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**Combined Nitrous Oxide and NO_x Abatement
in Nitric Acid Plants**

presented by

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About the IFA Technical Committee

The IFA Technical Committee encourages the development and adoption of technology improvements that can lead to greater production efficiencies and reduced emissions, as well as better health and safety standards throughout the fertilizer industry. Our mission is to actively promote the sustainable development of efficient and responsible production, storage and transportation of all plant nutrients. The Technical Committee accomplishes these objectives through a variety of channels, including:

- Technical and policy-oriented information materials. The committee regularly conducts surveys and produces reports on key industry metrics, including the IFA Energy Efficiency and CO₂ Emissions Report, the IFA Safety Report, and the IFA Emissions Report. This work enables member companies to assess their operations over time, make comparisons with similar facilities on an established level of performance, determine the need for technology improvements and identify good industrial and management practices.
- Regular exchange of information on technology developments and industrial practices. A key role of the IFA Technical Committee is to encourage ongoing technical innovation in the fertilizer industry through the development, compilation and exchange of technical information between members, researchers, engineers, equipment suppliers and other industry associations. To this end, the committee organizes a Technical Symposium every other year to examine progress in the production technology of fertilizers. Each Symposium traditionally features the presentation of 30-40 new technical papers from member companies worldwide, providing members with information on the latest technological developments. In the intervening years, the committee holds a variety of meetings to assess current industrial practices and standards, with an eye toward identifying key developments of interest to members.
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(as provided by the author for distribution in Alexandria)

Combined Nitrous Oxide and NO_x Abatement in Nitric Acid Plants

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 310 times the effect of carbon dioxide, and is also implicated in the destruction of the ozone layer there is a need for technologies to lower nitrous oxide emissions from nitric acid plants.

Responding to this need Uhde established a research and development programme to find a commercially viable method for removing nitrous oxide and NO_x from the tail gas of nitric acid plants. To gain practical long-term operating experience with possible catalysts, Uhde designed and built a catalyst test unit which could be connected to the tail gas section of a nitric acid plant. In a partnership with Uhde, the Linz, Austrian-based chemical company Agrolinz Melamine International GmbH (AMI) provided the nitric acid plant access and all the support needed for the trouble free and continuous operation of the catalyst test unit.

Based on the positive results obtained with the actual tailgas temperature of 435°C, a full-size EnviNOx[®] nitrous oxide and NO_x abatement reactor was designed and built, and the first commercial scale implementation of the new process successfully started up in September 2003 at AMI. In the first 1½ years of operation, 98% – 99% of the tail gas nitrous oxide has been consistently destroyed in the reactor and the outlet NO_x concentration lowered to 30 ppmv, allowing the Uhde EnviNOx[®] process to comfortably exceed performance requirements.

Building on the success of the new unit Uhde has gone on to extend the technology to temperatures lower than 400°C. The process, which has been comprehensively tested in the Uhde catalyst test unit at AMI in Linz, employs small quantities of a hydrocarbon, such as natural gas or propane, to reduce nitrous oxide to nitrogen and water vapour. Nitrous oxide removal rates of over 90% can be achieved.

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All papers and presentations prepared for the IFA Technical Committee Meeting in Alexandria will be compiled on a cd-rom to be released in May 2005.



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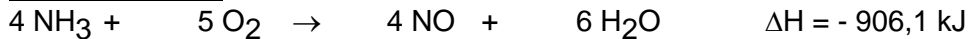
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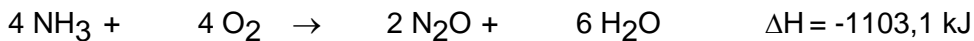
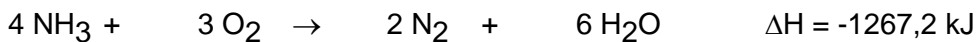
1. Formation of Nitrous Oxide in Nitric Acid Plants

Nitrous oxide and nitrogen are formed as unwanted by-products during the catalytic oxidation of ammonia in air over platinum-rhodium catalyst gauzes in the ammonia converter:

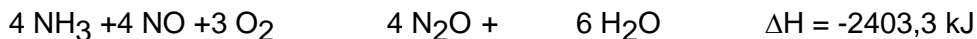
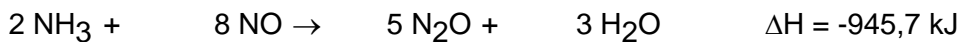
Desired reaction:



Undesired reactions:



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 that are normally installed below the catalyst gauzes for platinum recovery, catalyses these reactions.

The amount of nitrous oxide produced depends in part on the operating conditions, and also on the condition and type of the gauzes. With fresh gauzes in a medium pressure burner, less than 1.5% of the total ammonia may be converted to nitrous oxide, resulting in a tail gas nitrous oxide concentration under 1000 ppm. This can rise to 1500 ppm at the end of a campaign, corresponding to 2.5% ammonia loss to nitrous oxide (or about 9 kg N₂O / t HNO₃ product). A sudden rise in tail gas nitrous oxide can be indicative of damage to the gauzes allowing ammonia bypassing.



