Uhde EnviNOx® Technology for NO\textsubscript{X} and N\textsubscript{2}O abatement
– A contribution to reducing emissions from nitric acid plants –

by

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**Keywords:** N₂O oxide, NOₓ, nitrogen oxide abatement, greenhouse gas reduction, EnviNOx®, DeN₂O®.
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Abstract

N\textsubscript{2}O emissions from nitric acid production worldwide have been estimated at about 400 000 t/a, equivalent to 120 million t/a CO\textsubscript{2\,eq}, making nitric acid manufacture the largest single industrial process source of N\textsubscript{2}O. Uhde’s NO\textsubscript{X} and N\textsubscript{2}O abatement technology has been developed to permit high rates of N\textsubscript{2}O abatement for tail gas temperatures between 340\,°C and 600\,°C. For plants with a cooler tail gas it is often possible to raise the temperature to a suitable level by tail gas preheating. A large proportion of the world’s nitric acid plants can thus be equipped with Uhde’s N\textsubscript{2}O abatement technology. Existing abatement units routinely achieve N\textsubscript{2}O removal rates of 97\% - 98\% and above. This N\textsubscript{2}O abatement technology can thus play a significant role in lowering greenhouse gas emissions.
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1. Nitrogen Oxide Pollution

The nitrogen oxides NO and NO\textsubscript{2} which make up NO\textsubscript{X} have long been known as precursors of acid rain and smog. While ever more stringent emission limits apply in many countries there are still a large number of nitric acid plants which have no NO\textsubscript{X} abatement equipment installed. Nitrous oxide (N\textsubscript{2}O) is a powerful greenhouse gas being about 300 times more potent than carbon dioxide. Even though nitric acid plants represent the largest single industrial process source of this gas, most countries have not yet imposed emission limits on N\textsubscript{2}O, although steps in this direction are being made, for example, in the European Union. As nitric acid plants are point sources for N\textsubscript{2}O and NO\textsubscript{X} emissions they make good candidates for the implementation of cost effective greenhouse gas and NO\textsubscript{X} emission reduction technologies.

2. The Nitric Acid Process and N\textsubscript{2}O Emissions

Nitric acid is manufactured almost exclusively according to the Ostwald process (see flowsheet in Fig. 1) in which ammonia is catalytically oxidised over platinum-rhodium gauzes in the ammonia burner. The following reactions take place:

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Desired reaction:

\[
4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O} \quad \Delta H = -906.1 \text{kJ}
\]

Undesired reactions:

\[
4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O} \quad \Delta H = -1267.2 \text{kJ}
\]

\[
4 \text{NH}_3 + 4 \text{O}_2 \rightarrow 2 \text{N}_2\text{O} + 6 \text{H}_2\text{O} \quad \Delta H = -1103.1 \text{kJ}
\]

On and downstream of the catalyst gauzes further nitrous oxide is formed through reactions between unconverted ammonia and nitric oxide:

\[
2 \text{NH}_3 + 8 \text{NO} \rightarrow 5 \text{N}_2\text{O} + 3 \text{H}_2\text{O} \quad \Delta H = -945.7 \text{kJ}
\]

\[
4 \text{NH}_3 + 4 \text{NO} + 3 \text{O}_2 \rightarrow 4 \text{N}_2\text{O} + 6 \text{H}_2\text{O} \quad \Delta H = -2403.3 \text{kJ}
\]

Palladium, which is used in the catchment packs for platinum recovery that are often installed below the catalyst gauzes, enhances these reactions.

After the absorption of most of the NO\textsubscript{X} in water in the absorber to form nitric acid, the tail gas that remains consists mainly of nitrogen with smaller amounts of O\textsubscript{2}, H\textsubscript{2}O, NO\textsubscript{X} and N\textsubscript{2}O. It is reheated using energy from the process before being discharged to atmosphere via a gas turbine, to recover mechanical energy for powering the compressor in the plant. The temperature of the tail gas at the inlet of the tail gas turbine depends on the design of the plant and can be anywhere between around 200°C to well
above 600°C. Many plants, however, have a tail gas temperature between 300°C and 450°C.

![Flowsheet Diagram]

**Figure 1:** Simplified flowsheet of the nitric acid process showing possible locations for EnviNOx® N₂O and NOₓ abatement reactor

Apart from some possible losses due to high temperature decomposition, the N₂O leaving the ammonia burner takes no further part in the chemistry of the nitric acid process and is emitted to atmosphere in the tail gas.

