



# Abatement of $N_2O$ and $NO_X$ Emissions from Nitric Acid Plants with the Uhde Envi $NO_X$ Process

- Design, Operating Experience and Current Developments -

by

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Keywords: nitrous oxide, NOx, nitrogen oxide abatement, greenhouse gas reduction





# Abatement of N<sub>2</sub>O and NO<sub>X</sub> Emissions from Nitric Acid Plants with the Uhde EnviNOx<sup>®</sup> Process

# Design, Operating Experience and Current Developments –

# **Abstract**

Nitrous oxide (N<sub>2</sub>O) 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.

At the time of writing (January 2006) the first commercial scale implementation of Uhde's EnviNOx<sup>®</sup> combined N<sub>2</sub>O and NO<sub>x</sub> abatement technology for nitric acid plants has been in successful operation for over two years. During this time a consistent 98-99% rate of N2O removal has been achieved, while NO<sub>x</sub> emissions have been reduced to about 10 ppm. This process, which relies on the decomposition of N2O in the tail gas of nitric acid plants, works best at temperatures above ~425°C. For nitric acid plants with tail gas temperatures down to ~350°C Uhde has developed an EnviNOx® variant that uses small quantities of a hydrocarbon reducing agent and ammonia to achieve high N<sub>2</sub>O conversions and virtual elimination of NO<sub>x</sub> emissions.



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# - Design, Operating Experience and Current Developments -

# 1. The Greenhouse Effect and Climate Change

The greenhouse effect is a natural phenomenon. Without it the temperature of the earth would be around -15°C and life as we know it would not be possible. The main greenhouse gas is water vapour, which contributes over 60% of the total warming effect. Other important greenhouse gases include carbon dioxide, nitrous oxide and methane. Since the beginning of industrialisation the atmospheric concentration of these gases has been rising due to the burning of fossil fuels, the spread of agriculture, and deforestation. It is believed by a large body of scientific opinion that this change in the composition of the earth's atmosphere is leading to alterations in the global climate which may have a negative impact on human society.

## 2. Formation of Nitrous Oxide in Nitric Acid Plants

Nitric acid plants are significant emitters of the greenhouse gas nitrous oxide. Nitrous oxide is formed as an unwanted byproduct in the oxidation of ammonia over the platinum-rhodium gauzes in the ammonia burner.

The following reactions take place:

Desired reaction:

4 NH
$$_3$$
 + 5 O $_2$   $\rightarrow$  4 NO + 6 H $_2$ O  $\Delta H$  = - 906.1 kJ Undesired reactions:

$$4 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O}$$
  $\Delta H = -1267.2 \text{ kJ}$   
 $4 \text{ NH}_3 + 4 \text{ O}_2 \rightarrow 2 \text{ N}_2\text{O} + 6 \text{ H}_2\text{O}$   $\Delta H = -1103.1 \text{ kJ}$ 

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

$$2 \text{ NH}_3 + 8 \text{ NO} \rightarrow 5 \text{ N}_2\text{O} + 3 \text{ H}_2\text{O} \Delta \text{H} = -945.7 \text{ kJ}$$
  $4 \text{ NH}_3 + 4 \text{ NO} + 3 \text{ O}_2 \rightarrow 4 \text{ N}_2\text{O} + 6 \text{ H}_2\text{O} \Delta \text{H} = -2403.3 \text{ kJ}$ 

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

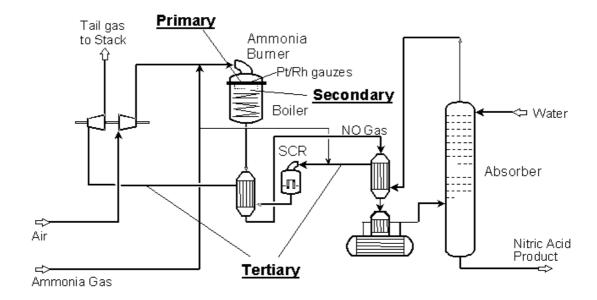
Apart from some possible losses due to high temperature decomposition, the nitrous oxide leaving the ammonia burner takes no further part in the chemistry of the nitric acid process and is emitted to atmosphere in the tail gas.



