# Emission monitoring in nitric acid plants

Dr. Michael Kamphus, Application Engineer for Process Gas Analysers at Emerson Process Management, Rosemount Analytical, takes an in-depth look at techniques for emission monitoring in nitric acid plants to support emission reduction and gain carbon trading credits.

Nitric acid is one of the world's 15 largest commodity chemicals, with an annual production of about 55 million t/a. Approximately 80% is used as intermediate in the production of nitrogenous fertilizers, primarily ammonium nitrate, and the remaining 20% is used in the production of various chemicals such as explosives or as intermediates for polymers like caprolactam, adipic acid or dinitrotoluene. Emission regulations on nitrogen oxide and nitrous oxide from nitric acid plants are being implemented in more and more areas around the world, and in other areas, emission level requirements are being tightened. These emission levels can only be achieved with additional measures, like abatement technologies, which have to be added to existing plants or considered for new plants. This paper details the various abatement technologies and the analytical measurements to control the abatement process and monitor the remaining emissions.
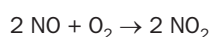
Nitric acid (HNO_3) is produced by oxidizing ammonia (NH_3) with air over a catalyst (platinum alloyed with rhodium) to nitrogen oxide (NO);
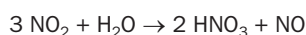
$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

As side products nitrogen (N_2) and nitrous oxide (N_2O) are formed:

$$4\ NH_3 + 3\ O_2 \rightarrow N_2 + 6\ H_2O$$

$$4\ NH3 + 4\ O_2 \rightarrow 2\ N_2O + 6\ H_2O$$
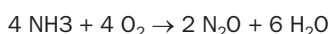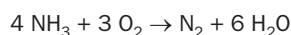
In a second step nitrogen oxide is oxidised to nitrogen dioxide (NO_2);

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Then NO_2 is absorbed in water to form nitric acid;

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

From the bottom of the absorption column, liquid nitric acid with concentration of 50-68% is withdrawn.

Gaseous emissions from nitric acid plants

In a typical nitric acid plant, continuous tail gas emissions at the absorber outlet may vary between the following limits, at a flow of 3,100-3,400 $Nm^3\ t^{-1}$ 100% HNO_3;

NOx: 100 to 3,500 ppmv
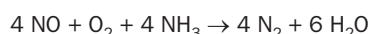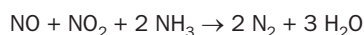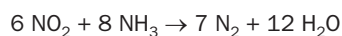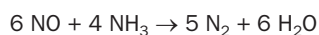**N_2O**: 300 to 3,500 ppmv
O_2: 1 to 4% by volume
H_2O: 0.3 to 2% by volume
N_2: balance

During start-up and shut-down of the process, the NOx concentrations will normally go up for several hours until the process is stabilised.

Part I: NOx

NOx emissions can be reduced by selective catalytic reduction (SCR). Ammonia or (evaporated) ammonia solutions are injected into the waste gas stream utilizing a catalyst to initiate the reaction. Depending on the catalyst, the tail gas needs to be heated to temperatures between 120 and 400°C. NOx and ammonia produce nitrogen and water vapour according to the following equations:

$$6\ NO + 4\ NH_3 \rightarrow 5\ N_2 + 6\ H_2O$$

$$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$$

$$NO + NO_2 + 2\ NH_3 \rightarrow 2\ N_2 + 3\ H_2O$$

$$4\ NO + O_2 + 4\ NH_3 \rightarrow 4\ N_2 + 6\ H_2O$$

The SCR process in nitric acid plants is quite different from power plants because the NO_2 ratio to NOx of 50-75% is substantially higher. This significantly affects the

catalyst behaviour, and as a consequence some of the catalysts used in power plants cannot be used in nitric acid plants. With SCR, NOx conversions of 80-97% can be achieved, resulting in emission levels of 74 - 100 ppm NOx. N_2O emissions are not reduced significantly by applying SCR.

