

# Nitric acid – without the emissions

Michael Groves, Meinhard Schwefer and Rolf Siefert explain Uhde's EnviNOx  $\text{N}_2\text{O}$  and  $\text{NO}_x$  abatement process

**PRODUCING nitric acid tends to have some undesirable side effects: not only does it produce  $\text{NO}_x$  – a major contributor to city smog – it also emits plenty of  $\text{N}_2\text{O}$ , a powerful greenhouse gas. Cutting emissions of these gases is therefore important, not only to comply with regulations, but also for the common good.**

Nitric acid is an important intermediate in the production of fertilisers, mining explosives and organic nitrogen chemicals such as toluene diisocyanate and methylene diphenyl diisocyanate. Practically all of the world's nitric acid is produced using the Ostwald process (see Figure 1), which involves the catalytic oxidation of ammonia in air over a platinum alloy gauze catalyst in the so-called ammonia burner. The main reaction product is nitric oxide ( $\text{NO}$ ), which is converted to nitrogen dioxide ( $\text{NO}_2$ ) and absorbed in water to form nitric acid ( $\text{HNO}_3$ ). Some of the ammonia, however, is converted to nitrous oxide ( $\text{N}_2\text{O}$ ), which takes no further part in the nitric acid process and is emitted to atmosphere in the tail gas together with the nitrogen of the reaction air and some residual  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) that was not converted to nitric acid in the absorber. The amount of  $\text{N}_2\text{O}$  generated is difficult to predict exactly but is known to be influenced by the operating parameters of the ammonia burner and the condition of the catalyst gauzes. The operating pressure, which is set during the design of a plant, has a particularly strong influence. Ammonia burners operating at atmospheric pressure have the lowest emissions of around 3–4 kg  $\text{N}_2\text{O}$ /t  $\text{HNO}_3$

product; the figure for medium pressure burners (~5 bar) is somewhat higher at 5–8 kg  $\text{N}_2\text{O}$ /t  $\text{HNO}_3$ , while high pressure burners operating at 10 bar and above can generate emissions up to 20 kg  $\text{N}_2\text{O}$ /t  $\text{HNO}_3$ . The platinum alloy catalyst gauzes deteriorate during use and need to be replaced at intervals ranging from less than 60 days for some high pressure burners to 6–12 months for medium and atmospheric pressure burners. As the gauzes age, emissions of  $\text{N}_2\text{O}$  usually rise.

$\text{N}_2\text{O}$  is the third most important anthropogenic greenhouse gas (GHG) after carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) and the most powerful of these, with 310 times the effect on global warming of  $\text{CO}_2$ . With current world nitric acid production at around 55m t/y and an overall average  $\text{N}_2\text{O}$  emission factor estimated at 7 kg  $\text{N}_2\text{O}$ /t  $\text{HNO}_3$ , annual emissions of  $\text{N}_2\text{O}$  from nitric acid plants are ~400,000 t  $\text{N}_2\text{O}$ , equivalent to 120m t  $\text{CO}_2$ /y. For comparison, this is about one-third of the size of the European Union's GHG emission reduction commitment under the Kyoto Protocol.

## process development programme

Uhde has long been involved in nitric acid technology as a part of its fertiliser process portfolio. During the 1990s, Uhde formed the view that nitrous oxide emissions from nitric acid plants were going to become a matter of concern and began an R&D programme aimed at testing and developing a catalyst and a process to lower these emissions. Under this programme, Uhde extended its laboratory facilities for catalyst characterisation and performance testing. Reliable conclusions about the suitability of any particular candidate catalyst can 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 Austrian-based Agrolinz Melamine International (AMI), which permitted the test unit to be installed in its 1000 t/d nitric acid plant in Linz. The catalyst test unit is operated by a distributed control system that also performs data logging. The temperature, pressure and flowrate can be set individually for each of the two

parallel reactor trains. 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 multi-component FT-IR analyser and a chemiluminescence detector for low  $\text{NO}_x$  concentrations.

After over five years of operation, the catalyst test unit is still in use to identify promising catalytic materials, evaluate process concepts and observe the long-term behaviour of catalytic materials. The data obtained is of sufficient quality to allow scale-up to full size industrial applications without requiring any intermediate pilot plant stage.

We found that certain specific iron zeolite materials are very suitable for  $\text{N}_2\text{O}$  and  $\text{NO}_x$  abatement in the tail gas of nitric acid plants. These materials have some interesting properties, which influence the configuration of the process. One of the materials investigated readily decomposes  $\text{N}_2\text{O}$ , especially in the presence of high concentrations of  $\text{NO}_x$ . A different iron zeolite material catalyses the reduction of  $\text{N}_2\text{O}$  with hydrocarbons. Surprisingly, here, the rate of  $\text{N}_2\text{O}$  reduction is greatly accelerated if  $\text{NO}_x$  is removed.