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. IPCC (Intergovernmental Panel on Climate Change) figures range from less than 2 to 19 kg N<sub>2</sub>O/tonne nitric acid. High pressure plants generally have a higher emission factor than medium (6-7.5 kg N<sub>2</sub>O/tonne nitric acid) or even atmospheric plants (4-5 kg N<sub>2</sub>O/tonne nitric acid). (To

#### 3. Classification of Nitrous Oxide Abatement Processes

estimate the corresponding tail gas concentration in ppmv multiply by 160).



Simplified flowsheet of the nitric acid process showing the classification of Figure 1: 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 Fig. 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.



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- 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. As nitrous oxide is metastable at the temperature used in the ammonia oxidation step and decomposes with first order kinetics, one method is to provide a space and thus high temperature residence time between the exit of the gauzes and the inlet of the cooler, normally the boiler. An alternative approach has a catalyst installed in the space below the gauzes before the inlet of the boiler.
- Tertiary: Nitrous oxide is removed from the tail gas downstream of the absorption tower, either by catalytic decomposition, the rate of homogeneous decomposition being negligible at the temperatures that typically prevail in tail gas streams, or by catalytic reduction. The optimum position for locating a tertiary abatement step is at the hottest position in the plant, immediately upstream of the expansion turbine.

# 4. Tertiary N<sub>2</sub>O Abatement Process Development Programme

During the 1990s Uhde formed the view that nitrous oxide emissions from nitric acid plants were going to become a matter of concern and decided to devote resources to finding ways to limit them. It was felt that a tertiary approach offered a number of advantages:

- The tertiary approach, as an end-of-pipe technology, is analogous to the various well-established catalytic NO<sub>X</sub> reduction processes. Acceptance was therefore not expected to present a problem, and there might be the possibility of combining the two technologies.
- With a tertiary process as opposed to a secondary one there would be no requirement to develop a particularly selective catalyst suitable only for destroying N<sub>2</sub>O but not NO or NO<sub>2</sub>.

It was therefore decided to concentrate efforts on tertiary measures and Uhde initiated an R&D programme with the aim of developing a technology for the reduction of nitrous oxide from nitric acid plants. The programme has a number of aspects:

- Contact with catalyst manufacturers, research institutes and universities working
  in the field of catalyst development who might be able to supply candidate catalyst
  materials and / or make their experimental facilities available for catalyst
  investigations.
- Construction of in-house laboratory facilities for independent catalyst testing work.
- Structural investigations to elucidate the parameters of most importance for high catalyst activity and stability.
- Co-operation with a nitric acid production plant owner for long term catalyst experiments under conditions actually found in real nitric acid production plants, and construction of a catalyst test unit for the purpose.
- Contact with catalyst manufacturers who would be able to undertake the large volume production of the catalysts resulting from the development work.

# 4.1 Catalyst test unit

An important component of the  $N_2O$  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 mtpd dual pressure nitric acid plant Line E. The unit has two independently operable test reactors and is controlled by a DCS which also performs data logging. The composition of the tail gas drawn from the nitric acid plant can be modified by supplying other gases from cylinders. Gas analysis is by a multicomponent FT-IR analyser and a chemiluminescence detector for  $NO_x$ .

# 4.2 Catalyst investigations

An initial screening identified iron zeolites as a promising class of material for N<sub>2</sub>O decomposition and detailed investigations were then carried out in Uhde's laboratories and the catalyst test unit and also for Uhde by external research institutes and university departments. The main results of these investigations are discussed in this section.

# **4.2.1** Effect of nitric oxide on N<sub>2</sub>O decomposition

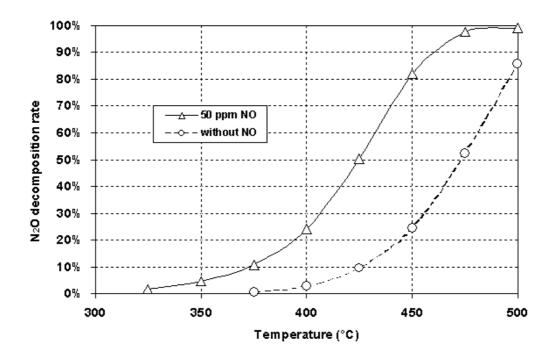


Figure 2: Effect of NO in enhancing N<sub>2</sub>O decomposition over an iron zeolite. Conditions: Total pressure 1 bar abs, Gas volume composition N<sub>2</sub>O 1000 ppm, H<sub>2</sub>O 0.5%, O<sub>2</sub> 4%, remainder N<sub>2</sub> with or without 50 ppm NO (from laboratory studies carried out for Uhde).



