



EnviNOx[®]: Process for N₂O and NO_x Abatement in Nitric Acid Plants

– Setting emission standards for nitric acid plants –

by

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Abstract

Nitrous oxide (N₂O) is an invisible by-product of the manufacture of nitric acid by the Ostwald process. It forms during the catalytic oxidation of ammonia over platinum / rhodium gauzes, the major product being nitric oxide (NO). Since nitrous oxide is a potent greenhouse gas with some three hundred times the effect of carbon dioxide, and nitric acid plants now represent the single largest industrial process source of the former gas, there is a need for technologies to lower nitrous oxide emissions from nitric acid plants.

The commercially tried and tested Uhde EnviNOx[®] process for the abatement of N₂O and NO_x emissions in nitric acid plants provides a highly viable solution to this problem, as it achieves almost complete removal of N₂O and NO_x.

To date some ten nitric acid plants have been equipped with EnviNOx[®] systems. These units continue to achieve N₂O removal rates of 98-99% with NO_x emissions being reduced to as low as 1 ppmv. The longest operating EnviNOx[®] unit has been running since 2003 to the complete satisfaction of its owner and still with the first charge of catalyst.

Basing their judgement on this successful track record and the exceptionally high rates of N₂O and NO_x abatement, the responsible European Union body has declared the EnviNOx[®] process to be Best Available Technique (BAT) for N₂O and NO_x abatement in nitric acid plants.

The performance of the EnviNOx[®] process makes it an ideal candidate for lowering greenhouse gas emissions from nitric acid plants under the Kyoto Protocol or to meet the most stringent of emission limits, and can provide nitric acid plant owners with an additional source of revenue and an environmentally clean production process.

Since some routes to caprolactam also employ the Ostwald oxidation of ammonia over noble metal gauzes a considerable number of caprolactam plants also emit N₂O in a tail gas stream and are thus candidates for being equipped with an EnviNOx[®] system for N₂O and NO_x emission reduction.



Abatement of N₂O and NO_x Emissions from Nitric Acid Plants with the Uhde EnviNOx[®] Process

– Design, Operating Experience and Current Developments –

1. Nitrogen Oxide Pollution

The nitrogen oxides NO and NO₂ which make up NO_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 quite a large number of nitric acid plants which have no NO_x abatement equipment installed.

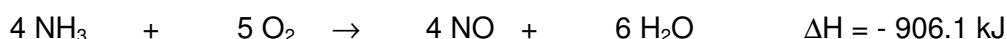
Nitrous oxide (N₂O) is a powerful greenhouse gas being about 300 times more potent than carbon dioxide. Even though nitric acid plants represent the largest single industrial process source of this gas, there are as yet no emission limits for most countries, although steps in this direction are taking place, for example, in the European Union. As nitric acid plants are point sources for N₂O (and NO_x) emissions they make good candidates for the implementation of cost effective greenhouse gas and NO_x emission reduction technologies.

2. Formation of Nitrous Oxide in Nitric Acid Plants

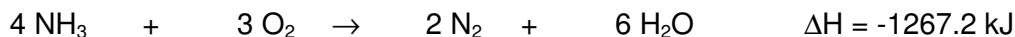
Nitrous oxide (N₂O) is formed as an unwanted by-product in the oxidation of ammonia over the platinum-rhodium gauzes in the ammonia burner.

The following reactions take place:

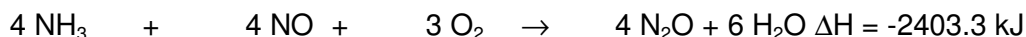
Desired reaction:



Undesired reactions:



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



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



Apart from some possible losses due to high temperature decomposition, the nitrous oxide 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, together with any NO_x that has not been converted to nitric acid in the absorption tower(s) or destroyed in a NO_x abatement unit.

The amount of nitrous oxide 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 nitrous oxide 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)¹ high pressure plants generally have the highest emission factor ($\sim 12 \text{ kg N}_2\text{O/tonne nitric acid}$), ahead of medium ($\sim 7 \text{ kg N}_2\text{O/tonne nitric acid}$) and atmospheric ammonia combustion plants ($\sim 5 \text{ kg N}_2\text{O/tonne nitric acid}$). (To estimate the corresponding tail gas concentration in ppmv multiply by 160).