$\text{NO}_x$  is a constituent of nitric acid plant tail gas, but due to regulations or client demand has to be reduced to a low concentration, typically less than 50 ppm for discharge to atmosphere. Another iron zeolite that we looked in our investigations was very effective as a  $\text{NO}_x$  reduction catalyst if ammonia was added.

These observations have resulted in the development of two process variants – marketed under the name EnviNOx – which both involve the combined removal of  $\text{N}_2\text{O}$  and  $\text{NO}_x$  from the tail gas.

## $\text{N}_2\text{O}$ decomposition

This two-stage process (Figure 2) exploits the observation that high levels of  $\text{NO}_x$  enhance the rate of  $\text{N}_2\text{O}$  decomposition. The  $\text{NO}_x$  concentration in untreated tail gas depends on the design and performance of the absorber and ranges from about 150 ppm up. The first catalyst bed destroys a large proportion of the  $\text{N}_2\text{O}$  by decomposition into nitrogen and oxygen. In the second bed the  $\text{NO}_x$  concentration is lowered to below

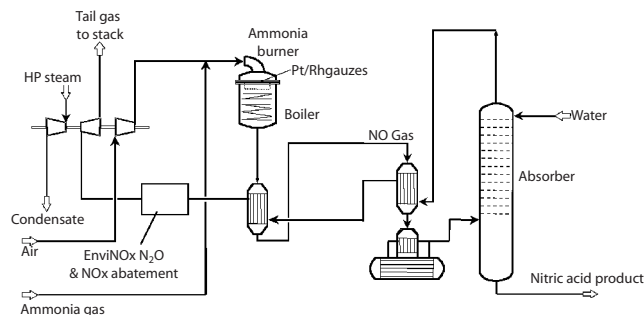


Figure 1: Simplified flowsheet of the Ostwald nitric acid process

Pictured (top): The process was tested at AMI's Linz nitric acid plant

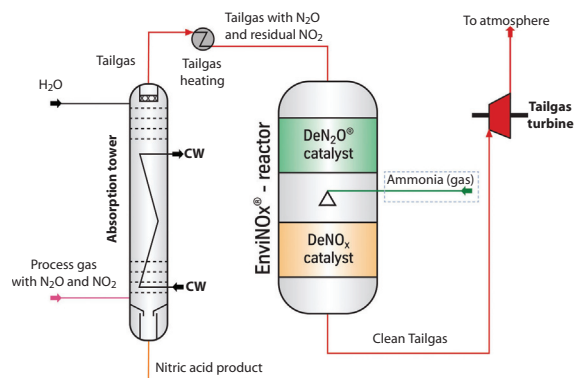
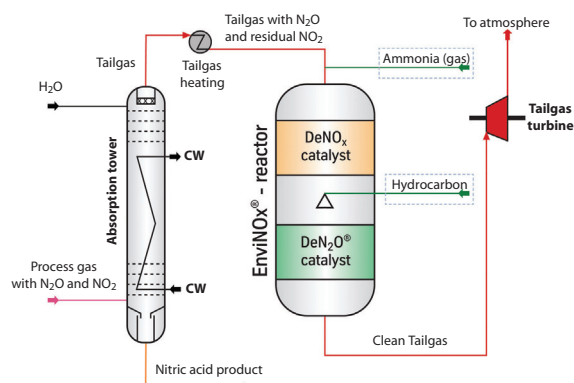
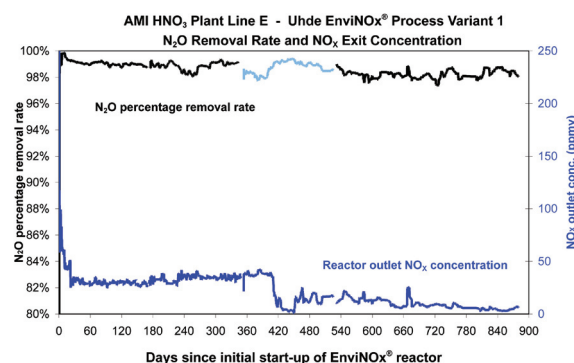


Figure 2: EnviNOx  $N_2O$  and  $NO_x$  abatement process variant 1 Linz Plant: The Uhde EnviNOx  $N_2O$  and  $NO_x$  abatement reactor at AMI, Linz reduces greenhouse gas emissions by over 0.5m t  $CO_2$  equivalent/year and lowers stack  $NO_x$  concentrations to below 10–15 ppm

(Below) Figure 3: Performance of EnviNOx  $N_2O$  and  $NO_x$  abatement reactor at AMI, Linz

Figure 4: EnviNOx  $N_2O$  and  $NO_x$  abatement process variant 2



the regulatory limit for discharge to atmosphere by reaction with the ammonia added between the beds.