It was found that nitric oxide greatly enhances the rate of  $N_2O$  decomposition on iron zeolites. This effect has been reported in the scientific literature and was also confirmed in the catalyst test unit. Measurements carried out on an iron zeolite for Uhde by an external research organisation are shown in Fig. 2. The gas composition approximates to that of a nitric acid tail gas except that in one case there are no nitrogen oxides present except for nitrous oxide, and in the other 50 ppm nitric oxide have been added to the gas. The addition of the nitric oxide shifts the temperature curve 50K to the left, or alternatively, at a given temperature, 450°C for example, the rate of nitrous oxide decomposition increases by over 50 percentage points.

# **4.2.2** Effect of pressure on N<sub>2</sub>O decomposition

Fig. 3 shows how the rate of  $N_2O$  decomposition over an iron zeolite catalyst varies with the pressure. The positive effect of higher pressure on  $N_2O$  conversion is significant. In this experiment an increase of system pressure from 1 to 6 bar g increased the rate of  $N_2O$  decomposition by about 24 percentage points.

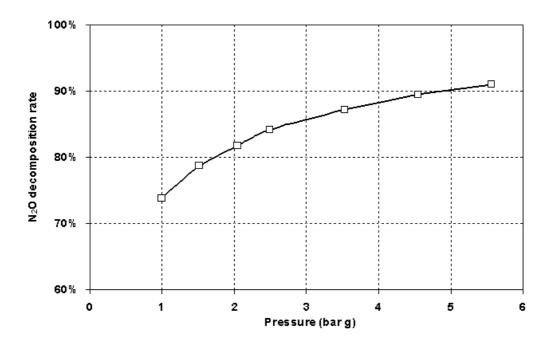


Figure 3: Effect of pressure on N<sub>2</sub>O decomposition over an iron zeolite. Feed composition: N<sub>2</sub>O 1000 ppm, NO<sub>x</sub> 500 ppm. (from Uhde catalyst test unit)

### **4.2.3** NO<sub>X</sub> abatement

The iron zeolites investigated were found to be very effective in reducing  $NO_X$  with ammonia. Fig. 4 shows that very high rates of removal of  $NO_X$  can be attained.



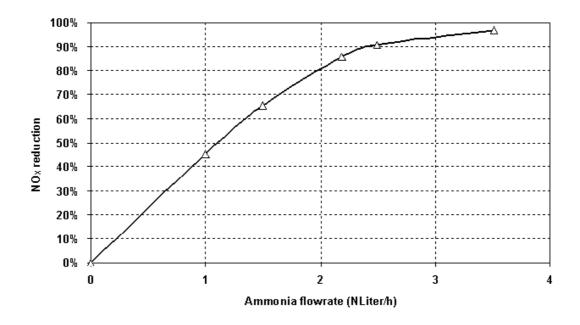


Figure 4:  $NO_X$  reduction with ammonia on iron zeolite catalyst.  $NO_X$  concentration in inlet gas 400 ppm (from Uhde catalyst test unit)

## 4.3 Long term operation of catalyst test unit

Apart from carrying out work on the effect on catalyst activity of parameters such as pressure, temperature or  $NO_X$  concentration the main use of the catalyst test unit is to gather data on the long term stability and activity of possible catalysts, to observe and understand trends in activity and to test catalyst modifications. The test unit has been in operation since 2000.

# 5. Process Concept for Combined N<sub>2</sub>O and NO<sub>X</sub> Abatement

By mid-2002 sufficient knowledge had been acquired to demonstrate the feasibility of an industrial scale implementation of the new technology. The process concept that was developed exploits the fact that the decomposition reaction of nitrous oxide is promoted by high concentrations of  $NO_X$  and that the reduction of  $NO_X$  with ammonia proceeds very effectively on the catalyst. These considerations result in a two bed reactor, with a gaseous ammonia feed between the catalyst beds. The reactor is located in the tail gas stream at the inlet side of the tail gas turbine where the tail gas temperature is at its highest. Fig. 5 illustrates the concept.