2. Approaches to Nitrous Oxide Abatement

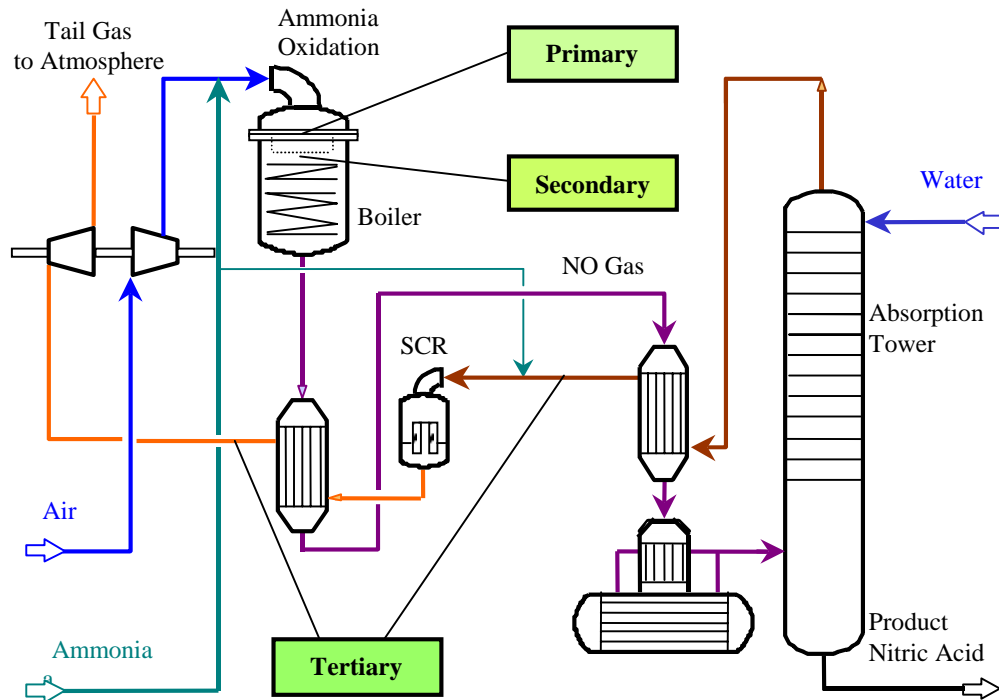


Figure 1: Simplified flowsheet of the nitric acid process showing the classification of nitrous oxide abatement methods according to the position in the process.

The possible ways of lowering nitrous oxide emissions from nitric acid plants can be broadly categorized into three groups (Fig. 1):

- Primary: suppression of nitrous oxide formation – requires modifications to the ammonia oxidation step.
- Secondary: removal of nitrous oxide from the gas stream between the ammonia oxidation and NO_x absorption steps – achieved by reduction or decomposition, catalytic or otherwise.
- Tertiary: removal of nitrous oxide from the tail gas downstream of the absorption tower – by reduction or decomposition.



3. Tertiary Abatement Catalyst Development Programme

It was decided to concentrate development efforts on tertiary measures. Some of the advantages of an approach aimed at treating the tail gas are:

- The main restriction on the size of reactor and therefore of nitrous oxide removal is economic rather than physical, thus very high rates of nitrous oxide removal are in principle possible.
- There is a clear separation between the abatement technology on the one hand, and the nitric acid end product or the intermediate nitrogen oxide product on the other, so any interference with or loss of product is not possible.