### operating experience

The first reactor employing this concept was designed by Uhde for AMI and has been in operation in the 1000 t/d Linz plant since September 2003. Of the 1000–1200 ppm  $N_2O$  entering the reactor, 98%–99% is destroyed, and the  $NO_x$  level is lowered from 400–500 ppm to ~10 ppm or less. Figure 3 shows the operating data for the first 2½ years.

### process concepts: $N_2O$ reduction

The EnviNOx process variant 1 is suited to temperatures higher than ~425 °C, since the rate of  $N_2O$  decomposition falls quite rapidly at lower temperatures. However, many nitric acid plants have tail gas temperatures below 425 °C. To cater for plants with tail gas temperatures down to around 350 °C we developed the EnviNOx process variant 2 (Figure 4) which utilises the knowledge gained

about  $N_2O$  reduction with hydrocarbons. As high concentrations of  $NO_x$  have a negative effect on  $N_2O$  reduction,  $NO_x$  is removed in the first bed of the reactor by reaction with ammonia. A hydrocarbon such as natural gas or LPG, depending on availability, is added to the tail gas between the beds and reacts with the  $N_2O$  in the second bed. In some situations the two beds can be combined and hydrocarbon and ammonia added together upstream of the reactor. We expect similarly high rates of  $N_2O$  and  $NO_x$  removal to those of process variant 1. In fact, the achievable outlet  $NO_x$  concentration is <1 ppm, making the tail gas very clean. Not only is process variant 2 useful in the low temperature range; at high temperatures a variant 2 reactor is significantly more compact than a variant 1 reactor using  $N_2O$  decomposition.

There is some additional emission of GHG, since the hydrocarbons are converted to  $CO_2$  in the reactor and there may be some  $CH_4$  slip if natural gas is used. However the additional GHG emission is low, less than 0.5% of the emission reduction due to the destruction of  $N_2O$ .

### industrial implementation

The first commercial-scale implementation of the EnviNOx process variant 2 will be in the 1830 t/d nitric acid plant of Abu Qir Fertilizers and Chemicals in Egypt. This plant is one of the biggest in the world and the expected GHG emission reduction is also large, at 1.2m t  $CO_2$  equivalent per year. This is roughly the same as the GHG emissions from a 250 MW gas-fired electricity generation plant. The catalyst for this and future EnviNOx systems will be manufactured by Süd-Chemie, an international speciality chemicals company with headquarters in Munich, Germany, at their facilities in South Africa.

If only  $NO_x$  but not  $N_2O$  abatement is required, a DeNOx reactor with a single zeolite bed and upstream ammonia addition can be used to reduce  $NO_x$  very effectively between ~200 °C and 500 °C.

### opportunities with Kyoto

With the 2008–2012 first commitment period of the Kyoto Protocol approaching, there is increasing interest in GHG emission reduction technology. Many countries which are committed to reducing GHG emissions under the Kyoto Protocol – the Annex 1 countries – will be unable to fulfill their obligations within their own borders. Kyoto therefore provides three flexible mechanisms that allow an Annex 1 country to be credited with emission reductions made outside its borders.

Emission trading allows companies within Annex 1 countries to trade emission rights with each other both nationally and across borders. The European Union Emissions Trading Scheme (EU ETS) started in 2005 but included only  $CO_2$  in its cap and trade system. The next round of the EU ETS starts in 2008. Presently, it is not clear whether other GHGs such as  $N_2O$  will be brought into the EU ETS. If this were the case, the installation of an  $N_2O$  abatement unit could be an interesting option for nitric acid plant owners in the EU.

With Joint Implementation (JI), the emission reductions of a project in a host Annex 1 country are transferred to a second Annex 1 country. Suitable host countries are those of Eastern Europe and Russia that have already fulfilled their Kyoto obligations due to the reduction in industrial activity since the baseline year of 1990. Reductions obtained under JI only count if they occur after the start of 2008.

The Clean Development Mechanism (CDM) is similar to JI except that the host country is a developing country without any Kyoto obligation and the emission reductions achieved now can be banked until the start of the first Kyoto commitment period. Thanks to the EU linking directive, emission reductions under CDM and JI can be acquired by organisations participating in the EU ETS in the same way as other emission rights within the EU ETS. CDM is subject to very strict rules aimed at preventing CDM projects from being unfairly credited with emission reductions. These rules are set down in the approved methodologies that are subjected to intense scrutiny by the public and experts before being passed or rejected by the CDM executive board. A CDM project without an approved methodology cannot generate saleable GHG emission reductions. The only currently-approved CDM methodology for  $N_2O$  abatement in nitric acid plants was for the Abu Qir project and is generally applicable to all EnviNOx process variants.

Provided a GHG emission reduction technology such as EnviNOx is available, the Kyoto Protocol and its flexible mechanisms can offer process plant owners interesting opportunities to improve the environment and their balance sheet. **tce**

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