Tail gas enters the reactor at a temperature of about  $425^{\circ}$ C or above. Because of the high  $NO_X$  concentration in the tail gas, 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.



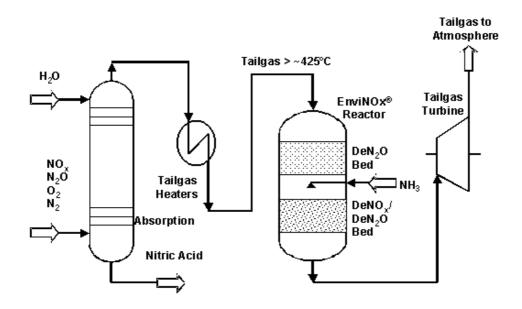


Figure 5: Process concept for combined N<sub>2</sub>O and NO<sub>X</sub> abatement for nitric acid plants using N<sub>2</sub>O decomposition.

#### 6. First Implementation of Process on Industrial Scale

### 6.1 Design and construction phase

The results from the catalyst test unit, including those on the long term performance of the nitrous oxide decomposition catalyst, were so convincing that AMI decided to equip their 1,000 mtpd dual pressure Line E nitric acid plant with a combined nitrous oxide and NO<sub>x</sub> abatement reactor using the new process. A contract for the basic engineering and the design of the reactor as well as the delivery of the catalyst was signed with Uhde in 2002. The detail engineering and erection was carried out by Chemserv Industrie GmbH, a Linzbased industrial service company. AMI retained the overall project management.

For the most part it was possible to carry out the erection work without impeding the nitric acid production. This applied to the casting of the foundations, the erection of the steelwork and a large part of the piping, as well as the installation of the reactor. Nitric acid production was shut down only for the actual tie-in of the pipework.



# 6.2 Commissioning

After the two beds of the reactor had been filled with catalyst and the reactor hood closed, a strainer that is permanently installed in the reactor outlet was equipped with an additional fine mesh gauze and the nitric acid plant operated for four hours on process air only, to capture loose catalyst particles and fines and prevent them from finding their way to the tail gas turbine and possibly causing damage. Afterwards the reactor was allowed to cool down and the strainer inspected. Only a very small quantity of particles and dust was found. Following this satisfactory result the additional fine mesh gauze was removed, so as not to cause unnecessary additional pressure drop in normal operation.

### 6.3 Startup

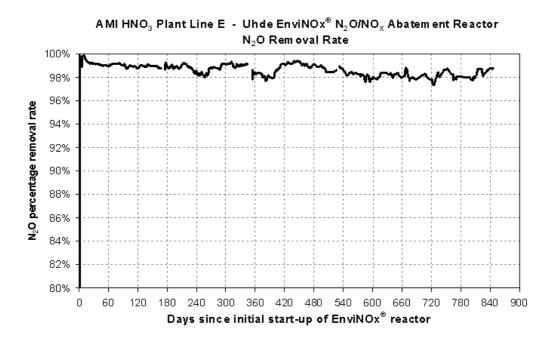
On 29th September 2003 the nitric acid plant was started up with ammonia in the customary way. A new set of ammonia oxidation gauzes had been installed. On reaching normal operating temperature in the combined nitrous oxide and NO<sub>x</sub> abatement reactor a rate of nitrous oxide removal of over 99% was observed immediately.

The ammonia supply system was started up shortly afterwards and the ammonia flow rate increased gradually. The NO<sub>X</sub> reduction worked satisfactorily.

## 6.4 Operating experience

The EnviNOx® reactor at AMI has been in operation for over two years. The original catalyst charge is still installed.