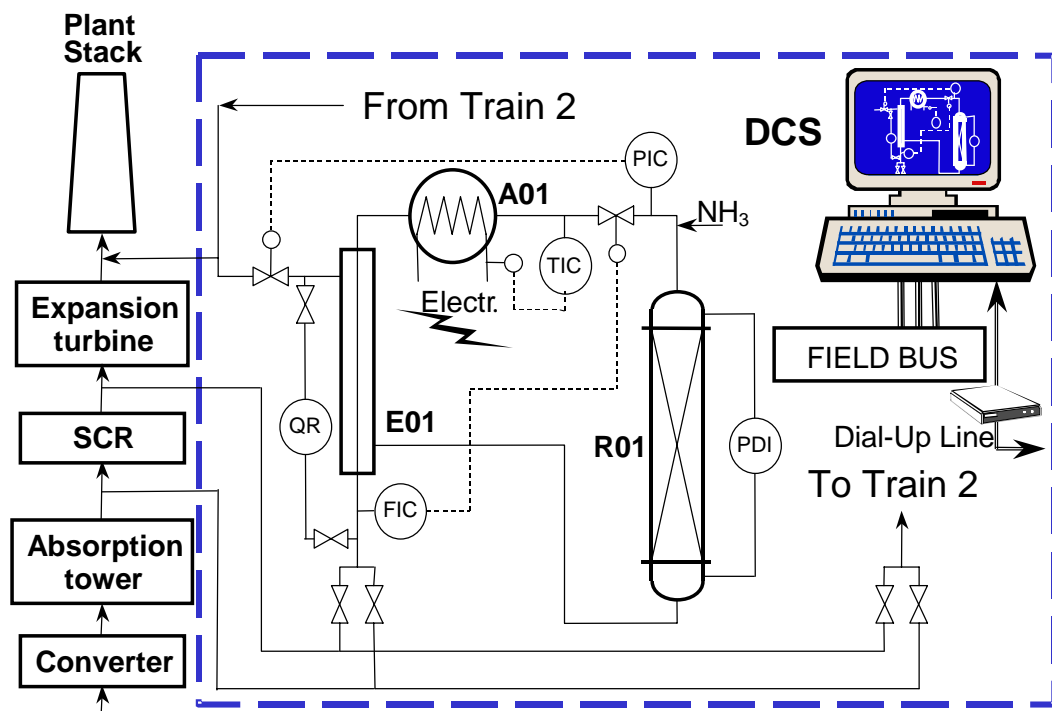


Figure 2: Flowsheet of Uhde nitrogen oxide abatement catalyst test unit.

Some five years ago Uhde initiated an R&D programme with the aim of developing a technology for the reduction of nitrous oxide from nitric acid plants. It was recognized 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 the purpose and was fortunate in finding a partner in AML, 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.



3.1. Uhde Catalyst Test Unit

The test unit (Fig. 2) consists of two parallel and independent reactor trains. It is connected to the tail gas side of the nitric acid production plant both upstream and downstream of the SCR (selective catalytic reduction unit for the removal of NO_x by reduction with ammonia). A process control system logs data and monitors and controls the unit and so enables it to be operated with minimal supervision.

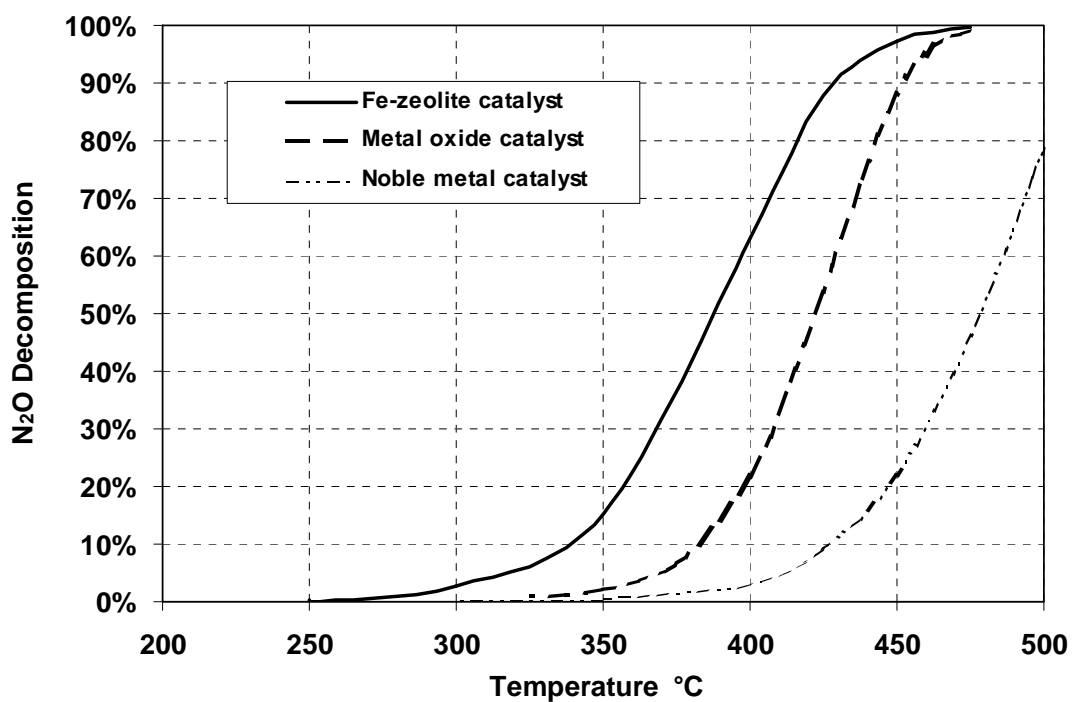


Figure 3 : Rates of N_2O decomposition vs. Temperature over different materials. Conditions: Total pressure 5 bar g, Gas volume composition N_2O 1000 ppm, H_2O 0.5%, O_2 2%, NO_x 0.01% remainder N_2 (from catalyst test unit).

An FT-IR (Fourier transform infra-red) online analyser measures concentrations of the main species N_2O , NO , NO_2 and H_2O at the inlet and outlet of the reactor of each train, while oxygen is detected with a zirconium oxide sensor. A CLD (chemiluminescence detector) is used for accurate measurement of low concentrations of NO_x . The outlet of the first train can be connected to the inlet of the second for more complex experiments, and ammonia and other compounds as required can be injected upstream of either reactor, for example for NO_x reduction trials.