The level of NO_x emissions, on the other hand, depends on the performance of the NO_x abatement unit, if present, or that of the absorption tower which is affected by its design and certain plant operating parameters such as pressure, cooling water flow and temperature and tail gas oxygen concentration.

3. Classification of Nitrous Oxide Abatement Processes

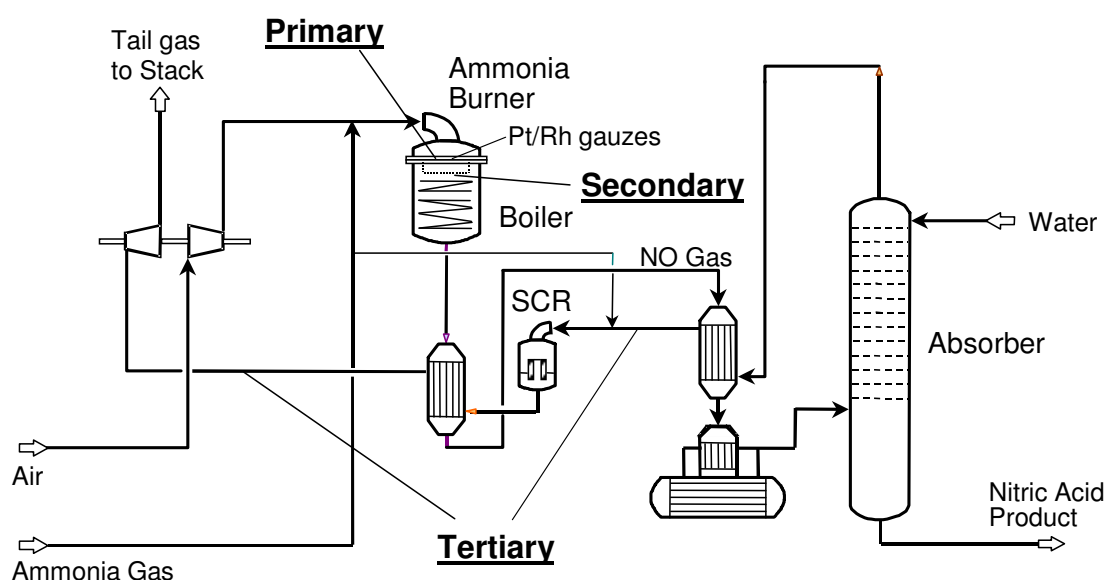


Figure 1: Simplified flowsheet of the nitric acid process showing the classification of nitrous oxide abatement methods according to the position in the process.



The possible ways of lowering nitrous oxide emissions from nitric acid plants can be categorised broadly into three groups (See the simplified nitric acid plant flowsheet in Figure 1):

- **Primary:** Nitrous oxide is prevented from forming in the first place. This requires modifications to the platinum gauzes to reduce nitrous oxide formation. Alternative materials can be employed as the ammonia oxidation catalyst. Cobalt oxide, for example, does not generate significant amounts of nitrous oxide by-product, but suffers from being less selective for the production of nitric oxide.
- **Secondary:** Nitrous oxide, once formed, is removed anywhere between the outlet of the ammonia oxidation gauzes and the inlet of the absorption tower. The position of choice for secondary methods is directly after the gauzes where the temperature is at its highest. Most technologies employ a catalyst in the form of pellets, either loose or enclosed in cages made of heat resistant wire, while some use honeycombs.
- **Tertiary:** Nitrous oxide is removed from the tail gas downstream of the absorption tower, either by catalytic decomposition into N_2 and O_2 , the rate of homogeneous decomposition being negligible at the temperatures that typically prevail in tail gas streams, or by catalytic reduction with a chemical reducing agent. The optimum position for locating a tertiary abatement step is normally at the hottest position in the plant, immediately upstream of the expansion turbine.