The amount of N₂O emitted depends in part on the operating conditions in the ammonia burner, and also on the condition and type of the gauzes. For this reason there can be considerable variation in N₂O emission between different kinds of nitric acid plant and during and between campaigns in the same plant. According to the IPCC (Intergovernmental Panel on Climate Change) high pressure plants generally have the highest emission factor (~12 kg N₂O/tonne nitric acid), ahead of medium (~7 kg N₂O/tonne nitric acid) and atmospheric ammonia combustion plants (~5 kg N₂O/tonne nitric acid). (To estimate the corresponding tail gas concentration in ppmv multiply by 160).

### 3. Destruction of N₂O and NOₓ in Nitric Acid Plants with EnviNOx®

N₂O and NOₓ emissions can be lowered by installing an Uhde EnviNOx® reactor in the tail gas stream at one of the positions indicated in the flowsheet of Fig. 1.
The EnviNOx® process is thus an end-of-pipe process which offers a number of advantages:

- It is analogous to the various well-established catalytic NO\textsubscript{X} reduction processes, so that acceptance among plant owners and operators is not considered to be a particular problem.

- As the NO\textsubscript{X} abatement performance of an EnviNOx® unit is typically equal or superior to most standard SCR/DeNO\textsubscript{X} systems, EnviNOx® can provide a one reactor solution to all nitrogen oxide emission problems in nitric acid plants (NO\textsubscript{X} and N\textsubscript{2}O), even where strict emission limits apply.

- There can be no undesired interactions between the EnviNOx® system and the actual process of making nitric acid since the EnviNOx® reactor is located in the waste tail gas stream downstream of the absorber where the nitric acid product is formed. Therefore the possibility of loss of nitrogen oxide (NO, NO\textsubscript{2}) intermediate or contamination of any downstream material manufactured from the nitric acid is completely eliminated.

- Within reason there are no externally dictated physical constraints on the arrangement of the EnviNOx® catalyst within the reactor or on the size of the reactor. Thus very high rates of N\textsubscript{2}O and NO\textsubscript{X} abatement combined with low pressure drop are no contradiction.

- For greenhouse gas emission reduction projects under the Kyoto Protocol or other schemes the EnviNOx® process offers a high degree of transparency. The baseline emissions of N\textsubscript{2}O (i.e., those which would have occurred had there been no N\textsubscript{2}O abatement system in place) can always be obtained in real time just by measuring the N\textsubscript{2}O concentration and tail gas flow rate upstream of the abatement system. Thus as soon as an EnviNOx® reactor has been installed it can start to generate verifiable emission reductions.

4. R&D Programme

Over the last decade Uhde has invested substantial resources in the development of the EnviNOx® process. As well as laboratory work carried out by Uhde and by universities and institutes on behalf of Uhde, an important mainstay of Uhde’s N\textsubscript{2}O and NO\textsubscript{X} abatement process development programme is the catalyst test unit. It was recognised that reliable conclusions about the suitability of any particular catalyst material could only be obtained by carrying out long term measurements in an industrial production facility. Uhde therefore designed a catalyst test unit for that purpose and was fortunate in finding a partner in Borealis AG (formerly AMI Agrolinz Melamine International GmbH), who permitted the test unit to be installed on their premises in Linz, Austria and connected up to their 1000 tonne/day dual pressure nitric acid plant. So persuasive were the results from the test unit that in 2003 Borealis installed an EnviNOx® system in this plant, the first in the world. The catalyst test unit, which has been in use since 2000, was recently given a complete overhaul and continues to yield valuable data for the further development of the EnviNOx® process.

After initial testing of a wide range of materials it was found that various types of iron zeolite are very suitable catalysts for NO\textsubscript{X} and N\textsubscript{2}O abatement in nitric acid plant tail gases. These catalysts are manufactured and supplied on an exclusive basis by the
international, Munich-based catalyst company Süd-Chemie under the trade names EnviCat®-NO<sub>X</sub> and EnviCat®-N<sub>2</sub>O.

The results of Uhde’s experimental investigations on these catalysts have been reported in detail in previous publications so the following sections only give a summary of the most important conclusions and the technology variants which have resulted.