3.2. Investigations on Tertiary Catalyst Materials

The research and development programme began by approaching potential sources of nitrous oxide abatement catalyst materials such as universities, institutes and commercial catalyst suppliers. An initial screening revealed that the most active material for nitrous oxide decomposition at the conditions of interest was an iron zeolite (Fig. 3). This material was examined in more detail both in the laboratory and in the catalyst test unit.

3.2.1. Effect of Nitric Oxide on the Decomposition of Nitrous Oxide

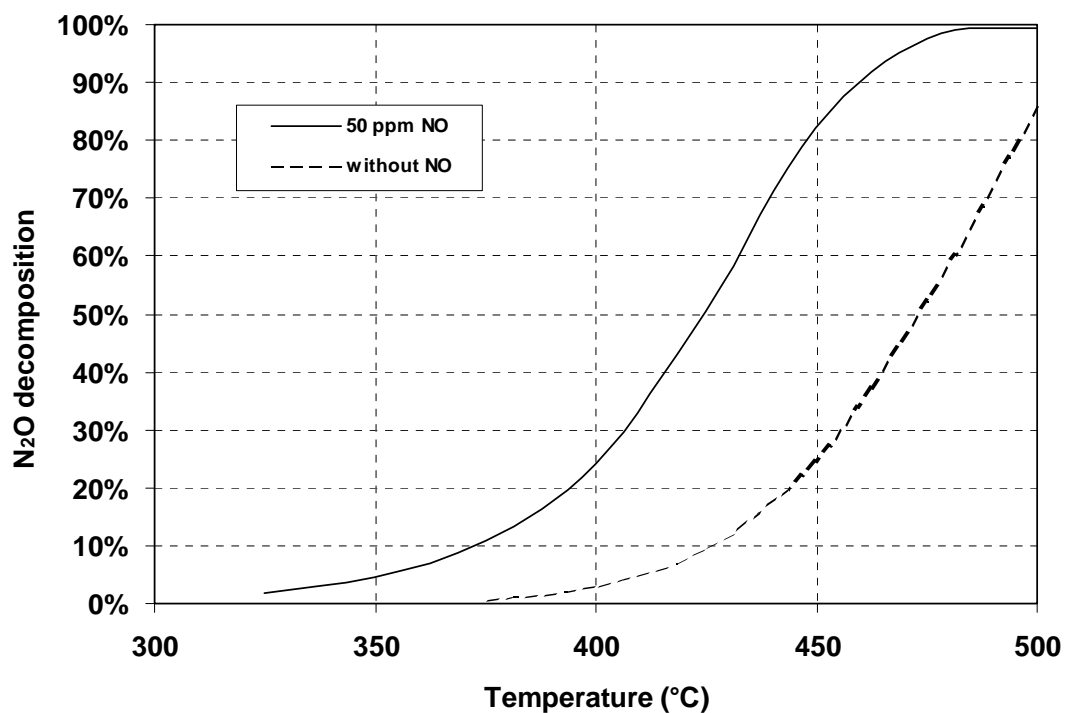


Figure 4 : Effect of NO in enhancing N₂O decomposition over an iron zeolite. Conditions: Total pressure 1 bar abs, Gas volume composition N₂O 1000 ppm, H₂O 0.5%, O₂ 4%, remainder N₂ with or without 50 ppm NO (from laboratory studies carried out for Uhde).

Iron zeolite catalysts show moderate activity in the decomposition of nitrous oxide, which, however, strongly increases in the presence of nitric oxide (NO). Quite small concentrations of NO are sufficient to cause a large increase in nitrous oxide decomposition rate, as Fig. 4 illustrates. The addition of 50 ppm of NO causes the temperature – decomposition rate curve to shift by approximately 50K to the left. NO is not consumed in the decomposition reaction but behaves as a co-catalyst.



3.3. NO_x Abatement

As work into nitrous oxide decomposition progressed it was found that the catalyst material used was a very effective NO_x reduction catalyst. Ammonia is used as the reducing agent. Fig. 5 illustrates that very high rates of removal of NO_x can be attained.