4. Advantages of EnviNOx[®] Tertiary N₂O Abatement Process

Tertiary N₂O and NO_x abatement with the EnviNOx[®] process offers a number of advantages compared with other approaches:

- As an end-of-pipe technology the tertiary approach is analogous to the various well-established catalytic NO_x reduction processes. Acceptance among plant owners and operators is therefore not considered to be a particular problem.
- As the NO_x abatement performance of EnviNOx[®] units is typically equal or superior to most standard SCR/DeNOx systems, EnviNOx[®] can provide a one reactor solution to all nitrogen oxide emission problems in nitric acid plants (NO_x and N₂O), even where strict emission limits apply.
- Since EnviNOx[®] is end-of-pipe there can be no undesired interactions with the actual process of producing nitric acid, in contrast to the situation with secondary technologies where there is intimate contact between the secondary abatement catalyst and the intermediate nitrous gas product which leaves the gauzes and is subsequently converted to nitric acid by reaction with water in the absorption column. Thus with an EnviNOx[®] system any possibility of loss of NO intermediate or contamination of any downstream material manufactured from the nitric acid is completely eliminated.
- Except in the case of new nitric acid plants a secondary N₂O abatement catalyst must be installed in a predetermined space, the geometry of which was fixed by considerations other than the requirements of the N₂O abatement technology. Thus there will be a trade-off between pressure drop and achievable N₂O destruction. Furthermore, in the case of a retrofit, the amount of secondary catalyst that can be installed may be limited by the maximum mechanical load that can be sustained by



the support construction of the ammonia oxidation catalyst basket rather than the physical space that is available. Even in the case of new nitric acid plants the cross-sectional area of the space available beneath the gauzes will, in the main, depend on the needs of the ammonia oxidation gauzes rather than those of the secondary abatement catalyst. In contrast, with a tertiary, end-of-pipe EnviNOx[®] system there are effectively no externally dictated physical constraints on the arrangement of the catalyst within the reactor or on the size of the reactor. Thus very high rates of N₂O and NO_x abatement combined with low pressure drop are no contradiction with an EnviNOx[®] system.

- For greenhouse gas emission reduction projects under the Kyoto Protocol or other frameworks tertiary technologies have a clear advantage over other N₂O abatement technologies in that the baseline emissions (i.e., those which would have occurred had there been no N₂O abatement system in place) can always be measured in real time just by measuring the N₂O concentration and tail gas flow rate upstream of the abatement system. Secondary technologies destroy the possibility of making this measurement as soon as they are installed, since there is no space for taking a representative sample between the gauzes where the N₂O is formed and the catalyst where the N₂O is destroyed. This makes it necessary to establish a baseline by making emission measurements for a representative period before it is permitted to install the N₂O abatement technology.

5. R&D Programme

The above-mentioned advantages were among the considerations that induced Uhde to invest 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 N₂O and NO_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 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 AMI 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 deliver vital 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_x and N₂O 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_x and EnviCat[®]-N₂O.

The results of Uhde's experimental investigations on these catalysts have been reported in detail in previous publications² so the following section only gives a summary of the most important conclusions and the technology variants which have resulted.



6. Uhde Technologies for NO_x and N₂O Abatement

6.1 Uhde DeNO_x process: NO_x 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_x (NO and NO₂) 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 N₂O, again in contrast to vanadium pentoxide, which is reported to generate N₂O at temperatures above 350 °C.³

This is the basis of the Uhde DeNO_x process, which has a similar NH₃ consumption to classical SCR/DeNO_x processes, is applicable over a wider range of temperatures and, in contrast to say vanadium pentoxide, a frequently used classical SRC/DeNO_x catalyst material, contains no environmentally hazardous substances, thus simplifying handling and disposal.

The Uhde DeNO_x process can be very conveniently combined with N₂O abatement as described below.

6.2 EnviNO_x® process variant 1: N₂O decomposition with NO_x reduction

The iron zeolite catalysts investigated decompose N₂O into its elements. An important phenomenon is that the rate of decomposition is greatly enhanced when NO_x is present in the waste gas stream. This fact, combined with the NO_x reducing properties of the iron zeolite catalysts, is exploited in the EnviNO_x® process variant 1, which is illustrated in Figure 2.

The EnviNO_x® 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_x concentration in the tail gas entering the reactor, a very large proportion of the incoming nitrous oxide 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_x is reduced to the level required for emission to atmosphere and some further decomposition of nitrous oxide also takes place.