#### 6.4.1 Nitrous oxide decomposition







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Figure 6: Nitrous oxide decomposition performance of Uhde EnviNOx $^{\otimes}$  combined nitrous oxide and NO $_{\times}$  abatement reactor in AMI nitric acid plant Line E (moving average)

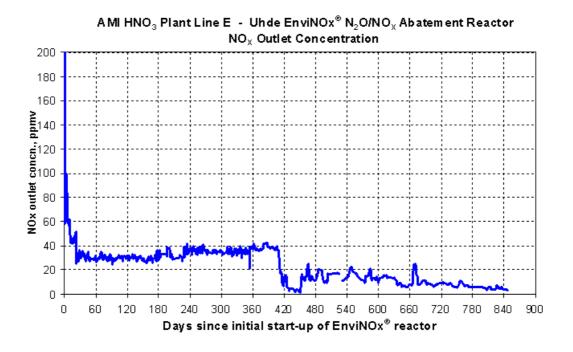
The nitrous oxide inlet concentration of the EnviNOx $^{\$}$  reactor is typically in the range 1000 – 1100 ppm. Short term fluctuations due to changing plant load are usually overlaid with a longer term trend to higher N<sub>2</sub>O concentrations as a gauze campaign advances. The gauzes are changed approximately twice a year.

Fig. 6 shows how the percentage reduction in nitrous oxide concentration over the  $N_2O/NO_X$  abatement reactor has changed over time. For the most recent 300 days of operation the  $N_2O$  conversion has been stable at about 98%. In the first year of operation an even higher 99% conversion was achieved. The  $N_2O$  concentration at the outlet of the EnviNOx® reactor is currently around 20 ppm.



#### 6.4.2 NO<sub>x</sub> reduction

Fig. 7 depicts the variation of NO<sub>X</sub> concentration in the tail gas leaving the EnviNOx<sup>®</sup> reactor over time.



Variation of tail gas total NO<sub>X</sub> (NO, NO<sub>2</sub>) concentration at outlet of Uhde Figure 7: EnviNOx<sup>®</sup> combined nitrous oxide and NO<sub>X</sub> abatement reactor in AMI nitric acid plant Line E (moving average)

The concentration of NO<sub>x</sub> at the inlet of the reactor depends on the conditions in the absorption tower, with the operating pressure, oxygen concentration, cooling water temperature and plant load all playing a role. Thus there is no long term trend in concentration variation, but rather the quantity of NO<sub>x</sub> fluctuates around a mean value of about 400 ppm. The outlet NO<sub>x</sub> concentration is determined by the quantity of ammonia that is supplied to the reactor. As confidence was gained with the operation of the reactor the ammonia flow controller was successively set to lower NO<sub>x</sub> concentrations. Initially the outlet NO<sub>x</sub> concentration was controlled at 60 ppmv, but soon lowered to 45 ppm. Thereafter outlet NO<sub>x</sub> was maintained at 30 to 40 ppm. After just over a year of operation the control strategy was modified to allow further NO<sub>x</sub> reduction. The EnviNOx<sup>®</sup> reactor is currently being operated with an outlet NO<sub>X</sub> concentration between 1 and 10 ppm, with the average value being around 5 ppm. Ammonia slip is not observed.



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# **6.4.3** Pressure drop

The design specification allowed for a total additional pressure drop attributable to the new  $EnviNOx^{®}$  combined  $N_2O/NO_X$  abatement reactor and connecting pipework of 100 mbar. At normal production capacity the pressure drop of the  $EnviNOx^{®}$  reactor is about 95 mbar and therefore within the limit for the project. The decrease in pressure at the inlet of the tail gas turbine caused by the new reactor would imply a reduction in energy recovery. However, in this case there is also a rise in temperature at the tail gas turbine inlet due to the exothermic nitrous oxide decomposition and  $NO_X$  reduction reactions. Calculations performed by AMI have shown that the overall effect is to increase slightly the amount of energy recovered.

# 6.5 Comparison of design and achieved performance

The process concept called for a nitrous oxide removal rate in the first bed of 80%. In the second bed the goal was to destroy 50% of the remaining nitrous oxide, thus achieving an overall reduction in nitrous oxide of 90%. The  $NO_X$  concentration was to be lowered to 80 ppm.

To date (January 2006) after over 2 years of operation the rate of nitrous oxide destruction has remained consistently high at between ~98% and 99%. The  $N_2O/NO_X$  abatement reactor operates with an inlet  $NO_X$  concentration of some 400 ppm and an outlet of less than 10 ppm. The stack plume is invisible. Pressure drop is within the limit of 100 mbar. The combined nitrous oxide and  $NO_X$  abatement reactor has therefore comfortably met and exceeded the process design specification.