5. Uhde Technologies for NO<sub>X</sub> and N<sub>2</sub>O Abatement

5.1 Uhde DeNOx process: NO<sub>X</sub> reduction with ammonia

It was found that one of the iron zeolites materials tested was a very efficient catalyst for the selective reduction of NO<sub>X</sub> (NO and NO<sub>2</sub>) with ammonia. This catalyst has the advantage that it can be used over a large range of temperatures, from ~200°C to over 500°C, while classical vanadium-pentoxide-based SCR catalysts for nitric acid plants generally cannot be used at temperatures much above ~400°C. A further advantage is that it generates no N<sub>2</sub>O, again in contrast to vanadium pentoxide, which is reported to produced N<sub>2</sub>O at temperatures above 350°C (Jouannic et al. 1984).

This is the basis of the Uhde DeNOx process, which has a similar ammonia consumption to classical SCR/DeNOx processes, is applicable over a wider range of temperatures and, in contrast to frequently used classical SRC/DeNOx catalyst materials, contains no environmentally hazardous substances, thus simplifying handling and disposal.

The Uhde DeNOx process can be very conveniently combined with N<sub>2</sub>O abatement as described below.

5.2 EnviNOx® process variant 1: N<sub>2</sub>O decomposition with NO<sub>X</sub> reduction

The iron zeolite catalysts investigated decompose N<sub>2</sub>O into its elements. An important phenomenon is that the rate of decomposition is greatly enhanced when NO<sub>X</sub> is present in the waste gas stream. This fact, combined with the NO<sub>X</sub> reducing properties of the iron zeolite catalysts, is exploited in the EnviNOx® process variant 1, which is illustrated in Figure 2.

The EnviNOx® reactor is typically located in the tail gas stream on the inlet side of the tail gas turbine where the tail gas temperature is at its highest.

Because of the high NO<sub>X</sub> concentration in the tail gas entering the reactor, a very large proportion of the incoming N<sub>2</sub>O is catalytically decomposed to nitrogen and oxygen in the first bed. Ammonia is mixed with the tail gas between the beds, the ammonia distribution and mixing equipment being incorporated into the reactor. In the second bed the NO<sub>X</sub> is reduced to the level required for emission to atmosphere and some further decomposition of N<sub>2</sub>O also takes place.
Figure 2: EnviNOx® process variant 1: Combined N₂O and NOₓ abatement for nitric acid plants using N₂O decomposition and NOₓ reduction with ammonia

EnviNOx® process variant 1 is currently suitable for tail gas temperatures between about 425°C and 520°C. High rates of N₂O removal are possible with 98% typically achieved in commercial installations and NOₓ emissions can be reduced to low levels depending on the amount of ammonia supplied, with 5 – 40 ppmv being usual. As with the Uhde DeNOx processes ammonia consumption is similar to that of classical SCR/DeNOx processes.

5.3 EnviNOx® process variant 2: N₂O & NOₓ reduction by hydrocarbons & NH₃

There are, of course, a great many nitric acid plants with tail gas temperatures below 425°C. The solution for a large number of these plants is the EnviNOx® process variant 2, which relies on another significant phenomenon which was intensively investigated during development work.

While N₂O in nitric acid tail gas can be reduced by reaction with a hydrocarbon over certain iron zeolite catalysts, the effectiveness of the reduction is greatly enhanced if the NOₓ is removed almost entirely from the tail gas. Even a few ppm of NOₓ is sufficient to cause strong inhibition of the reactions of hydrocarbons with N₂O. This property combined with the NOₓ reducing properties of the iron zeolite catalysts with ammonia leads to the EnviNOx® process variant 2, depicted in Figure 3.
Figure 3: **EnviNOx® process variant 2: Combined N₂O and NOₓ abatement for nitric acid plants using N₂O reduction with hydrocarbons and NOₓ reduction with ammonia**

Ammonia is mixed with the tail gas entering the EnviNOx® reactor in such an amount that NOₓ is completely reduced in the first DeNOx bed. The virtually NOₓ-free tail gas is then mixed with a hydrocarbon and passed over the second catalyst bed where the N₂O is reduced to a very low level by reaction with the hydrocarbon. Tail gas with nearly no NOₓ and a very low concentration of N₂O leaves the reactor. It is important to recognise that the hydrocarbon acts as a chemical reagent and is not used as a fuel to raise the temperature of the catalyst to a level at which high rates of N₂O decomposition can occur. Because of their favourable costs and availability the hydrocarbons of choice are natural gas or propane. Consumptions of both ammonia and hydrocarbon are quite moderate. The EnviNOx® process variant 2 works best at temperatures between about 340°C and ~520°C.