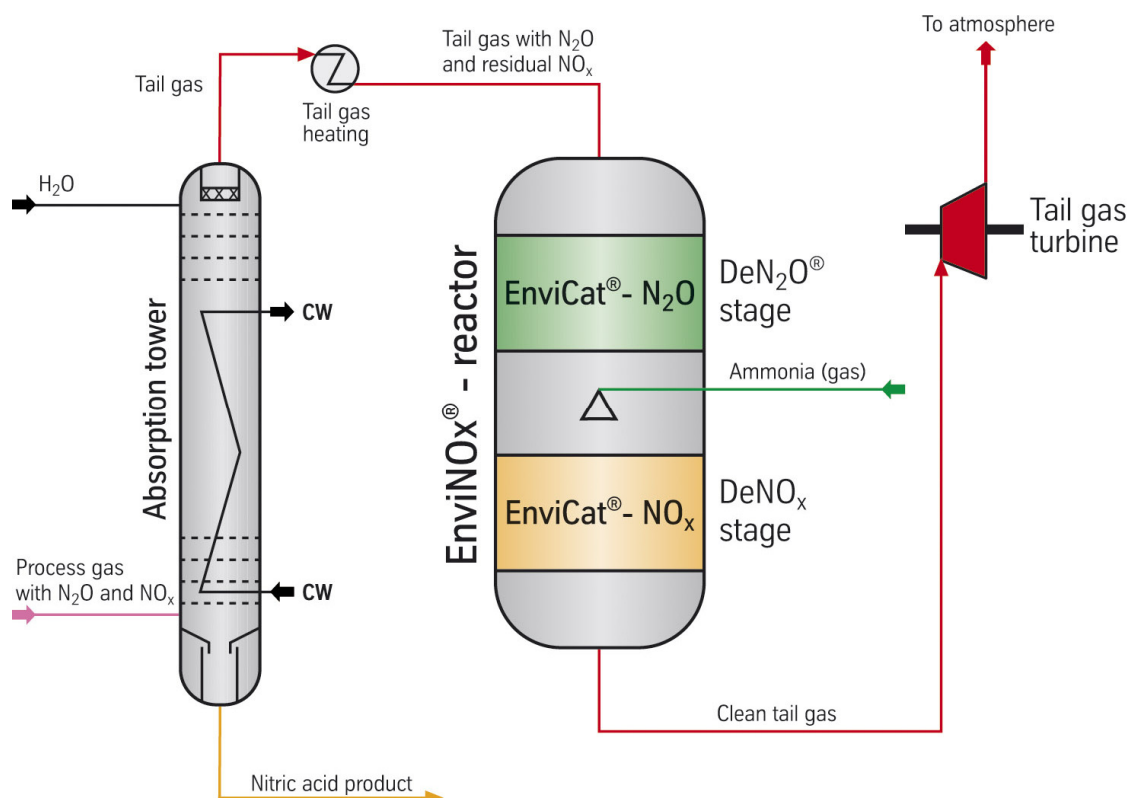


Figure 2: EnviNOx[®] process variant 1: Combined N₂O and NO_x abatement for nitric acid plants using N₂O decomposition and NO_x reduction with ammonia

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 NO_x emissions can be reduced to low levels depending on the amount of ammonia supplied, with 5 – 25 ppmv being usual. As with the Uhde DeNOx process ammonia consumption is similar to that of classical SRC/DeNOx processes.

6.3 EnviNOx[®] process variant 2: N₂O & NO_x 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 NO_x is removed almost entirely from the tail gas. Even a few ppm of NO_x is sufficient to cause strong inhibition of the reactions of hydrocarbons with N₂O. This property combined with the NO_x reducing properties of the iron zeolite catalysts with ammonia leads to the EnviNOx[®] process variant 2, depicted in Figure 3.