#### 6.6 Impact on the environment

The expected performance of the new reactor according to the process concept corresponds to an emission reduction of 1600 tonne/year  $N_2O$ . Applying the Kyoto Protocol value of the global warming potential for nitrous oxide of 310 results in an expected emission reduction equivalent to 500 000 tonne/year  $CO_2e$ . In fact the better than expected performance of the reactor has meant that the emission reduction is in the region of 700 000 tonne/year  $CO_2e$ . With this single measure AMI have cut their greenhouse gas emissions at the Linz site by over 30%. The reduction corresponds to more than half of Austria's climate gas emission reduction target of 1 250 000 tonne/year  $CO_2e$  in the field of manufacturing industry and trade and therefore represents a significant contribution to climate protection.

# 7. N₂O Abatement at Tail Gas Temperatures Below ~425°C

The  $N_2O$  decomposition process implemented successfully at AMI is suited to tail gas temperatures above about 425°C. (The  $NO_X$  reduction component functions efficiently over the much wider temperature range of 200°C to 500°C.) At lower temperatures, particularly below 400°C, the activity of the iron zeolite for  $N_2O$  decomposition falls increasingly rapidly. A reactor designed for a high rate of  $N_2O$  conversion at these temperatures would be unattractively large. There are, however, many nitric acid plants with tail gas temperatures below 425°C. Uhde therefore started work to develop a nitrous oxide abatement process applicable to such plants.



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# 7.1 Laboratory and pilot plant investigations on N₂O reduction

Investigations conducted by Uhde and others organisations on behalf of Uhde demonstrated that a hydrocarbon might be a promising reducing agent for  $N_2O$  in industrial applications. A readily available hydrocarbon is natural gas, which consists mainly of methane and smaller amounts of higher hydrocarbons, nitrogen and carbon dioxide. Methane was used in laboratory and pilot plant investigations carried out by Uhde.

If a typical tail gas composition is treated with methane or higher hydrocarbons over an iron zeolite catalyst the amount of  $N_2O$  conversion is rather small, or, putting it another way, large quantities of hydrocarbon are required to effect a significant reduction in  $N_2O$  concentration. The  $NO_X$  present in the tail gas inhibits the reaction between  $N_2O$  and  $CH_4$ . The iron zeolite is, however, a very effective  $NO_X$  reduction catalyst if supplied with ammonia. Thus the idea was born to combine the destruction of all the unwanted nitrogen oxides species  $N_2O$  and  $NO_X$  in one step by supplying hydrocarbon together with ammonia to the iron zeolite catalyst. Using this approach very effective abatement of both  $N_2O$  and  $NO_X$  is possible.

This can be seen in Fig. 8 which shows the results of an experiment carried out in the Uhde catalyst test unit. A fixed amount of methane, 525 ppm, was mixed with a tail gas stream containing 15 ppm  $NO_X$  and 1700 ppm  $N_2O$  and the resulting gas contacted with an iron zeolite catalyst held at 350°C. Ammonia was then added in increasing concentrations, to react with the  $NO_X$  and remove it.

Initially, before any ammonia had been added, only about 13% of the nitrous oxide could be destroyed. As more and more ammonia was supplied to the reactor the  $NO_X$  outlet concentration continued to decrease. The  $N_2O$  conversion increased slowly at first. As the  $NO_X$  concentration was lowered from 2 ppm to around zero there was a rapid rise in  $N_2O$  conversion from 30% to 80%. Further additions of ammonia over the amount required to remove the  $NO_X$  entirely had but slight effect on  $N_2O$  conversion.

The maximum  $N_2O$  conversion, 85%, observed in the experiment of Fig. 8 is determined by the amount of methane that was used. Fig. 9 shows the experiment that was performed immediately after the experiment of Fig. 8. The same tail gas feed stream with 1700 ppm  $N_2O$  and 15 ppm  $NO_X$  was used. The ammonia concentration was kept at a constant 50 ppm, a level at which maximum  $N_2O$  conversion was obtained in the experiment of Fig. 8, and the flow of methane was varied. The curve of Fig. 9 demonstrates that the  $N_2O$  conversion changes smoothly as a function of the amount of methane added and that very high  $N_2O$  conversions, here 97%, are possible.