Measurement of NOx

NOx is typically measured with continuous measurements. There are two common technologies available: chemiluminescence detectors (CLD) and photometry in the IR and UV. In the chemiluminescence detector NO is reacting with ozone (O_3) which is generated from oxygen (O_2) with a UV lamp or by electrical discharge to form NO_2 in an excited state. The NO_2 molecule in the excited state relaxes into the ground state by emitting a photon. The photons are detected with a photomultiplier or a photodiode and the intensity of the detected light is proportional to the NO concentration (Fig. 1). NO_2 is not reacting with ozone; it needs to be converted to NO. Here, typically vitreous carbon converters at temperatures of 400°C are used, which besides NO_2, do not convert other nitrogen species e.g. NH_3. In the NO mode the sample gas is by-passing the converter and only NO is measured. In the NOx mode the sample is flowing over the converter and the sum of NO and NO_2 is measured.

NO measurements with a photometer can be done in the ultraviolet or the infrared. In the UV, 225 nm light sources are used. With this wavelength very low ranges down to 0-10 ppm NO can be achieved, but the light source is very expensive. Therefore most of the NO measurements are done in the infrared using the NO absorption band at 5.3 μm. Sensitivities at this wavelength are good enough to measure in the tail gas of nitric acid plants behind

Fig 1: **CLD reaction chamber showing the reaction of NO and O_3 to form NO_2 in an excited state**
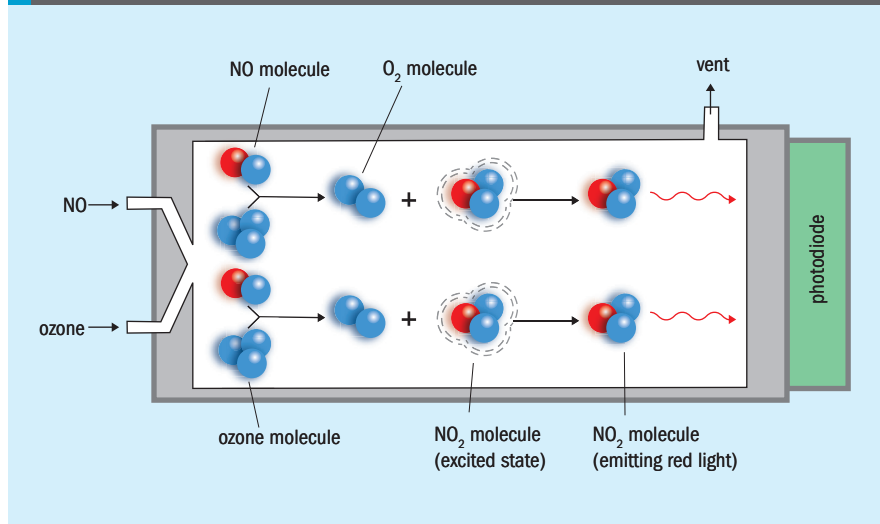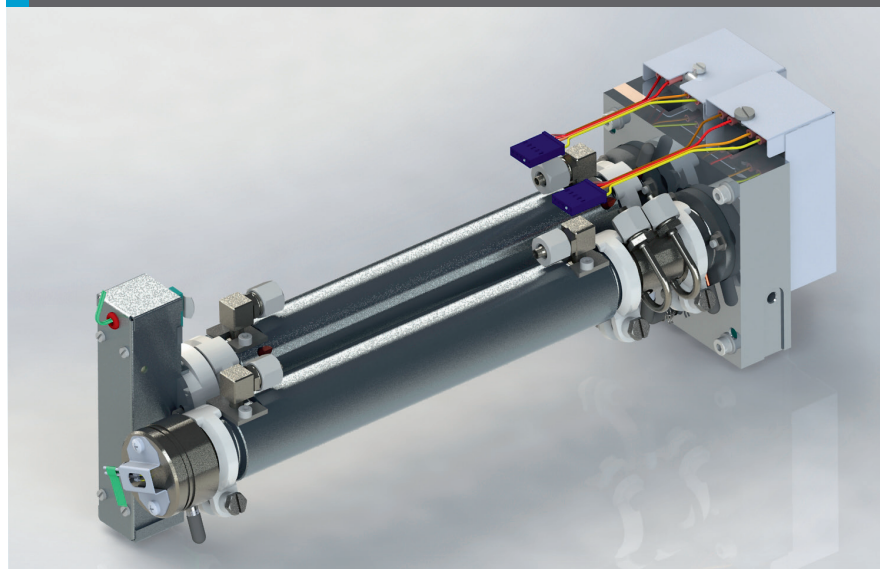

