

# Combating NOx in acid plants

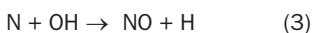
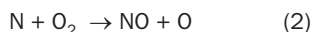
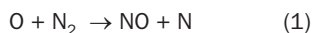
Nitrogen oxides can be formed via several mechanisms in the upstream operations of sulphuric acid plants. NOx levels may need to be controlled to ensure acid quality and good operation. Several methods of NOx removal are available to meet these needs.

**N**itrogen oxides (NOx) typically refer to different compounds that are formed out of nitrogen and oxygen, e.g. NO, N<sub>2</sub>O, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>. A typical specification for NOx in commercial grade sulphuric acid is 5 ppmw oxides of nitrogen as nitrates (equivalent to 10 ppm HNOSO<sub>4</sub>). Depending on the plant design, this would limit the concentration of NOx in the feed gas to between 5 to 15 ppmv in order to produce a product acid that would require no additional treatment.

The NOx that occurs in an acid plant can be formed through a number of mechanisms in the upstream operations<sup>1,2</sup>.

## Thermal NOx

The formation of thermal NOx occurs through the reaction of nitrogen and oxygen:

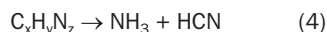


The thermal formation of NOx starts at temperatures below 1,000°C but typically results in significant concentrations at temperatures above 1,300°C. The rate of NOx generation is a function of temperature and oxygen concentration. As the kinetics of the reaction is relatively slow, even at temperatures of 1,600°C the equilibrium will be reached after seconds, hence the concentrations of NOx are significantly below the thermodynamic equilibrium value in sulphur combustion processes. Metallurgical plants, on the other hand, may receive more NOx in the feed gas as the primary smelting units generally operate at higher temperatures than sulphur or acid regeneration furnaces.

The increased use of oxygen enrichment in smelters and acid regeneration plants tends to increase the quantity of NOx formed due to the effect of higher temperatures and higher oxygen concentration. When using oxygen enrichment, the NOx content peaks in the 35-50 vol-% oxygen range. Beyond this level, the quantity of nitrogen present and available to form thermal NOx decreases.

## Fuel NOx

Organic bound nitrogen present in some fuels, particularly heavy fuel oils, is readily converted to NOx in the combustion process. This conversion is difficult to prevent when using heavy fuel oil. The formation of fuel NOx can result in significant NOx concentrations even at lower temperatures compared to thermal NOx (<900°C). The main reactions are:



NOx in the gas stream to the acid plant is undesirable for several reasons: it leads to nitrates in the product acid which may exceed specifications, thus affecting acid quality; it leads to NOx in stack gas exceeding permitted concentrations and causing a visible yellow to brown plume, it can also directly affect the operation of acid plants by blocking candle filters or fouling equipment such as heat exchangers.

## Feed NOx

Some feeds to furnaces and smelters contain organic nitrogen compounds. For

instance, methyl methacrylate spent acid contains significant quantities of organic nitrogen compounds. It consists of almost 35% ammonium sulphate and some concentrates, particularly zinc concentrates. While the operating conditions in an acid regeneration furnace can be adjusted to minimise the production of NOx, the operation of the smelter/roaster is controlled more by metallurgical considerations. However the formation of NOx in the off-gas is ensured in either case.

## NOx in sulphuric acid plants

In sulphur based sulphuric acid plants, NOx is mainly formed as thermal NOx. The formation is influenced by temperature and the combustion system. In general, higher temperatures will result in higher NOx concentration and more compact burner/furnace systems will result in reduced NOx concentrations. In a few plants, an increased NOx level, due to nitrogen containing impurities in the feedstock (contamination of sulphur), have been reported.

In acid plants processing metallurgical off-gases, the NOx content results solely from the upstream pyrometallurgical process and can reach high values (>>100 mg/Nm<sup>3</sup>). For example, the excessive use of oxygen in the smelter process results in high temperatures and/or nitrogen containing components in the treated concentrate.

Plants treating off-gases from spent acid decomposition plants, which typically operate at lower temperatures (< 1,000°C), can also show a significant amount of NOx (>>100 mg/Nm<sup>3</sup>) due to nitrogen containing components in the feedstock.