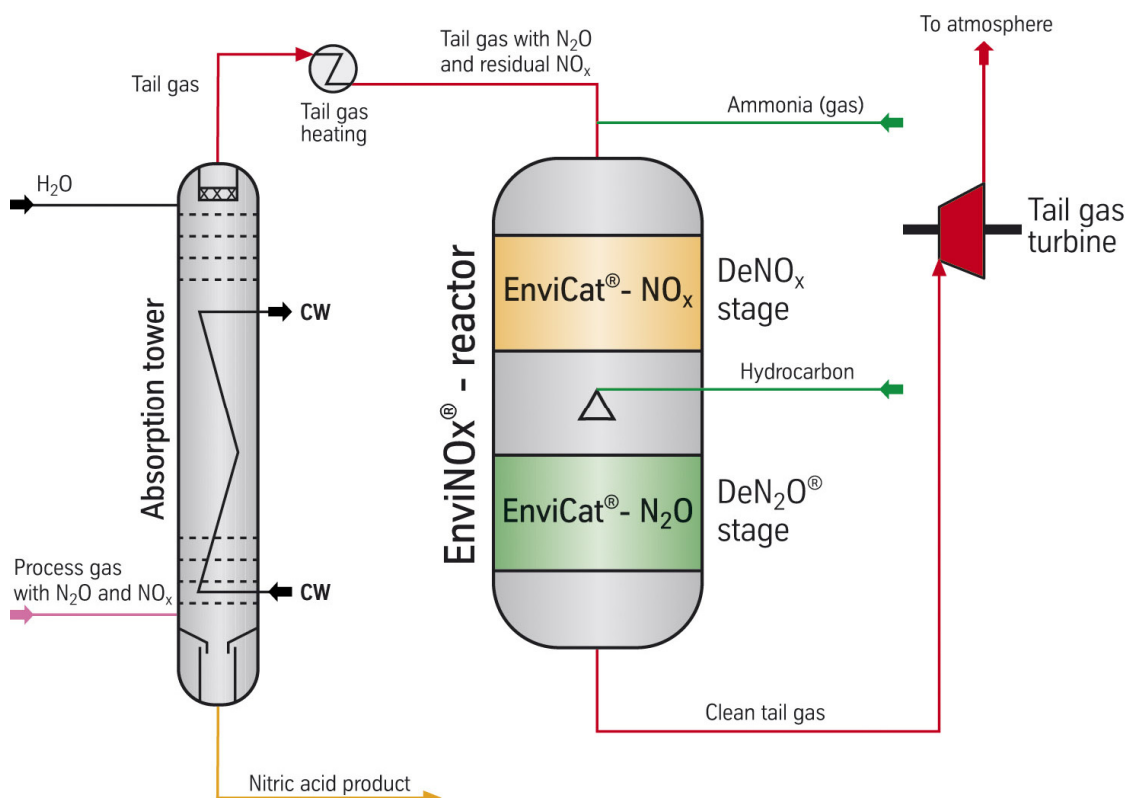


Figure 3: *EnviNOx® process variant 2: Combined N_2O and NO_x abatement for nitric acid plants using N_2O reduction with hydrocarbons and NO_x reduction with ammonia*

Ammonia is mixed with the tail gas entering the EnviNOx® reactor in such an amount that NO_x is completely reduced in the first DeNO_x bed. The virtually NO_x -free tail gas is then mixed with a hydrocarbon and passed over the second catalyst bed where the N_2O is reduced to a very low level by reaction with the hydrocarbon. Tail gas with nearly no NO_x and a very low concentration of N_2O 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 N_2O 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.

6.4 Uhde DeN2O® process: N_2O decomposition without NO_x abatement

If there is no requirement to lower NO_x emissions, the N_2O decomposition catalyst described above can be used on its own. The catalyst achieves high N_2O abatement performance up to temperatures of about 600 °C, substantially increasing the range of nitric acid plants which can be equipped with N_2O abatement. In such plants a NO_x abatement unit can also be installed if necessary, provided an appropriate tail gas temperature level between about 200 °C and 500 °C plus is available.



7. Operating Data of Commercial EnviNOx[®] Installations

EnviNOx[®] systems have been in commercial operation since September 2003 and continue to deliver high rates of NO_x and N₂O abatement on the first catalyst charge.

7.1 Operating data for EnviNOx[®] process variant 1 installations

7.1.1 AMI Line E, Austria – Start Up 2003

Figure 4 show the percentage rate of N₂O removal in the 1000 tonne/day nitric acid plant of AMI, Linz, Austria over the first 1200 days of operation. The N₂O removal rate averaged over 98%. The outlet NO_x concentration is controlled at around 5 – 10 ppmv.