Fig 2: **Compact photometer for NOx**

SCR installations at levels of 10-50 ppm. NO_2 is typically measured in the UV around 360 nm with low ppm ranges. In principle, NO_2 detection in the IR would be possible, but cross interferences from other gases complicate the measurement in the IR. To measure NOx, typically an NO measurement in the IR is combined with an NO_2 measurement in the UV. With a calculator functionality the sum of NO and NO_2 can be calculated as NOx. For optimised packaging and serviceability, both measurements should be built into one single analyser housing, preferentially on one chopper. With this setup, complexity and number of spare parts are reduced (Fig. 2).

The NOx measurement can also be done with an NO photometer channel only.

Similar to the CLD, a converter is used to convert NO_2 to NO. The analyser is measuring NO and NO_2 as a sum when the sample gas is flowing over the converter. Although this is the cheapest option to measure NOx, it has some minor drawbacks which have to be taken into consideration. The analyser is measuring NOx only. If NO_2 or NO concentrations need to be determined, the converter has to be bypassed and calculations have to be performed for NO_2. Also the converter efficiency has to be checked regularly. Finally, the NO_2 detection over a converter with an NO IR photometer is not as sensitive as an NO_2 UV photometer channel or a CLD.

NOx is typically measured on a dry basis. The sample gas is going over a

sample gas cooler at temperature around 5°C. Ammonia which might still be present in the sample gas (NH_3 slip from SCR) is strongly soluble in water and therefore is removed with the condensing moisture. Thus a NOx analyser can work at standard temperatures and there is no danger of forming ammonium nitrates in the core parts of the analyser.

Legislation on NOx emissions from nitric acid plants

In January 2011, the Industrial Emissions Directive 2010/75/EU of the European Commission set NOx emissions levels in Europe based on Best Available Technologies (BAT) as 5-75 ppmv NOx as NO_2 in new plants, and in existing installations 5-90 ppmv are allowed (up to 150 ppmv where safety aspects due to deposits of AN restrict the effect of SCR or with the addition of H_2O_2 instead of applying SCR). In the US, NOx emissions from nitric acid plants built before October 2011 are limited to 1.5 kg nitrogen oxides, expressed as NO_2 per metric ton of acid produced (3.0 lb/t), the production being expressed as 100% nitric acid. For plants built after October 2011 the NOx limit expressed as NO_2 is 0.50 lb/t of nitric acid produced.

Part II: N_2O

Nitrous oxide is produced as a side product during the oxidation of ammonia. Typical N_2O concentrations at the absorber outlet are between 300-3,500 ppm. In a study from 1998 it was found that a typical European nitric acid plant emits 6 kg of N_2O per tonne of HNO_3. N_2O is a greenhouse gas with a global warming potential (GWP) of 298 on a 100-year time horizon, which means that N_2O is 298 times more impactful than CO_2. The Intergovernmental Panel on Climate Change (IPCC) in its recent report from 2013 states that N_2O is now likely to be the third largest well mixed greenhouse gas contributor to relative forcing.

In the US, chemical production contributes to 9% of N_2O emissions. Other sources are agricultural soil management, manure management, transportation and stationary combustion. The two industrial processes contributing most to N_2O emissions are nitric acid and adipic acid production.

Emission trading under the UNFCCC

The United Nations Framework Convention on Climate Change (UNFCCC) is an international environmental treaty negotiated

at the United Nations Conference on Environment and Development (UNCED), held in Rio de Janeiro in 1992. The objective of the treaty, which does not set binding limits of greenhouse gas emissions, is to "stabilize greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system." It provides a framework for negotiating specific international treaties called protocols that may set binding limits on greenhouse gases.