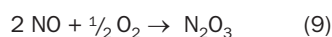
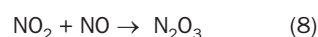
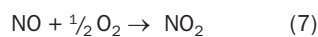
NOx in the process gas, regardless of the feed source, enters the acid plant

Fig 1: NO<sub>x</sub> emission from candle filter during cleaning



PHOTO: OUTOTEC

mainly as nitrogen oxide (NO), which does not react with sulphuric acid nor does it have a tendency to form sulphate. NO is a gas with a very low boiling point and it cannot be captured in the gas cleaning system of an acid plant, nor can it be separated in the gas cooling section or drying tower in significant amounts. The key component for the reaction with sulphuric acid is dinitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), which is formed once NO enters the catalytic stages of the acid plant. At lower temperatures, NO is converted to N<sub>2</sub>O<sub>3</sub> in the presence of vanadium pentoxide catalyst:



In the first stage of the converter approximately 50% of the NO will be converted to N<sub>2</sub>O<sub>3</sub>. N<sub>2</sub>O<sub>3</sub> reacts with sulphuric acid mist to form nitrosyl-sulphuric acid (NOHSO<sub>4</sub>), which tends to be a vapour initiator:



NOHSO<sub>4</sub> aerosols will be precipitated from the gas in the candle filters of the intermediate- and final absorber. Measurements have shown that 30-85% of the total NO<sub>x</sub> is collected in the candle filter systems, the majority can be found in the final absorber. Typically 85-400g NOHSO<sub>4</sub> per kg H<sub>2</sub>SO<sub>4</sub> are dissolved in the candle filters. As the solubility of NOHSO<sub>4</sub> is (depending on temperature and acid concentration) approximately 600g NOHSO<sub>4</sub> per kg H<sub>2</sub>SO<sub>4</sub>, fluctuations in the process conditions can result in blockages of candle filters due to crystallisation of NOHSO<sub>4</sub>, which will disturb the plant operation due to the high pressure drop. The cleaning of NO<sub>x</sub> polluted candle filters requires additional pre-

cautions, as during the cleaning process the reverse reaction (10) will result in NO<sub>x</sub> emissions as seen in Fig. 1.

When the NOHSO<sub>4</sub> enriched acid is drained from the candle filters directly to the product acid, the NO<sub>x</sub> concentration in product acid can exceed the specified value (typically < 5 ppm) and the NO<sup>+</sup> species can result in corrosion of equipment (e.g. cold heat exchanger) and will form coloured compounds (Fe-complexes). The resulting treatment of the NOHSO<sub>4</sub> in the product acid by chemicals (e.g. hydrazine, hydroxylamine, urea, etc.) will create additional cost, thus lowering the product margin.

## NO<sub>x</sub> control

The following strategies can be employed to control NO<sub>x</sub> in sulphuric acid plants:

- prevention;
- elimination in gas cleaning;
- partial NO<sub>x</sub> reduction;
- selective catalytic reduction

### Prevention

If possible adjustments or modifications should be made at the furnace to prevent or minimise the formation of NO<sub>x</sub>. Low NO<sub>x</sub> burners can be retrofitted and the gas flow paths in the furnace adjusted to eliminate hot spots that favour the formation of NO<sub>x</sub>. CFD analysis is used to assist in optimising the gas flow path in the furnace.

### Elimination in gas cleaning

The first opportunity to eliminate the NO<sub>x</sub> after it is formed occurs in gas cleaning. Here ozone can be added to the gas to oxidise NO to NO<sub>2</sub> which is then scrubbed in the gas cleaning and purged in the weak acid effluent. The disadvantages with this approach is that oxidation with ozone is not very efficient, the ozone rapidly decomposes leading to significant ozone loss before it reacts with the NO<sub>x</sub>, additionally the ozone will react with significant quantities of SO<sub>2</sub> resulting in additional SO<sub>3</sub> formation thereby increasing the quantity of weak acid effluent. Also the weak acid effluent after neutralisation will now contain nitrates which can be a far greater discharge problem than an effluent containing limited concentrations of dissolved sulphates.