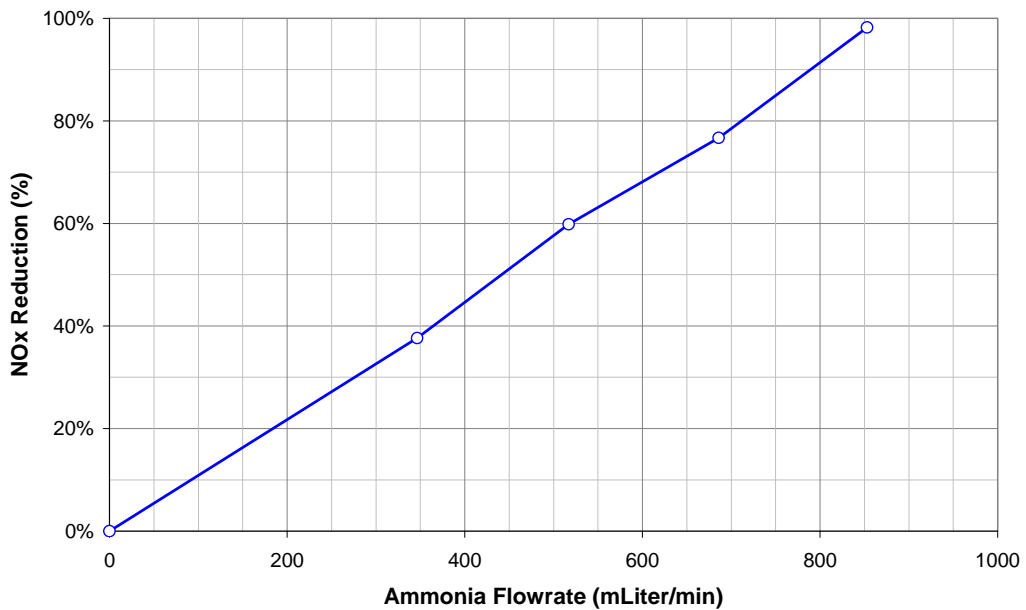


Figure 5 : NO_x reduction with ammonia on iron zeolite catalyst. NO_x concentration in inlet gas 400 ppm (from measurements in catalyst test unit).

3.4. Long Term Operation of Catalyst Test Unit

Apart from carrying out investigations 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 went into operation in 2000.



4. Commercial Scale Implementation of EnviNOx[®] Process

4.1. Process Concept for Combined N₂O and NO_x Abatement

By mid-2002 sufficient knowledge had been acquired to enable a convincing case for the feasibility of an industrial scale implementation of the new technology to be made. The process concept that was developed exploits the fact that the decomposition reaction of nitrous oxide is promoted by high concentrations of NO, one of the constituents 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 expansion turbine where the tail gas is at its hottest. Fig. 6 illustrates the concept.

In the first bed a very large proportion of the incoming nitrous oxide is catalytically decomposed to nitrogen and oxygen because of the high NO_x concentration in the tail gas. 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. Very high overall rates of nitrous oxide and NO_x removal are achievable.

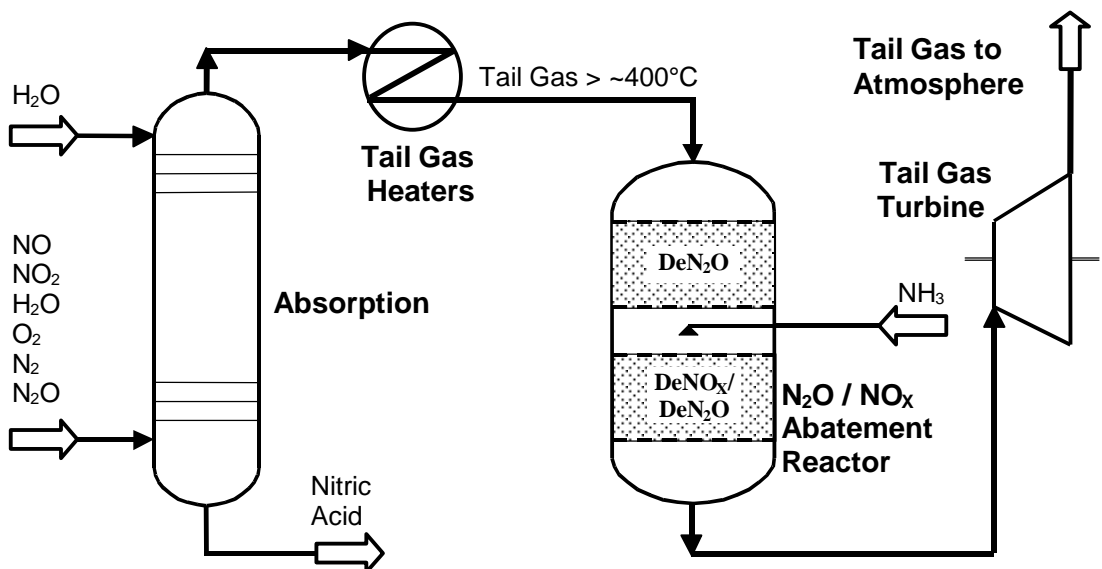


Figure 6 : Uhde process concept for combined nitrous oxide and NO_x abatement for nitric acid plants (nitrous oxide decomposition).



4.2. 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 persuasive, that AMI decided to equip their 1 000 mtpd dual pressure Line E nitric acid plant with a combined nitrous oxide and NO_x abatement reactor using the Uhde EnviNOx[®] 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 mid-2002. The detail engineering and erection was carried out by Chemserv Industrie GmbH, a Linz-based 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 only shut down for the actual tie in of the pipework. During the shutdown the opportunity was used to carry out other unrelated work in the plant.