The Kyoto Protocol sets emissions targets for developed countries which are binding under international law. The first commitment period applies to emissions between 2008 and 2012, and the second commitment period applies to emissions between 2013 and 2020. The 37 parties with binding targets (Annex I parties) in the second commitment period are Australia, the European Union, Belarus, Iceland, Kazakhstan, Liechtenstein, Norway, Switzerland, and Ukraine. Belarus, Kazakhstan and Ukraine have stated that they may withdraw from the Protocol or not put into legal force the amendment with second round targets. Japan, New Zealand, and Russia have participated in Kyoto's first-round but have not taken on new targets in the second commitment period. Other developed countries without second-round targets are Canada (which withdrew from the Kyoto Protocol in 2012) and the United States (which has not ratified the Protocol).

International emission trading allows developed countries to trade their commitments under the Kyoto Protocol. They can trade emissions quotas among themselves, and can also receive credit for financing emissions reductions in developing countries. There are three flexibility mechanisms set out in the Kyoto Protocol to help countries with binding greenhouse gas emissions targets to meet their obligations: Emissions Trading, Joint Implementation and the Clean Development Mechanism. Emissions trading allows Annex I parties to buy emission permits for greenhouse gas from other countries to help meet their domestic emission reduction targets. Joint Implementation (JI) is a mechanism which allows any Annex I country to invest in an emission reduction project in any other Annex I country as an alternative to reducing emissions domestically. Most projects are expected to take place in so-called "economies in transition," noted in Annex B of the Kyoto Protocol, where reducing emission might be

cheaper. Emission reduction projects are awarded credits called Emission Reduction Units (ERUs), which represent an emission reduction equivalent to one tonne of CO_2. As of December 2013 there are 55 projects on N_2O emission reduction from a total of 760 Joint Implementation projects. From these projects 53 million ERUs from a total of 829 million ERUs have been issued between 2008 and 2012.

The Clean Development Mechanism (CDM) allows Annex I countries to meet part of their emission reduction commitments by buying Certified Emission Reduction units (CER) from CDM emission reduction projects in developing countries (non-Annex I parties). Between 2001 and 2012, the CDM issued 1 billion CER units. As of June 2013, 19% of all CERs had been issued for projects based on destroying N_2O. Any proposed CDM project has to use an approved baseline and monitoring methodology to be validated, approved and registered. Baseline methodology will set steps to determine the baseline within certain applicability conditions. Monitoring methodology will set specific steps to determine monitoring parameters, quality assurance, and equipment to be used, in order to obtain data to calculate the emission reductions. For N_2O, there are five approved methodologies (see Table 1) with 108 projects, of which 101 are for nitric acid plants.

In AM0021 and AM0028 the CDM states that accuracy of the N_2O emissions monitoring is to be ensured by installing a monitoring system that has been certified to meet (or exceed) the requirements of the prevailing best industry practice or monitoring standards in terms of operation, maintenance and calibration. The latest applicable European standards and norms (EN 14181) could be used as the basis for selecting and operating the monitoring system. According to AMC0019 (which replaced AM0034 and AM0051) the monitoring system is to be installed
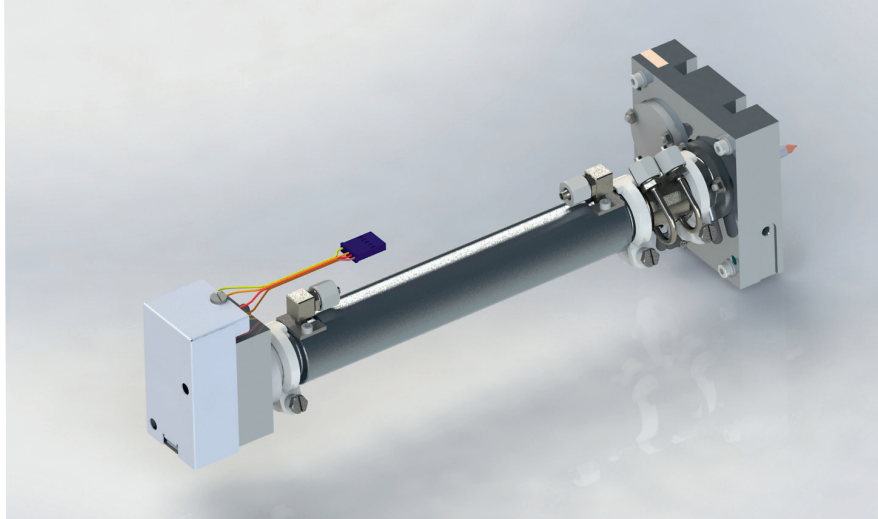
and maintained throughout the crediting period based on the European Norm 14181 (2004), or any more recent update of that standard.