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

The approximately 90% of the NO<sub>x</sub> that is measured in the strong acid occurs through capture in the acid mist droplets

formed at the inlet to the absorption towers. These mist droplets are themselves subsequently collected in the mist eliminators located in the top of the towers and drained back to the bulk of the acid.

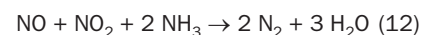
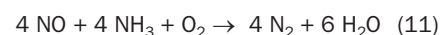
Absorption towers that are fitted with Brownian Diffusion candle-type mist eliminators have an effective method for trapping and diverting these mist droplets containing the absorbed NO<sub>x</sub>. However the quantity of NO<sub>x</sub> captured in the acid is at maximum only 65% of the total NO<sub>x</sub> feed and the NO<sub>x</sub> segregated in the candle drips is 90% of the total captured. The remaining NO<sub>x</sub> in acid is sufficient to exceed the quantity permitted by the acid quality specification.

Segregating the candle drips requires additional treatment for both the candle drips and the product acid.

The simplest approach for treating the candle drips is to just dilute with water and sewer or neutralise the candle drips. However this creates an acid yield loss and an additional effluent from the acid plant. Also care must be taken when diluting. The rapid hydrolysis and heat of dilution when the candle drips come into contact with water will result in the release of copious brown NO<sub>x</sub> fumes. In most cases it will be necessary to use a scrubber to avoid the release of NO<sub>x</sub>.

### Selective catalytic reduction (SCR)

Another technique for the removal or destruction of NO<sub>x</sub> in gases is selective reduction using a reducing agent such as ammonia. The process involves the reaction of NO and NO<sub>2</sub> with ammonia to form nitrogen and water:



Although these reactions can occur at high temperature (above about 900°C, i.e. at the conditions of the smelter or furnace outlet) without a catalyst in the typical hot smelter or furnace gas it is believed that the relatively high levels of dust and, of course, SO<sub>2</sub> will make the reaction largely ineffective.

At more moderate temperatures (180-600°C) a catalyst is used. Selective catalytic reduction of NO<sub>x</sub> by ammonia over vanadia/titania type catalysts is by far the most important commercial process today for removal of NO<sub>x</sub><sup>3</sup>.

However, the process to date has had only limited application on a commercial scale in sulphuric acid plants.

## The SCR DeNOx process

Figure 2 shows a schematic diagram of the SCR DeNOx process. The process is generally the same whether applied to flue gases, exhaust gases, or to other off-gases.

The main components of the SCR process consist of a reactor containing the catalyst and an ammonia storage and injection system. The ammonia can be in the form of liquid, water-free ammonia (under pressure) or an aqueous ammonia solution (at atmospheric pressure). A solution of urea can also be used if warranted by safety.

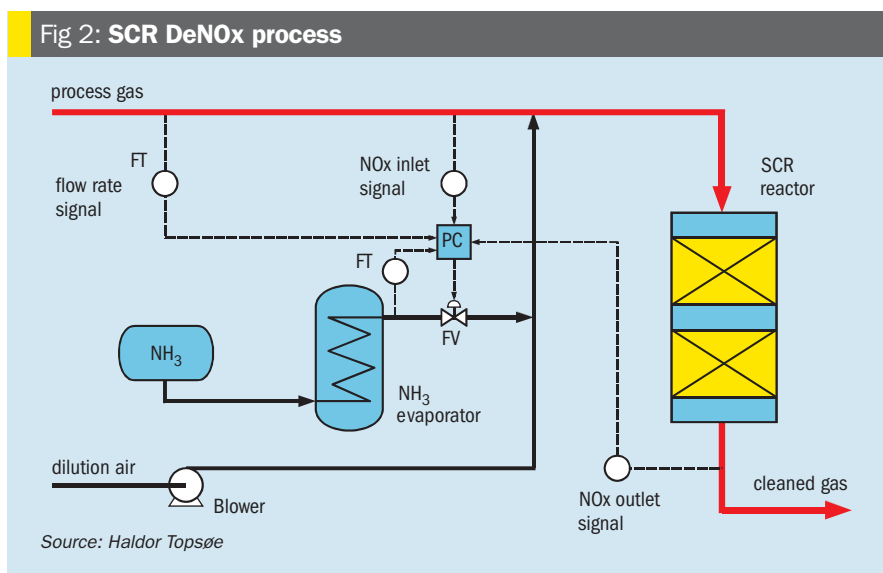
The ammonia is evaporated in an electrically, steam, or hot water heated evaporator and is subsequently diluted with air before the mixture is injected into the process-gas duct. The injection of the ammonia/air normally takes place through a grid of nozzles in order to achieve a uniform mixing of the ammonia with the process gas. A system of one or more static mixers may be placed in the duct to further improve mixing. This mixing is important so that the resulting gas-ammonia mixture has the uniform  $\text{NH}_3/\text{NO}_x$  ratio required to ensure efficient removal of  $\text{NO}_x$  and to minimise the ammonia slip ("leakage") from the SCR reactor.