4.3. Commissioning

After the two beds of the reactor had been filled with catalyst, 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 expansion 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.

4.4. Start-Up

On 29th September 2003 the nitric acid plant was started up with ammonia in the customary way. On reaching normal operating temperature in the combined nitrous oxide and NO_x abatement reactor a rate of nitrous oxide removal of over 99% was observed immediately.

The ammonia injection system was started up shortly afterwards and the ammonia flow rate increased gradually. The NO_x reduction worked satisfactorily.

4.5. Operating Experience since the Initial Start-Up

4.5.1. Nitrous Oxide Decomposition

Fig. 7 shows tail gas nitrous oxide concentrations upstream and downstream of the EnviNOx[®] reactor for the first three production campaigns of the nitric acid plant that followed the installation of the EnviNOx[®] reactor. By a "campaign" is meant the interval between changes of the platinum-rhodium ammonia oxidation gauzes. Campaign lengths of around six months are typical for this plant.



As the upper set of curves clearly shows, the amount of nitrous oxide in the tail gas varies both during and between campaigns. Short term alterations in nitrous oxide concentration can be correlated with changes in plant load. At lower plant throughputs the ammonia loading of the catalyst gauzes is also reduced, which favours the main nitric oxide formation reaction over the formation of nitrous oxide.

An example of this phenomenon was observed during the second campaign. The rather large drop in nitrous oxide concentration starting at around day 220 is associated with a reduction in nitric acid production for reasons unconnected with the EnviNOx® unit.

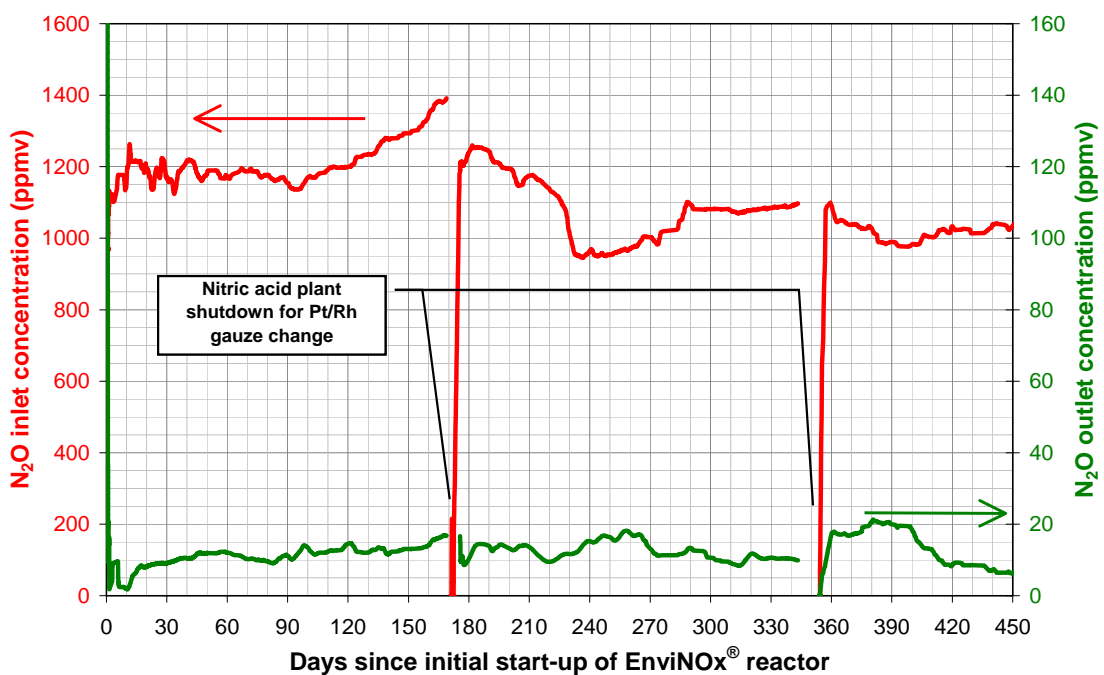


Figure 7 : Variation of tail gas nitrous oxide concentration at inlet and outlet of Uhde EnviNOx® combined nitrous oxide and NO_x abatement reactor in AMI nitric acid plant Line E.

The lower curve in Fig. 7, for which the right hand axis applies, shows the nitrous oxide concentration downstream of the reactor. For almost the entire period of operation the outlet nitrous oxide concentration has remained within the range 10 to 20 ppm, which corresponds to a rate removal of some 98% to 99%, as Fig. 8 illustrates.