European Norm 14181

This standard specifies procedures that shall be carried out to cover quality assurance of automated measuring systems (AMS) installed on industrial plants for the determination of the flue gas components and other flue gas parameters. The AMS consists of a complete system from sample probe through sample conditioning to the analyser. Within the EN 14181 quality assurance levels (QAL) are defined. QAL 1 describes a suitable AMS and refers to EN 15267-3 (Air quality - Certification of automated measuring systems - Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources; EN 15267-3:2007) for the test procedures. Notified bodies carry out the certification with two identical AMS in the laboratory and in the field. During the certification, the AMS are tested with respect to several performance criteria:

- Lack of fit
- Biggest interference (15% CO_2, 3% O_2, 20 mg/m³ CO, etc …)
- Span shift in field test
- Zero shift in field test
- Sensitivity to sample volume flow
- Sensitivity to sample pressure
- Sensitivity to sample temperature
- Sensitivity to ambient temperature
- Dependence on supply voltage
- Repeatability at span
- Field reproducibility
- Uncertainty of test gas at reference point

A total expanded uncertainty is calculated from the performance criteria, which has to be below 15% of the certified measuring range. Then the AMS is type approved and every AMS built in the same way is

	N_2O
Table 1: Approved methodologies for N_2O emission reduction.	
AM0021	Decomposition of N_2O from existing adipic acid production plants.
AM0028	Catalytic N_2O destruction in the tail gas of nitric acid or caprolactam production plants.
AM0034	Catalytic reduction of N_2O inside the ammonia burner of nitric acid plants.
AM0051	Secondary catalytic N_2O destruction in nitric acid plants.
ACM0019	N_2O abatement from nitric acid production.

Fig 3: **N₂O IR photometer bench with negative filtering**

allowed to be installed in Continuous Emission Monitoring applications in the European Union. QAL 2 describes the correct installation and calibration of an AMS at site and also lists the standard reference methods to be used for validation. These reference methods need to be applied to check if the AMS is installed properly. QAL 3 ensures continuous functionality of the AMS by defining an annual surveillance test (AST) and other measures. QAL 1 is the responsibility of the AMS manufacturer whereas QAL 2 and QAL 3 are the operator's responsibility. In addition to the N_2O concentration measurement in the tail gas flow, the total gas volume flow also has to be measured to calculate the carbon credit amount. This flow measurement needs to be certified according to EN14181.

Measurement of N₂O

N_2O is typically measured with a photometer in the IR either at 4.5 µm or at 7.8 µm. Higher sensitivities are achieved when measuring at 4.5 µm, where cross interferences from CO_2 and CO complicate the analysis. At 7.8 µm cross interferences come from CH_4 and SO_2. As in emission monitoring, low concentrations need to be detected, and the setup at 4.5 µm is more common. In tail gas from nitric acid plants, CO_2 and CO concentrations are very low compared to flue gas applications. Nevertheless, an N_2O analyser for nitric acid plant emissions should have low cross interferences from CO_2 and CO because interferences are tested during the QAL 1 certification, and are used for calculating the total expanded uncertainty of the AMS. This value is taken into account when cal-

culating the number of carbon credits from the amount of destroyed N_2O. Therefore a low total expanded uncertainty helps in earning carbon credits.

In an N_2O analyser, low cross interferences from CO_2 and CO are typically achieved with optical filters, but for an optimized performance, additional measures have to be taken (e.g. by implementing negative filtering). In this case, a special N_2O gas filter is placed into the setup of the photometer, so that the N_2O absorption lines become smaller (wings of the absorption lines are faded out) and cross interferences are decreased. As always, when selectivity is increased the sensitivity goes down, but is still good enough for a 0-100 ppm range (Fig. 3).