### 5.4 **Uhde DeN2O® process: N₂O decomposition without NOₓ abatement**

If there is no requirement to lower NOₓ emissions, the N₂O decomposition catalyst described above can be used on its own. The catalyst achieves high N₂O abatement performance up to temperatures of about 600°C, substantially increasing the range of nitric acid plants which can be equipped with N₂O abatement. In such plants a NOₓ abatement unit can also be installed if necessary, provided an appropriate tail gas temperature level between about 200°C and 500°C is available.
6. Operating Data of Commercial EnviNOx® Installations

EnviNOx® systems have been in commercial operation since September 2003 and continue to deliver high rates of NO\textsubscript{X} and N\textsubscript{2}O abatement on the first catalyst charge.

6.1 Operating data for EnviNOx® process variant 1 installations

Figure 4 shows the percentage rate of N\textsubscript{2}O removal in the 1000 tonne/day nitric acid plant of Borealis AG, Linz, Austria over the first 1200 days of operation. The N\textsubscript{2}O removal rate averaged over 98%. The outlet NO\textsubscript{X} concentration is controlled at around 5 – 10 ppmv by adjusting the amount of ammonia supplied.

As part of a Kyoto CDM project the Uhde-built HU CHEMS #4 nitric acid plant was equipped with an EnviNOx® variant 1 system in early 2007. 98% N\textsubscript{2}O removal is achieved with the NO\textsubscript{X} outlet concentration being controlled at 25 ppm by addition of ammonia. After nearly six years of operation the catalyst is showing no signs of loss of activity.

DSM Agro have EnviNOx® process variant 1 systems in operation in two Stamicarbon-designed dual pressure nitric acid plants in the Netherlands. The EnviNOx® reactor in the 1600 mtpd No. 5 nitric acid plant at Geleen was started up in October 2007 and continues to achieve rates of N\textsubscript{2}O abatement of 99.5% - 100%. The second EnviNOx® system was started up around the beginning of 2008 in the 700 mtpd No. 5 nitric acid plant at IJmuiden and continues to destroy 100% of the N\textsubscript{2}O entering it, resulting in zero N\textsubscript{2}O emissions from this plant. In 2008 DSM Agro were awarded the Responsible Care Prize of the Dutch Chemical Industry Association (VNCI) for their achievements in lowering N\textsubscript{2}O emissions from their nitric acid plants.

![Figure 4: EnviNOx® process variant 1, N\textsubscript{2}O decomposition and NO\textsubscript{X} reduction with ammonia: Borealis AG, (formerly AMI), Linz, Austria, Percentage rate of N\textsubscript{2}O destruction](image-url)
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6.2 Operating data for EnviNOx® process variant 2 installations

The first commercial scale implementation of the EnviNOx® process variant 2 went into operation in October 2006 as a Kyoto CDM project in the Uhde-built 1830 tonne/day Abu Qir 2 nitric acid plant of Abu Qir Fertilizer Co. near Alexandria in Egypt. N₂O is reduced with natural gas. N₂O abatement rates in excess of 99% and NOₓ outlet concentrations of around 1 ppmv are being consistently achieved, making for a very clean nitric acid plant tail gas. Figure 5 shows some performance data.

![Graph](image)

**Figure 5:** EnviNOx® process variant 2, N₂O reduction with natural gas and NOₓ reduction with ammonia: Abu Qir Fertilizer Co., Egypt, Percentage rate of N₂O destruction and NOₓ outlet concentration

As natural gas was not available on site, commercial propane was used as the reducing agent for N₂O in two implementations of the EnviNOx® process variant 2 in the 300
tonne/day #2 and #3 nitric acid plants of HU CHEMS, Yeosu, Korea. High rates of N\textsubscript{2}O removal of 98% are again being achieved, while NO\textsubscript{x} emissions are below 5 ppmv.

