Unlike with N₂O decomposition, the NOx content of the tail gas inhibits the N₂O reduction reaction. It is therefore necessary to completely eliminate the NOx in the tail gas. Depending on the tail gas composition and the particular operating conditions, this can be accomplished in a DeNOx unit located upstream of the DeN₂O® stage or, preferably, simultaneously with the N₂O reduction in a single common stage. In the latter case, a separate upstream DeNOx 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 300°C and 520°C depending on the specific conditions in the nitric acid plant. Current developments are aimed at widening this temperature window.

### DeNOx reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
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<tbody>
<tr>
<td>6 NO₂ + 8 NH₃</td>
<td>7 N₂ + 12 H₂O</td>
</tr>
<tr>
<td>4 NO + O₂ + 4 NH₃</td>
<td>4 N₂ + 6H₂O</td>
</tr>
</tbody>
</table>

### DeN₂O® reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2n+1) N₂O + CₙH₂n+₂</td>
<td>(2n+1) N₂ + n CO + (n+1) H₂O</td>
</tr>
<tr>
<td>(3n+1) N₂O + CₙH₂n+₂</td>
<td>(3n+1) N₂ + n CO₂ + (n+1) H₂O</td>
</tr>
</tbody>
</table>
The Uhde DeN$_2$O process

Fig. 5: Uhde DeN$_2$O® process:
catalytic N$_2$O decomposition process (without reducing agents)

**N$_2$O abatement by catalytic decomposition**

The Uhde DeN$_2$O® process consists of the first DeN$_2$O® stage of the EnviNOx® variant 1 as a single catalyst bed reactor. The DeN$_2$O® process requires a tail gas temperature between about 425°C and 600°C. Currently research activities regarding the installation at higher temperatures are ongoing.

<table>
<thead>
<tr>
<th>DeN$_2$O® reactions:</th>
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<tr>
<td>$2 \text{N}_2\text{O} + 2 \text{NO}$</td>
<td>$\rightarrow$</td>
</tr>
<tr>
<td>$2 \text{NO}_2$</td>
<td>$\rightleftharpoons$</td>
</tr>
<tr>
<td>$2 \text{N}_2\text{O}$</td>
<td>$\rightarrow$</td>
</tr>
</tbody>
</table>

$^{14}$NO$_2$ levels may be unchanged
Commercial scale implementation

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

Process variant 1 has been in operation in the 1,000 mtph 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 NOx 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 NOx abatement obtained with this technology can be controlled by varying the amount of ammonia added and the NOx 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 NOx 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 NOx abatement than conventional SCR processes.

Overall, nitrous oxide emissions from this plant are reduced by some 2,400 metric tons per year, equivalent to a reduction of around 750,000 metric tons per 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.
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 Nm$^3$/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 N$_2$O (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 CO$_2$ 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 N$_2$O and NO$_x$ are natural gas and ammonia respectively.

Further EnviNOx® process variant 2 systems are also in operation with similar very high N$_2$O abatement rates (98% and above), e.g. in South Africa, Hungary and Korea. A reference list with more details is available on request.
Starting from initial laboratory experiments, Uhde 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 NOₓ (down to nearly zero ppm) abatement that can be achieved in a single reactor vessel mean that current and future N₂O and NOₓ 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 EnviNOx® technology and the feedstock, 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.

CDM or JI projects using EnviNOx® technology can be executed rapidly due to the existence of the approved methodology AM 0028, which is suitable for all EnviNOx® process variants. Projects using EnviNOx® technology can generate a particularly large yield of carbon credits due to the very high rates of N₂O removal that can be achieved and verified. Uhde acts as the technology supplier in such projects. For the CDM/JI business side of these projects, Uhde can put clients in contact with experienced carbon traders who can act either as the carbon trader only or also as the investor in and possibly owner of the EnviNOx® system, depending on the specific needs of the client.

For more information, please contact one of the Uhde offices in your area or visit www.uhde.eu.

### Advantages that speak for themselves

The Uhde EnviNOx® process for the combined reduction of N₂O and NOₓ 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).

### N₂O emission level*

| M/M, M/H | New plants | 0.12 - 0.6 | 20 - 100 |
| M/H | 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/N - Mono Medium/Medium, M/H - Dual Medium/High, H/H - Mono High/High

### NOₓ emission level as NO₂

| New plants | – | 5 - 75 |
| Existing plants | – | 5 - 90* |
| NH₃ 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.

NOₓ emission levels associated with the application of BAT for the production of HNO₃.

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 NOₓ emissions reduction can be combined in a single reactor vessel
- High NOₓ removal rates (down to nearly zero ppm NOₓ)
- 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:
  - Uhde DeNOₓ process: 200 - 520°C
  - Uhde DeN₂O®: 425 - 600°C
  - Uhde EnviNOx® process variant 1: 425 - 520°C
  - Uhde EnviNOx® process variant 2: 330 - 520°C
Süd-Chemie Catalyst

In cooperation with Süd-Chemie AG, Uhde has developed special iron-exchanged zeolite catalysts for use in its EnviNOX® process. They are produced by Süd-Chemie and marketed jointly by Uhde and Süd-Chemie exclusively for the EnviNOX® process under the brand names EnviCat®-N₂O and EnviCat®-NOₓ.

Zeolites are synthetic microporous aluminosilicates which are characterised by high thermal and hydrothermal stability. As a result of their internal structure, they also have a large specific surface area and, consequently, high reactivity. Apart from their conventional use as adsorbents, zeolites are therefore used as catalysts in a wide range of chemical processes, for example for fuel production at refineries or in the plastics industry. In addition, the use of zeolites in waste gas treatment processes is also becoming more commonplace. For example, they are used to store cold-start emissions in car exhaust catalysts and as active substances to reduce nitrogen oxides in diesel truck exhaust gases. Süd-Chemie is a leading producer of special zeolites with many years of experience in the field of zeolite synthesis and the use of zeolites. The company has a number of certified facilities worldwide for the production of zeolite powders and the catalysts formed from them.

Süd-Chemie’s production of EnviCat®-N₂O and EnviCat®-NOₓ zeolite catalysts, especially the addition of iron to the base zeolite, is based on a special patented process which is responsible for the high activity of the iron zeolite catalyst. Painstaking production and specific adaptation of the structure and composition of the zeolites guarantee a long service life of the catalysts and high selectivity with respect to the catalysed reactions. The zeolite catalysts EnviCat®-N₂O and EnviCat®-NOₓ are manufactured in pellet form and, unlike conventional vanadium-based DeNOₓ catalysts, contain no toxic substances.

Further advantages of EnviCat® zeolite catalysts compared to conventional DeNOₓ catalysts are their resistance to typical catalyst poisons, such as sulphur or chlorine, and their operating range over a wide temperature window of approximately 200 – 600°C. The ability of EnviCat® zeolite catalysts to selectively oxidise ammonia to nitrogen and water at temperatures above approximately 300°C permits a slightly higher than stoichiometric admixture of ammonia and thus an almost complete reduction of NOₓ while, at the same time, preventing undesired ammonia slip. This reduces the risk of hazardous ammonium nitrate formation, thus obviating the need to install an additional ammonia guard catalyst.

About Süd-Chemie

Süd-Chemie AG is an independent, specialty chemical company headquartered in Munich. Core activities are directed towards energy, the environment and the conservation of natural resources. This is reflected in the numerous products and services supplied by the company’s Catalysts and Adsorbents divisions. Süd-Chemie operates globally and has the determination and capability to expand its leading positions in many markets by focussing on innovation to satisfy its customers’ needs.