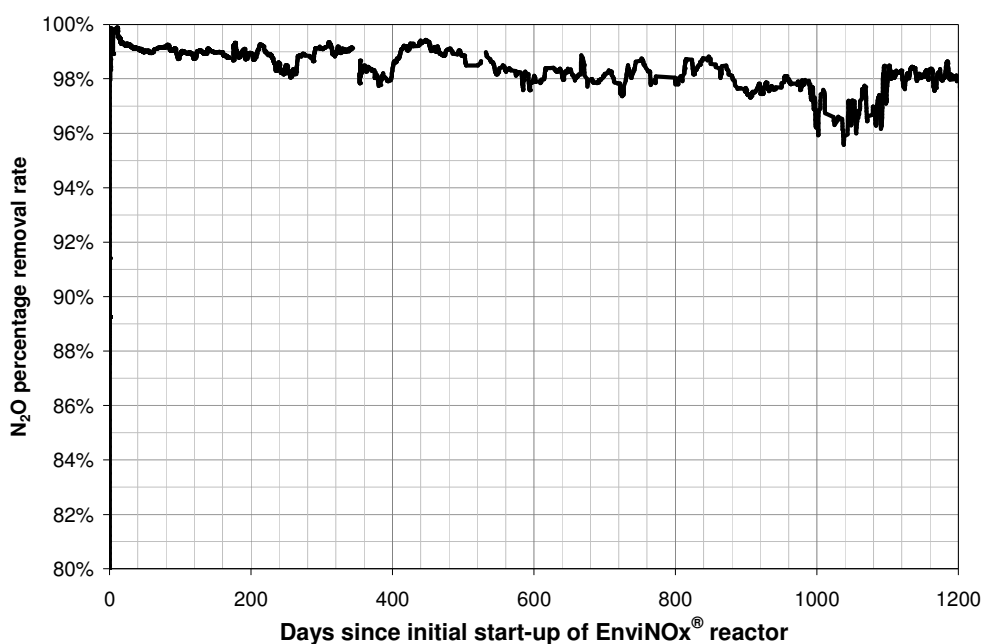


Figure 4: EnviNOx[®] process variant 1, N₂O decomposition and NO_x reduction with ammonia: AMI, Linz, Austria, Percentage rate of N₂O destruction



7.1.2 HU CHEMS #4 NA Plant, Yeosu, Korea – Start Up in early 2007

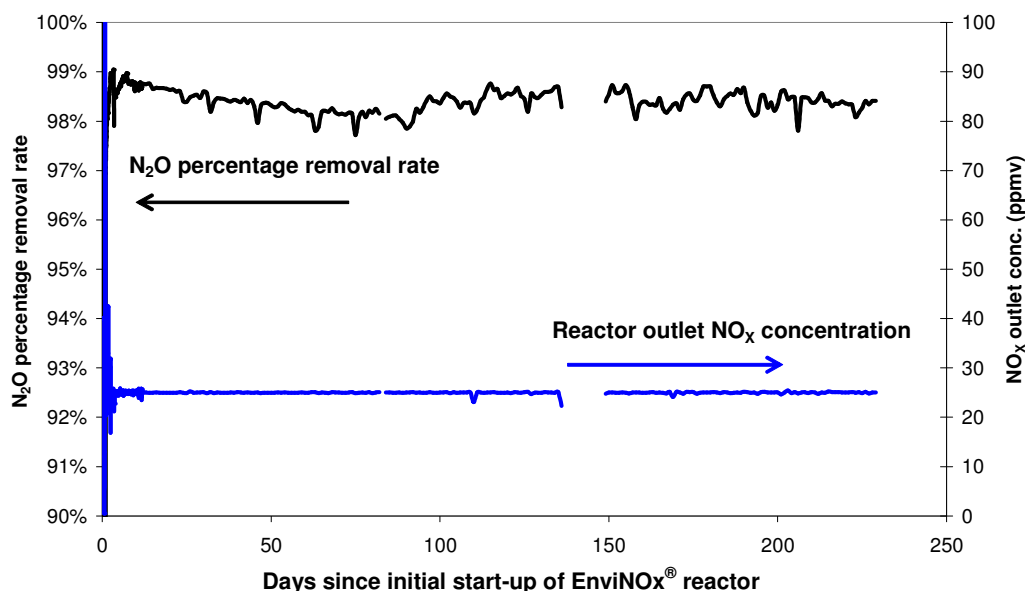


Figure 5: *EnviNOx®* process variant 1, N_2O decomposition and NO_x reduction with ammonia: HU CHEMS No. 4 Nitric Acid Plant, Yeosu, Korea, Percentage rate of N_2O destruction and NO_x outlet concentration

As part of a Kyoto CDM project the Uhde-built HU CHEMS #4 nitric acid plant was equipped with an EnviNOx® variant 1 system.