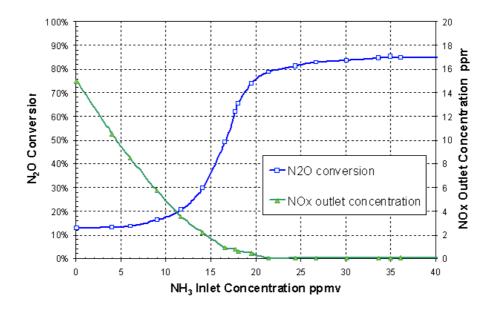


Figure 8: Nitrous oxide reduction with methane over iron zeolite with NO<sub>X</sub> reduction with ammonia, illustrating inhibiting effect of NO<sub>X</sub> on N<sub>2</sub>O reduction reaction. Temperature 350°C, feed composition: CH<sub>4</sub> 525 ppm, NO<sub>X</sub> 15 ppm, N<sub>2</sub>O 1700 ppm, NH<sub>3</sub> variable. (from Uhde catalyst test unit)

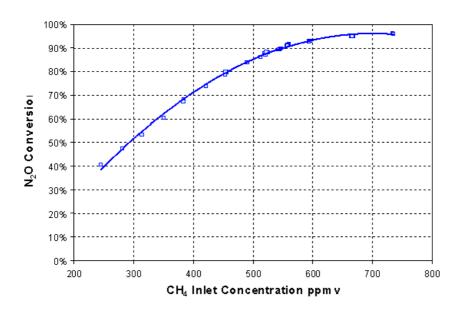
In other experiments it was demonstrated that the same high  $N_2O$  conversions can be obtained if the  $NO_X$  removal step is carried in a separate bed upstream of the  $N_2O$  reduction.

Similar results were obtained in investigations with higher hydrocarbons, which were found to be as active in reducing  $N_2O$  as methane. Higher, more typical  $NO_X$  concentrations have no adverse effect on the  $N_2O$  conversion provided the appropriate amount of ammonia is supplied to reduce the  $NO_X$  concentration to zero.

Summarising the results of these and other experiments carried out by Uhde it can be stated:

- Tail gas N<sub>2</sub>O can be effectively reduced with methane and higher hydrocarbons if the NO<sub>X</sub> is removed.
- High N<sub>2</sub>O conversion rates can be achieved.
- The amount of N<sub>2</sub>O conversion can be easily set to the figure required by adjusting the flow of hydrocarbon. This could be of value if an emission limit such as the 407 ppm (0.80 g/m³) of the German TA Luft must be observed, as only the precise amount of hydrocarbon required to achieve the limit and no more must be supplied.





Nitrous oxide reduction with methane over iron zeolite with NO<sub>X</sub> reduction Figure 9: with ammonia. Temperature 350°C, feed composition: NO<sub>X</sub> 15 ppm, N<sub>2</sub>O 1700 ppm, NH<sub>3</sub> 50 ppm, CH<sub>4</sub> variable (from Uhde catalyst test unit).

- The consumption of hydrocarbon is low in the experiments described above less than <sup>1</sup>/<sub>3</sub> mol CH<sub>4</sub> / mol reactor inlet N<sub>2</sub>O was necessary to achieve 90% N<sub>2</sub>O conversion. At higher temperatures the hydrocarbon consumption is even lower.
- The tail gas NO<sub>X</sub> concentration is lowered to effectively zero.
- The NO<sub>X</sub> can be removed in parallel with the N<sub>2</sub>O reduction with hydrocarbons or equally well be carried out in an upstream catalyst bed.
- The role of ammonia is to reduce NO<sub>x</sub>. Adding additional ammonia over and above the amount required for reaction with the NO<sub>X</sub> only has a fairly small effect on N<sub>2</sub>O conversion and excess ammonia is converted to nitrogen and water.
- At the present stage of development N<sub>2</sub>O reduction with hydrocarbons combined with NO<sub>X</sub> reduction with ammonia is feasible down to a temperature of ~350°C.

It is noteworthy that the role of NO<sub>x</sub> in the reduction of N<sub>2</sub>O with hydrocarbons is the opposite of that in N<sub>2</sub>O decomposition on iron zeolites. NO<sub>X</sub> enhances the rate of N<sub>2</sub>O decomposition but inhibits N<sub>2</sub>O reduction with hydrocarbons.