The SCR process requires precise control of the ammonia injection rate. Insufficient injection results in low conversion of  $\text{NO}_x$  and an injection rate which is too high results in an undesirable leakage of unconverted ammonia from the SCR reactor. SCR control strategies in general use a combination of feedback control and feedforward control. The primary control variable is the SCR outlet  $\text{NO}_x$  concentration. The feedforward signal is comprised of two major components, one related to the gas flow rate into the SCR and the other representing the inlet  $\text{NO}_x$  concentration.

## SCR in a sulphuric acid plant

The SCR reactor usually consists of one or more layers of catalyst. The normal operating temperature of the catalyst is between  $300^\circ\text{C}$  and  $425^\circ\text{C}$  but through the use of special catalysts the SCR process can be applied at temperatures down to  $180^\circ\text{C}$  and up to  $600^\circ\text{C}$ .

The application of SCR technology in a sulphuric acid plant requires in the first place a consideration for the location of the catalyst bed. Possible locations for the SCR reactor in a metallurgical off-gas based plant are:



- before gas cleaning in the hot gas;
- before the stack;
- after gas cleaning and before the drying tower;
- in the dry-gas section.

**Before gas cleaning in the hot gas:** The gas at this point is in the ideal temperature range for the operation of an SCR unit. Unfortunately the gas will contain significant quantities of dust and catalyst poisons such as arsenic, fluorides and chlorides that make this location unacceptable.

**Before the stack:** Another obvious location for the DeNOx catalyst is immediately prior to the acid plant stack, as the gas constituents at this location would be roughly similar to hundreds of other SCR applications. However, this location has some serious disadvantages in that  $\text{NO}_x$  will still be absorbed into the product acid in the acid plant, requiring an expensive chemical treatment, and that the gas must be reheated following the final absorption tower, requiring installation of additional gas-gas heat exchangers and auxiliary fuel firing.

**After gas cleaning and before the drying tower:** This location has the major disadvantage of having to heat the gas from near ambient temperature.

**In the dry-gas section:** The benefits of locating the SCR in the dry gas section of the contact plant before the first catalyst bed are:

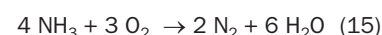
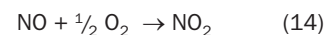
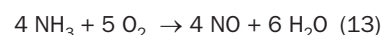
- the gas is hot and within the required temperature range;
- the  $\text{NO}_x$  is destroyed before it encoun-

ters any acidic residues where it can be absorbed to create later problems during maintenance;

- the  $\text{NO}_x$  is reduced to a level so that candle drip segregation is unlikely to be required and consequently eliminating the disposal or treatment problem;
- the  $\text{NO}_x$  is reduced to a level so that product treatment is not required and eliminating the requirement to use potentially hazardous reagents.

Also, this location is virtually free of  $\text{SO}_3$  so there is minimum risk of a reaction of  $\text{SO}_3$  with ammonia resulting in the production of ammonium bisulphate. This reaction would lead to fouling and equipment plugging as well as catalyst deactivation and rules out the possibility of locating the SCR further downstream the contact section. The DeNOx reaction results in a small increase in the moisture content of the gas stream (1.5 mole of water formed per mole of  $\text{NO}_x$  converted). The water formed will react with  $\text{SO}_3$  to form gaseous sulphuric acid. Any resultant dew point and mist considerations need to be addressed.