Other commercial scale implementations include the EnviNOx\textsuperscript{®} reactor installed in the new Grande-Paroisse-designed 1500 tonne/day nitric acid plant of Nitrogénnművek, Pétfürdő, Hungary. The EnviNOx\textsuperscript{®} system went into successful operation in mid-2007 with N\textsubscript{2}O abatement above 99%. Natural gas is used to reduce N\textsubscript{2}O and ammonia to reduce NO\textsubscript{x}. Another EnviNOx\textsuperscript{®} variant 2 reactor using natural gas and ammonia has been in operation since January 2008 in the Uhde-built 750 tonne/day nitric acid plant of Omnia Fertilizer Ltd., Sasolburg, South Africa. N\textsubscript{2}O removal rates of 98% to 99% are being achieved with 0 – 1 ppmv NO\textsubscript{x} in the tail gas leaving the plant.

7. EnviNOx\textsuperscript{®} and Best Available Technique

Under the IPPC (Integrated Pollution Prevention and Control) Directive 96/61/EC Member States of the European Union are required to issue operating permits for certain kinds of industrial installations. The permits must contain conditions based on best available techniques (BAT). BAT Reference Documents (BREFs) are produced by the European IPPC Bureau and are required to be taken into account by EU Member States. The BREF that is relevant to nitric acid plants gives the N\textsubscript{2}O and NO\textsubscript{x} emission levels reproduced in Table 1 below as being those that should be achieved when BAT is used. These values are generally applicable and do not refer to any specific technology.

The EnviNOx\textsuperscript{®} process (variant 1) is explicitly named in the BREF as being a BAT, and in fact even the lowest BAT emission levels of N\textsubscript{2}O and NO\textsubscript{x} given in the BREF can easily be attained with an EnviNOx\textsuperscript{®} system, as the performance figures given in the present paper illustrate.

<table>
<thead>
<tr>
<th></th>
<th>(\text{N}_2\text{O}) emission level associated with BAT (ppmv)</th>
<th>(\text{NO}_x) emission level associated with BAT (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New plants</td>
<td>20 – 100</td>
<td>5 – 75</td>
</tr>
<tr>
<td>Existing plants</td>
<td>20 – 300</td>
<td>5 – 90</td>
</tr>
<tr>
<td>(\text{NH}_3) Slip from SCR</td>
<td></td>
<td>&lt;5 ppmv</td>
</tr>
</tbody>
</table>

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

\textit{Table 1: \(\text{N}_2\text{O}\) and \(\text{NO}_x\) emission levels from nitric acid plants associated with the use of Best Available Technique according to EU BREF LVIC 2007}

8. Current Developments

Work is currently underway to widen the upper and lower temperature range of the EnviNOx\textsuperscript{®} technology to permit it to be applied to an even broader selection of nitric acid plants. Applications in other kinds of industrial waste gas streams are also being developed. The results of ongoing investigations are promising.
9. Conclusion

The EnviNOx® process for the combined abatement of NO\textsubscript{X} and N\textsubscript{2}O emissions from nitric acid plants has proven itself in installations around the world which are now operating at temperatures between 340°C and 510°C. Typically, N\textsubscript{2}O emissions are reduced by ~98% – 99% while NO\textsubscript{X} emission levels of 1 to ~25 ppmv are achieved, depending on the process variant.

Independent confirmation of the high N\textsubscript{2}O abatement performance of EnviNOx® systems can be obtained at the web site of the United Nations Framework Convention on Climate Change (www.unfccc.org/cdm) where the monitoring reports of N\textsubscript{2}O abatement projects under the Clean Development Mechanism of the Kyoto Protocol can be studied and downloaded. EnviNOx® projects with published monitoring reports include those for Abu Qir Fertilizers, HU CHEMS and Omnia.

The EnviNOx® process can be applied in nitric acid plants with tail gas temperatures between about 340°C and 600°C covering an estimated 70% – 80% of all nitric acid production worldwide. For many of the nitric acid plants with tail gas temperatures outside this range, relatively simple plant modifications are possible to enable a nitrous oxide abatement system to be installed. The EnviNOx® process can thus make a useful contribution to lowering greenhouse gas emissions.

EnviNOx® is an “operator friendly” technology since the EnviNOx® catalysts are easy to handle, environmentally uncontroversial materials with a long operating lifetime. Furthermore as an end-of-pipe process EnviNOx® does not interact in any way with the plant product or its precursors.
10. References