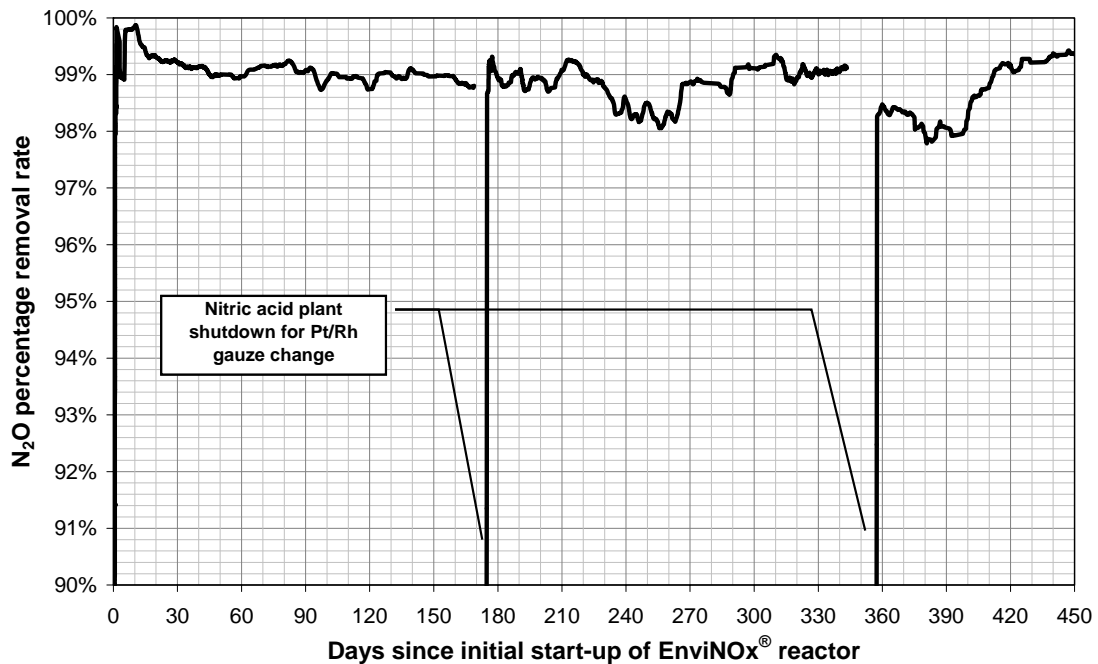


Figure 8 : Percentage rate of nitrous oxide decomposition in Uhde EnviNOx® combined nitrous oxide and NO_x abatement reactor in AMI nitric acid plant Line E.

4.5.2. NO_x Reduction

The concentration of NO_x at the inlet to the EnviNOx® reactor (upper curve of Fig. 9) 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, but rather the NO_x concentration is subject to short term fluctuations in the range 300 to 500 ppm.

The lower curve in Fig. 9 shows the NO_x concentration at the reactor outlet. At the start of the first campaign it might appear that the reduction catalyst improved over the campaign. In fact the NO_x concentration was lowered in successive steps by the operators as confidence was gained with the new reactor. After the initial phase of adjustment in the first few days of the first campaign, the outlet NO_x concentration was successively lowered from 60 ppm down to 45 ppm and thereafter 30 to 35 ppm. Investigations carried out in the Uhde catalyst test unit indicated that even lower outlet concentrations of NO_x should be achievable, without ammonia slip.

The reduction in NO_x concentration starting at around day 410 marks the start of AMI's successful attempt to test this prediction in the commercial scale reactor. Using a modified ammonia injection control system AMI have achieved NO_x outlet concentrations of below 5 ppm.