Also, it must be taken into consideration that unconverted ammonia from the DeNOx reactor will be oxidised partly to  $\text{NO}_x$  and partly to elemental nitrogen in the  $\text{SO}_2$  converter:



This means that the ammonia slip from the SCR reactor will by and large end up as nitrates in the acid.

Fig 3: Haldor Topsøe DNX<sup>®</sup> SCR catalyst

PHOTO: TOPSØE

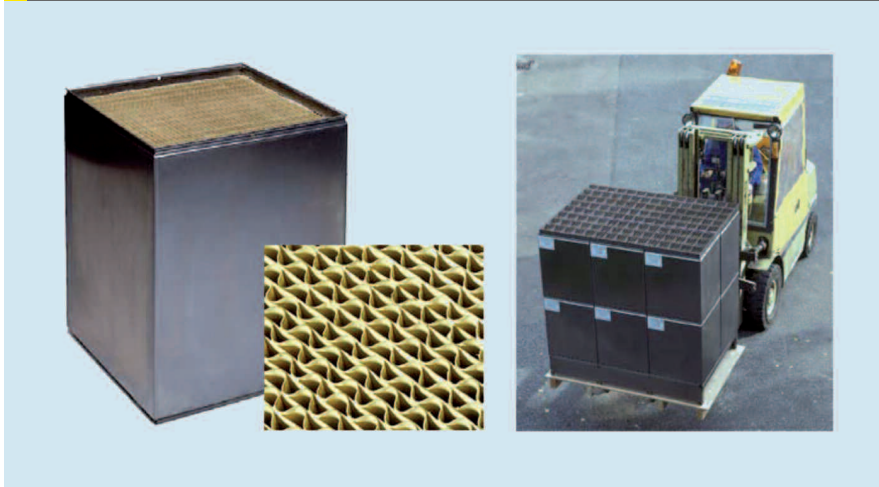
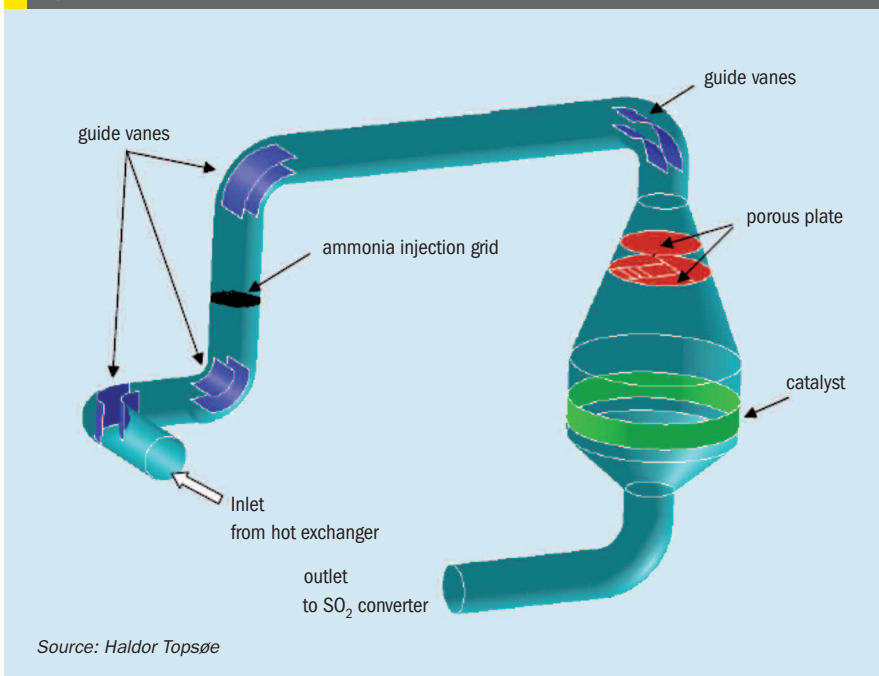


Fig 4: The single-bed SO<sub>2</sub> converter with risers holding the DeNOx catalyst at Nyrstar Budel Zink, The Netherlands

PHOTOS: AKER SOLUTIONS



Fig 5: General layout of duct and SCR DeNOx reactor for Japanese zinc smelter



Source: Haldor Topsøe

## The SCR DeNOx catalyst

SCR catalysts are normally based on a titanium dioxide (TiO<sub>2</sub>) carrier, with a combination of vanadium pentoxide and tungsten trioxide as the active material.