Thus the process concept for a nitrous oxide abatement by reduction with hydrocarbons is different from that described above for N<sub>2</sub>O decomposition.



# 7.2 Process concept for N<sub>2</sub>O abatement by reduction with hydrocarbons

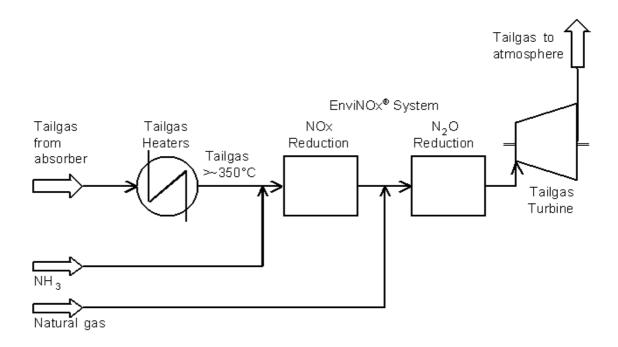


Figure 10: Process concept for combined NO<sub>X</sub> and N₂O abatement by reduction with ammonia and natural gas, respectively.

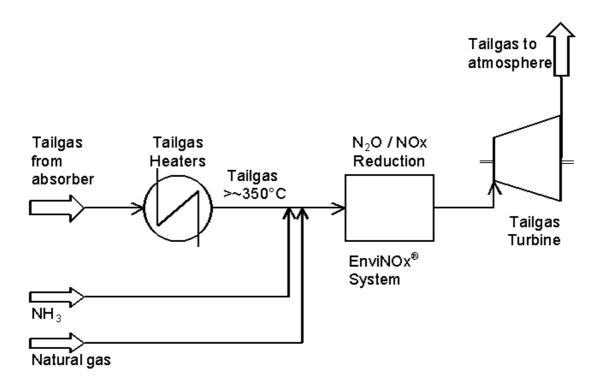


Figure 11: Process concept for simultaneous NO<sub>X</sub> and N₂O abatement by reduction with ammonia and natural gas, respectively.

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The prime requirement for efficient  $N_2O$  reduction is to lower the concentration of  $NO_X$  to a very low level.  $NO_X$  removal by reaction with ammonia must therefore take place before or during the reduction of  $N_2O$  with hydrocarbon (Figs. 10 and 11).

In Fig. 10 the  $NO_X$  is removed in an upstream  $NO_X$  reduction reactor or catalyst bed before any  $N_2O$  reduction takes place. It is equally possible to combine the  $NO_X$  and  $N_2O$  reduction steps in one vessel as in Figure 11.

Other hydrocarbons may be used instead of natural gas.

N<sub>2</sub>O abatement by reduction with hydrocarbons works well down to ~350°C.

#### 8. Conclusion

For the cost effective reduction of greenhouse gas emissions a nitrous oxide abatement measure implemented in a nitric acid plant is an attractive proposition, because of the point nature of the emission source and the high global warming potential of nitrous oxide. An applied research and development programme started in 1999 by Uhde has generated a nitrous oxide emission reduction technology for nitric acid plants which is also capable of being combined with a process step for the practically complete reduction of other nitrogen oxides ( $NO_X$ ). The first industrial scale implementation of the technology for the combined removal of nitrous oxide and  $NO_X$  has been in operation for over two years, and continues to perform satisfactorily. The technology, which is based on the catalytic decomposition of nitrous oxide, is applicable to new or existing nitric acid plants with a tail gas temperature of ~425°C or higher. The  $NO_X$  abatement component can be used on its own and is suitable for the wider temperature range from about 200°C to 500°C.

For nitric acid plants with tail gas temperatures of  $\sim 350^{\circ}\text{C}$  and above, Uhde has developed an EnviNOx® process variant based on nitrous oxide reduction, which uses small amounts of a hydrocarbon such as natural gas, and ammonia, to virtually eliminate NO<sub>X</sub> emissions and lower N<sub>2</sub>O concentrations to very low levels.

The catalysts for all  $EnviNOx^{@}$  process variants are supplied by  $S\ddot{u}d$ -Chemie and are marketed under the trade names  $EnviCat^{@}$ -NOx for  $NO_X$  reduction and  $EnviCat^{@}$ -N<sub>2</sub>O for  $N_2O$  abatement.