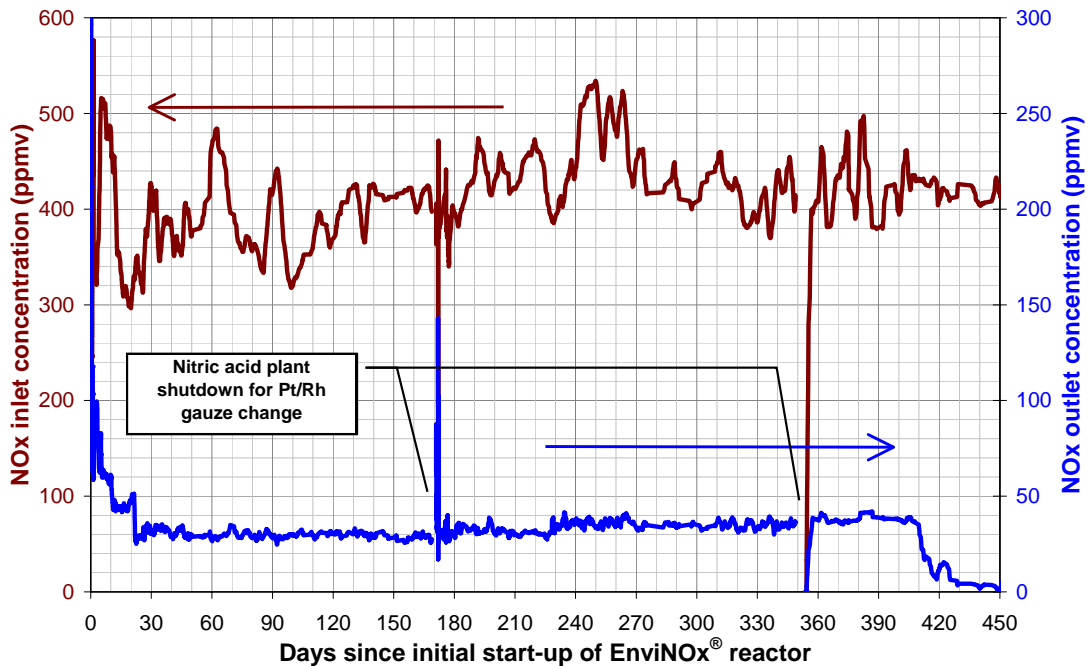


Figure 9: Variation of tail gas NO_x (NO, NO₂) concentration at inlet and outlet of Uhde combined nitrous oxide and NO_x abatement reactor in AMI nitric acid plant Line E.

4.5.3. Pressure Drop

At normal production capacity the pressure drop of the combined nitrous oxide and NO_x abatement reactor is about 90 mbar and therefore within the 100 mbar specification allowed for the project. A pressure reduction at the tail gas expansion turbine implies a reduction in energy recovery. However, the reduction in pressure was more than compensated by an increase in temperature at the tail gas turbine inlet, due to the exothermal nitrous oxide decomposition and NO_x reduction in the new reactor.

4.6. 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 remove 50% of the remaining nitrous oxide, thus achieving an overall rate of nitrous oxide removal of 90%. The NO_x concentration was to be lowered to 80 ppm.

Since the first start-up the rate of nitrous oxide destruction has remained consistently high at between 98% to 99%. The EnviNOx® reactor operates with an inlet NO_x concentration of some 400 ppm and an outlet of 30 ppm, and in the recent past less than 5 ppm. The stack plume is invisible.

Thus the EnviNOx® combined nitrous oxide and NO_x abatement reactor is comfortably exceeding expectations.



4.7. Impact on the Environment

The expected performance of the EnviNOx® reactor according to the process concept corresponded to an emission reduction of 1600 mtpy N₂O. Nitrous oxide has a “Global Warming Potential” of 310. That is, one tonne of emitted nitrous oxide is considered to make the same contribution to the greenhouse effect as do 310 tonnes of carbon dioxide. Thus the expected performance of the reactor is equivalent to a reduction in carbon dioxide emissions of 500 000 mtpy, the actual current performance being even better.

With this single measure AMI have cut their greenhouse gas emissions at the Linz site by over 30%. The reduction corresponds to more than 40% of Austria’s climate gas reduction target in the field of manufacturing industry and trade and therefore makes a significant contribution to climate protection. For this reason AMI won the “Climate Pioneer” award of the Federal Government of Upper Austria. Uhde received the EEP Silver Award 2004 from the European Environmental Press, an association of 13 leading European environmental periodicals, for the EnviNOx® technology. The EEP Awards are presented on an annual basis for major innovations in environmental protection.

5. Alternative N₂O Reduction Technology for Lower Temperatures

The technology in use in the reactor that is currently in successful operation at AMI relies on the catalytic decomposition of nitrous oxide at tail gas temperatures above about 400°C. To cater for nitric acid plants which have lower tail gas temperatures Uhde has developed a low temperature variant of the EnviNOx® technology that is based on the catalytic reduction of nitrous oxide to water vapour and nitrogen. The reducing agent is a hydrocarbon.

As only small amounts of hydrocarbon are used (~0.3 mol hydrocarbon/mol N₂O removed) the increase in greenhouse gas emissions due to the additional carbon dioxide arising from the oxidation of the hydrocarbon is minimal in comparison with the reduction in greenhouse gas emissions gained by the removal of the nitrous oxide. (Additional greenhouse gas emissions from use of hydrocarbon = ~0.3% of emission reduction due to N₂O abatement.) Rates of nitrous oxide reduction of more than 90% can be achieved. The process is applicable to tail gas temperatures down to about 300°C.



6. Conclusion

The first commercial scale implementation of the EnviNOx® combined nitrous oxide and NO_x abatement process for nitric acid plants has been in operation for 18 months and continues to exceed expectations. This technology destroys nitrous oxide by catalytic decomposition and is applicable to new or existing nitric acid plants with a tail gas temperature in excess of about 400°C. The NO_x abatement component can be used on its own and is suitable for the temperature range 180°C to 480°C.

The pace of development of the new technology is noteworthy – from gram-scale laboratory experiments to the start-up of the first commercial-scale reactor in just four years – and is in no small part due to the close co-operation between AMI and Uhde and the commitment of both parties to the success of the venture.

For nitric acid plants with tail gas temperatures in the range 300°C to 400°C Uhde has developed a variant of the EnviNOx® technology that employs a hydrocarbon to reduce nitrous oxide. Uhde is thus in a position to offer nitrous oxide and NO_x abatement technology for a large proportion of the world's nitric acid plants.