Certification of an AMS for N₂O emissions

In nitric acid plants, N_2O emissions are measured in the tail gas behind the absorption tower either before or behind the tail gas turbine. Therefore, the sample handling system of the AMS should be configurable with a pump for ambient pressure conditions behind the tail gas turbine or with a pressure reduction if the sample is withdrawn prior to this. Both variations should be mentioned in the description of the AMS on the QAL 1 certificate. The gas temperature at the sampling point is still high, as (N)SCR reactions are performed at temperatures up to 400°C. Temperatures below 180°C need to be avoided at the (N)SCR stage because nitrogen oxides and ammonia could form ammonium nitrate particulates which could plug and damage equipment. This is especially

critical during start-up and shut-down. The build-up of ammonium nitrates could also plug the sample gas lines to the analyser if they are not heated; 130°C is sufficient if the lines are cleaned every year during annual maintenance. With a special vortex cooler and additional particulate filter, sample gas temperature can be reduced before the analyser so that a standard analyser can be applied without any danger of fouling the photometer parts of the analyser due to salt formation. The configuration of the sample handling system to avoid build-up of ammonium salts in the analyser without changing the N_2O concentration is crucial for a properly working AMS. Problems with the N_2O measurement often originate from the sample handling system and not from the analyser itself.

N₂O abatement technologies

Depending on the location of the N_2O abatement, there are three main techniques: primary controls reduce the amount of N_2O formed in the ammonia oxidation step; secondary controls reduce N_2O directly after it is produced in the oxidation reactor; and tertiary controls reduce N_2O by installing a catalytic reactor either upstream or downstream of the tail gas expansion unit following ammonia oxidation.

Primary controls
a) Oxidation catalyst and campaign length
Although often platinum recovery systems are applied, catalysts (platinum with 5-10% rhodium and up to 5% palladium) in the oxidation stage need to be exchanged about one to four times a year. N_2O emissions are increasing with the campaign length. A sudden increase of N_2O levels can indicate that damage to the catalyst gauze has occurred, thus allowing ammonia to bypass the gauzes.

b) Optimisation of oxidation step
The NO yield in the oxidation step is the highest at an NH_3/air ratio of 9.5 to 10.5% ammonia (from stoichiometry 14.38% would be optimal), at low pressures of 1 bar and temperatures of 750 to 900°C. Nitrous oxide (N_2O) is unstable at temperatures of 850-950°C and is partly reduced to N_2 and O_2. A long residence time and a high temperature in the catalytic reactor promote this reduction.

c) Alternative oxidation catalysts
Modification in the composition and geometry of platinum-based oxidation catalysts

can lead to higher NO yields and/or lower N_2O emissions (30 - 50% reduction). Additionally, an extension of campaign length is possible. Alternative oxidation catalysts like Co_3O_4 or two-step catalysts can also reduce N_2O emission, but generally have a lower NO yield, and thus increase the NH_3 consumption.

d) N_2O decomposition by extension of reaction chamber

With the extension of the reaction chamber behind the catalyst, the gases have a longer residence time (1-3 seconds) at elevated temperatures and N_2O (which is metastable at a temperature of 850 to 950°C) can be reduced to 70 to 85%.

Secondary controls

e) Catalytic N_2O decomposition in the oxidation reactor

With a selective De-N_2O catalyst right behind the oxidation catalyst, reduction of emission levels to 130-325 ppm can be achieved. With the additional catalyst volume, a pressure drop is introduced which might decrease NO yields, however.

Tertiary controls

f) Combined NOx and N_2O abatement in tail gases

With a special dual stage catalyst in front of the tail gas turbine, NOx and N_2O can be reduced simultaneously. In the first stage at temperatures of 420-480°C, N_2O is decomposed to N_2 and O_2 over an Fe zeolite at full NOx load, as NOx promotes the reaction. Then ammonia is injected before the second catalyst which reduces the NOx but also further decomposes the N_2O. With this approach, plants can achieve N_2O and NOx removals close to 99%.