The catalytic reaction is essentially a surface reaction. In order to maximise the activity the catalyst must provide a large external surface area and is therefore manufactured with a large number of parallel channels arranged in a honeycomb structure. The size of the channels depends on the content of particulate matter (dust) in the gas and typically ranges from 2 mm (dust-free gas) up to 10 mm (dust contents of > 30 g/Nm<sup>3</sup>). Figure 3 shows Haldor Topsøe's SCR DeNOx catalyst which is based on a fibre-reinforced titania carrier in a corrugated structure. Owing to the carrier's high porosity the catalyst is very resistant to thermal shocks and the weight is considerably lower than traditional extruded or plate-type catalysts.

The catalyst is manufactured in monolithic blocks with 466 mm x 466 mm cross section and a height of e.g. 500 mm, and is housed in a steel casing forming elements. The elements are usually combined into modules, to facilitate handling and installation of the catalyst. The modules are tailored in size to varying design requirements.

One drawback of locating the DeNOx catalyst before the converter is the high level of SO<sub>2</sub> in the gas stream, much higher than seen in SCR's on e.g. boiler flue gas. A major ingredient of the DeNOx catalyst is vanadium pentoxide, which catalyses the oxidation of SO<sub>2</sub>. This reaction competes with the DeNOx reaction and therefore the catalyst must be specially formulated to ensure that it maintains a high activity for DeNOx operation. By using a high-porosity catalyst it is ensured that a large number of active sites are available for the DeNOx reaction.

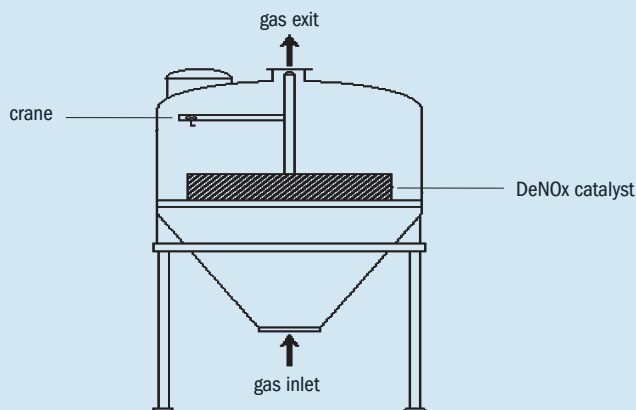
## Haldor Topsøe case studies

### Nyrstar Budel Zink, The Netherlands

The SCR technology was successfully implemented on a zinc smelter operated by Nyrstar Budel Zink in the Netherlands in 1999. The DeNOx catalyst was incorporated within a new Bed 1 converter also containing catalyst for SO<sub>2</sub> conversion. The new converter was supplied by Aker Chemetics and Haldor Topsøe supplied the catalyst and part of the basic engineering of

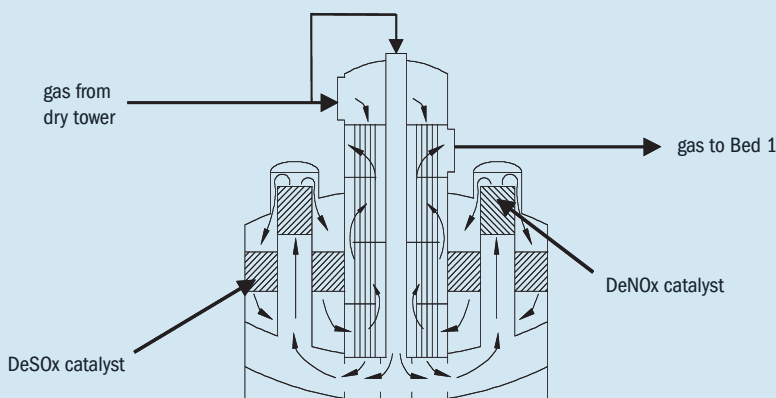


Fig 8: DeNO<sub>x</sub> catalyst vessel



Source: Aker Solutions

Fig 9: Single bed converter flow diagram



Source: Aker Solutions

or power since the acid flows by gravity. The equipment is simple, reliable, and small (a 12" packed column will treat the candle drips from a 2000 s.t/d acid plant).