As the operating data in Figure 5 shows, N_2O destruction rates of over 98% are consistently achieved while the outlet NO_x concentration is controlled at 25 ppmv by addition of the appropriate quantity of ammonia.

7.2 Operating data for EnviNOx® process variant 2 installations

7.2.1 Abu Qir 2, Egypt – Start Up October 2006

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. N_2O is reduced with natural gas. N_2O abatement rates in excess of 99% and NO_x outlet concentrations of around 1 ppmv are being consistently achieved, making for a very clean nitric acid plant tail gas. Figure 6 shows some performance data.

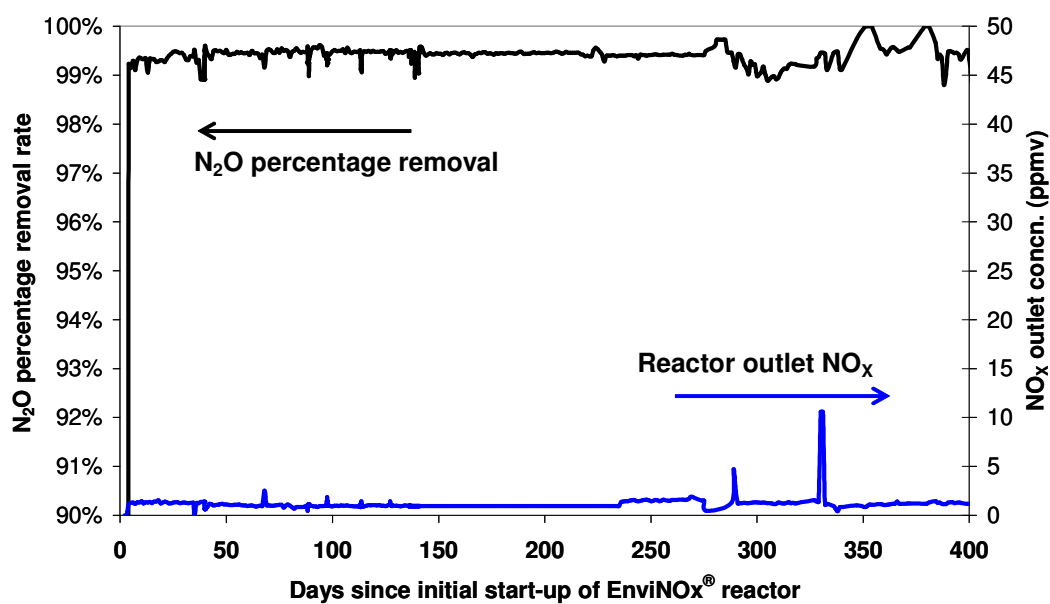


Figure 6: EnviNOx[®] process variant 2, N_2O reduction with natural gas and NO_x reduction with ammonia: Abu Qir Fertilizer Co., Egypt, Percentage rate of N_2O destruction and NO_x outlet concentration



7.2.2 HU CHEMS #2 and #3 NA Plants, Yeosu, Korea – Start Up in early 2007

As natural gas was not available on site, commercial propane was used as the reducing agent for N_2O 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. As Figure 7 illustrates for plant #3, high rates of N_2O removal are again being achieved, while NO_x emissions are below 5 ppmv.