In a variant of this technology, NH_3 is injected into the tail gas before the combined reactor to remove NOx (similar to an SCR). Then hydrocarbons are injected in between the first and the second catalytic stage to remove N_2O. This variant is favoured at lower tail gas temperatures and shows lower NOx emissions close to 0 ppm at N_2O decomposition efficiencies of 99%.

g) Non-selective catalytic reduction (NSCR) of NOx and N_2O in tail gases

In an NSCR reaction, fuel, either natural gas or methane (CH_4), hydrogen (H_2) or ammonia plant purge gas (mainly H_2), is added to the tail gas at temperatures of 200-300°C for H_2 and 450-575°C for natural gas over a catalyst (typically based on

platinum, vanadium pentoxide, iron oxide or titanium). The fuel first reacts with excess oxygen, but then reduces N_2O and NOx to N_2. With the oxidation of the fuel (especially at conditions with 3% excess O_2), the gas temperature can go above 800°C. Then a dual stage approach with intermediate cooling is necessary. When fossil fuels are used, CO and CO_2 as reaction products are introduced into the tail gas. Hydrocarbons can also be present. The CO_2, which is built in the NSCR reaction, has to be taken into account when carbon credits are calculated from the amount of abated N_2O. Emission levels of 50 ppm N_2O and 100-150 ppm NOx can be achieved with this technology.

For tertiary controls, additional measurements are often necessary to optimise the abatement reaction. Reactor inlet measurements of NOx are typically performed with an NO IR and NO_2 UV photometer (as described in Part I: NOx measurement). For N_2O inlet measurements, an IR photometer is used. In the new ACM0019, the initial N_2O concentration for calculation of carbon credits does not need to be measured anymore. Instead a baseline emission factor is applied which represents current Best Available Technology (BAT) for N_2O emissions from nitric acid production without any N_2O abatement technology. Nevertheless, the N_2O concentration in the tail gas upstream of the abatement reactor is a powerful indicator for the catalyst efficiency in the ammonia oxidation reaction. Beside NOx and N_2O measurements in the outlet of the abatement reactor, oxygen and fuel (H_2 or CH_4/natural gas) analysis is important. The fuel measurement helps to avoid slips when injecting fuel into the abatement reactor, while the O_2 measurement is a safety measure to avoid explosive conditions by injecting fuel into the reactor when too much oxygen is present. For space and maintenance reasons the controlling and safety measurements should be combined in one analyser with the emission measurements instead of installing single channel units.

Other controls

h) Optimisation of absorption stage

NO oxidation to NO_2 and NO_2 absorption in H_2O is favoured by pressures above atmospheric. In mono-pressure plants, operating pressures are medium between 1.7 and 6.5 bar, as a compromise with the oxidation stage which shows high yields

at low pressures. In dual pressure plants the absorption stage can be operated at a higher pressure of 6.5 to 13 bar, while the oxidation section is operated at low pressures. With high feedstock and energy prices and for large capacities, dual pressure plants are favourable. As the reactions are exothermic, low temperatures also increase the nitric acid yield while decreasing NOx emissions. Optimisation of the contact between NOx, O_2 and H_2O by design changes in the absorption tower will also improve nitric acid yields.

i) Addition of H_2O_2 to the absorber stage

Introducing H_2O_2 in the absorber stage increases the absorption efficiency thus lowering NOx emissions. This solution was tested at a plant where the tail gas could cool down below 85°C in the expander and the NH_3 slip from the SCR process could react with the remaining NOx to form ammonium salts in the expander. Due to this safety concern, an installation of an SCR was turned down and a H_2O_2 injection system was applied instead. With this technology, NOx emission levels of 150 ppm were achieved. In a study from 2001, the different N_2O reduction strategies didn't show a difference in investment cost which were EUR 0.71-0.87/ t CO_2-eq. reduced and EUR 0.98-1.20/t HNO_3 produced.

Legislation on N_2O emissions from nitric acid plants

In January 2011, the Industrial Emissions Directive 2010/75/EU of the European Commission went into force and had to be transposed into national legislation by member states by January 2013. Within this directive the European Commission defined best available technologies for different industry sectors. Within the best available technology reference document (BREF) on Large Volume Inorganic Chemicals - Ammonia, Acids and Fertiliser Industries, emission levels for N_2O from nitric acid plants are given in Table 2.