Another method involves the creation of a solution of SO<sub>2</sub> in weak sulphuric acid, by passing some of the process gas leaving the blower through a dilute sulphuric acid solution. The candle drips are then mixed with the SO<sub>2</sub> solution, and the NO<sub>x</sub> is reduced to nitrogen by reaction with the SO<sub>2</sub> in the liquid. The reduction reaction leaves no NO<sub>x</sub> or HNO<sub>3</sub> by-product for disposal.

Even if the candle drips can be segregated, unless the NO<sub>x</sub> content is below 15 ppmv, the acid plant product will not meet a NO<sub>x</sub> specification of less than 5 ppm. In this case the acid product must be chemically treated to reduce the NO<sub>x</sub>. Reduction can be accomplished by adding one of the reducing agents in the series (in order of decreasing cost and decreasing efficiency):

- Hydrazine N<sub>2</sub>H<sub>4</sub>
- Hydroxylamine HONH<sub>2</sub>
- Hydroxylamine sulphate (HONH<sub>2</sub>)<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub>
- Sulphamic acid H<sub>2</sub>N.SO<sub>3</sub>H
- Urea H<sub>2</sub>N.CO.NH<sub>2</sub>

For instance if hydrazine is used as a reducer, and the NO<sub>x</sub> level in the acid is high, the cost may be as high as \$2.00 per ton of product acid.

Aker Solutions has had particular success with the installation of selective catalytic reduction units for NO<sub>x</sub> in sulphuric acid plants. The catalytic DeNO<sub>x</sub> system at Nystar's Budel plant (described above) is a particularly good example. Since startup in late 1999 the NO<sub>x</sub> emissions to the stack have been continuously monitored and have been in the order of 3ppmv until mid 2008. More recently the emissions have gradually increased to 5 to 6 ppmv average with catalyst activity estimated at

60 to 86%. This is after close to 10 years of continuous operation without catalyst replacement. The mechanical integrity of the DeNO<sub>x</sub> Reactor is also good and has exhibited no significant problems since start-up in 1999.

The DeNO<sub>x</sub> bed has been incorporated in two locations in the acid plant, after the cold exchanger and after the hot exchanger. With different operating temperatures, different DeNO<sub>x</sub> catalysts exhibiting different activities are employed in the different locations. The DeNO<sub>x</sub> catalyst, assembled into cassettes and modules, is installed in a separate vessel. The vessel design is more robust than the typical SCR container because of the requirement for the unit to operate at a higher pressure than occurs in a power plant flue gas installation. A diagram of a typical DeNO<sub>x</sub> catalyst vessel designed for use in a sulphuric acid plant is shown in Fig. 8.

It may be advantageous to expand or otherwise modify the existing sulphuric acid plant at the same time as the DeNO<sub>x</sub> catalyst is installed. One project incorporated the DeNO<sub>x</sub> catalyst within a new Bed 1 converter also containing catalyst for the conversion of SO<sub>2</sub> to SO<sub>3</sub>. The unit also contained a new internal hot exchanger for additional maintenance benefits. A diagram of the combined DeNO<sub>x</sub> and DeSO<sub>x</sub> unit with the internal hot exchanger is shown in Fig. 9.

A DeNO<sub>x</sub> removal requirement of 95% or greater is typically required for these systems. This can only be achieved if the criteria of even ammonia distribution within the gas and even distribution of the gas over the catalyst are obtained. The catalyst criterion is that flow deviations through the catalyst mass should be not greater than +/- 15%. This is achieved by performing extensive CFD analysis on the flow patterns in the catalyst vessel. ■

## References

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