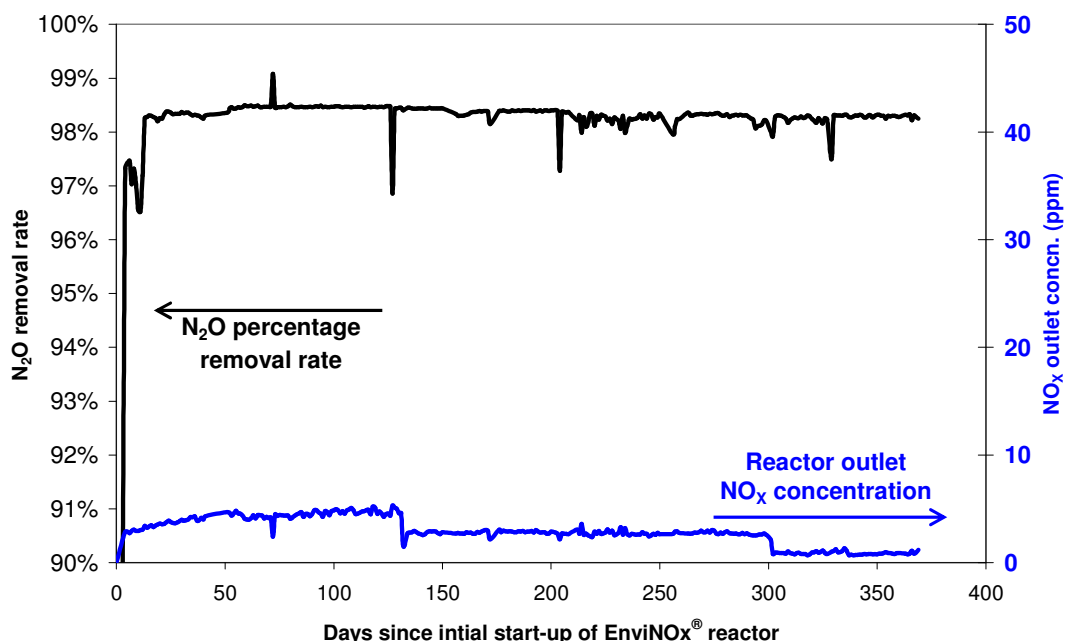


Figure 7: EnviNOx[®] process variant 2, N_2O reduction with propane and NO_x reduction with ammonia: HU CHEMS Nitric Acid Plant #3, Yeosu, Korea, Percentage rate of N_2O destruction and NO_x outlet concentration

7.3 Other commercial scale EnviNOx[®] units

The EnviNOx[®] systems described in the previous sections are not the only ones currently in operation. Other commercial scale implementations include the EnviNOx[®] reactor installed in the new Grande-Paroisse-designed 1500 tonne/day nitric acid plant of Nitrogénművek, Pétfürdő, Hungary. The EnviNOx[®] system went into successful operation in mid-2007 with N_2O abatement above 99%. Natural gas is used to reduce N_2O and ammonia to reduce NO_x .

Another EnviNOx[®] variant 2 reactor using natural gas and ammonia has been in operation since early this year in the Uhde-built 750 tonne/day nitric acid plant of Omnia Fertilizer Ltd., Sasolburg, South Africa. N_2O removal rates of 98% to 99% are being achieved with 0 – 1 ppmv NO_x in the tail gas leaving the plant.

More EnviNOx[®] units are in operation in Western European nitric acid plants, and further reactors are expected to come on stream in 2009.



8. EnviNOx[®] 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 plants⁴ gives the N₂O and NO_x emission levels reproduced in the table 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.

	N ₂ O emission level associated with BAT (ppmv) ***	NO _x emission level associated with BAT (ppmv)
New plants	20 – 100	5 – 75
Existing plants	20 – 300	5 – 90
NH ₃ Slip from SCR		<5 ppmv

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

The EnviNOx[®] process (variant 1) is explicitly named in the BREF as being a BAT, and in fact even the lowest BAT emission levels of N₂O and NO_x given in the BREF can easily be attained with an EnviNOx[®] system, as the performance figures given in the present paper illustrate.

9. Current Developments

Work is currently underway to widen the upper and lower temperature range of the EnviNOx[®] technology to permit it to be applied to an even broader selection of nitric acid plants. The results of ongoing investigations are promising.



10. Conclusion

The EnviNOx[®] process for the combined abatement of NO_x and N₂O emissions from nitric acid plants has proven itself in installations around the world which are now operating at temperatures between 340 °C and 520 °C. Typically, N₂O emissions are reduced by ~98% – 99% while NO_x emission levels of 1 to ~25 ppmv are achieved, depending on the process variant.

Independent confirmation of the high N₂O 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 N₂O 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 to 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 most of the nitric acid and caprolactam plants with tail gas temperatures outside this range, relatively simple plant modifications are possible to enable these plants to enjoy the low N₂O and NO_x emission benefits of an EnviNOx[®] system. As an end-of-pipe process EnviNOx[®] does not interact in any way with the plant product or its precursors.

The EnviNOx[®] catalysts are easy to handle, environmentally friendly materials with a long operating lifetime.

In 2007 the Uhde EnviNOx[®] process was declared to be BAT (Best Available Technique) in the European Union. Present BAT emission levels for NO_x and N₂O can easily be met, and with its high performance the EnviNOx[®] process will be able to meet any realistically conceivable future limits on gaseous emissions from nitric acid plants, too.

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