In existing plants, N_2O emission levels are allowed to be 20 - 300 ppm, whereas new plants are only allowed to emit 20-100 ppm. In December 2009, US EPA stated under section 202(a) of the Clean Air Act (CAA) that six greenhouse gases in the atmosphere – CO_2, CH_4, N_2O, hydrofluorocarbons, perfluorocarbons, and sulphur hexafluoride – may reasonably be anticipated to endanger both public health and public welfare. The Climate Action Reserve,

Table 2: N_2O emission levels from EU nitric acid plants.			
		N_2O emission level*	
		kg/tonne 100% HNO_3	**ppmv**
M/M, M/H and H/H	New plants	0.12-0.6	20-100
	Existing plants	0.12-1.85	20-300
L/M plants		No conclusion drawn	

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

founded as the California Climate Action Registry by state legislation in 2001, is a private 501c(3) non-profit organization and encourages voluntary reporting and reductions of GHG emissions and develops protocols to track GHG emissions and reductions. In its nitric acid production project protocol, guidance to account for, report and verify GHG emission reduction by N_2O abatement from nitric acid plants is given. The protocol does not apply to new plants constructed after December 2009 or plants restarted after December 2007 after being out of operation for a period of 24 months or longer. If there have already been emission reduction measures in place when registering for a project, special rules apply. Secondary or tertiary catalyst projects are treated under Climate Action Reserve projects. Reduction calculations were derived from internationally accepted methodologies (AM0028, AM0034 and ACM0019). The US Code of Federal Regulations Title 40 (40 CFR), Part 60 and Part 75 outline the minimum requirements for the installation, evaluation, monitoring and record keeping for NOx CEMS and are also applicable to N_2O emission testing at nitric acid plants. Initial certification requirements of the 40 CFR Part 75 include:

● 7-day calibration error test
● Linearity check

● Relative Accuracy Test Audit (RATA)
● Bias test
● Cycle time test
● Automated data acquisition and handling system (DAHS) verification

All RATA of CEMS must be conducted by a testing body conforming to the requirements of ASTM D7036-04. Differing from Europe, in the US there is no type approval for CEMS. After initial certification of the CEMS, daily, quarterly and (semi-) annual assessments have to be performed. The N_2O abatement from Climate Action Reserves is traded as CRT (Climate Reserve Ton), which represents one metric tonne of carbon dioxide equivalent emissions reduction. The Climate Action Reserve currently has five nitric acid production projects, including four secondary catalysts and one tertiary catalyst. Some 5,116,007 CRTs (tCO_2e) have been issued to four of these projects so far. The fifth project has not yet gone through verification.

Since January 2011, the EPA has phased in regulations for GHG emissions from major sources (emitting more than 100,000t CO_2e per year) under the Clean Air Act. New plants or major capacity extensions have to apply for a Title V permit. Title V generally does not add new pollution control requirements, but sources will need to address GHG-related information in their Title V permit applications. This Title V, known as the "Tailoring Rule," also requires Prevention of Significant Deterioration (PSD) permits. An assessment

of Best Available Control Technology (BACT) for GHGs will be required as part of the PSD permitting process.

Conclusion

Prices for CERs and ERUs with an all-time low of less than €1/tCO_2e make projects for the installation of N_2O abatement technology unattractive compared to the years before where prices have been much higher, so that the return on investment was achieved within a short period. The main reason for the low prices is the economic crises, and politicians are discussing cutting down CO_2 emission allowances. Nevertheless, emission regulations on NOx and N_2O from nitric acid plants are implemented in more and more world areas, or emission levels are tightened. These emission levels can only be achieved with additional measures (abatement technologies) which have to be added to existing plants or need to be considered for new plants. Beside the N_2O and NOx emission measurements, for some of the abatement technologies, control measurements are needed to optimize the abatement reactor and avoid explosive conditions. In European legislation and for CDM and JI type approved analysers need to be installed, whereas in the U.S. the suitability of a CEMS is proven after installation. Besides suitable analysers, some of which need type approval, the sample handling systems are also an integral part of the analytical system required to obtain reliable emission data. ■

Rosemount Analytical MLT family of N_2O analysers from Emerson Process Management.