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Uhde EnviNOx® process for the combined reduction of N_2O und NO_X emissions from nitric acid plants

I EnviNOx® reactor installed at AMI Agrolinz Melamine International GmbH in Linz, Austria

N_2O emissions in the production of nitric acid

The industrial production of nitric acid (HNO_3) involves oxidizing ammonia (NH_3) with air on a platinum/rhodium gauze catalyst to produce nitrogen oxides. This process yields nitrogen monoxide (NO), which is then reacted with oxygen and water to form nitric acid. However, it also produces nitrous oxide (N_2O) – a known greenhouse gas and ozone killer – as an undesired by-product. Unlike NO, the nitrous oxide does not undergo any further reaction in the HNO_3 production process and is emitted into the atmosphere in the tailgas | Fig. 1 |.

Approximately 2% of the ammonia is oxidized to N_2O, which leads to the emission of about 7 kg of N_2O per metric ton of HNO_3. An estimated 400,000 metric tons of nitrous oxide are emitted each year by nitric acid plants worldwide.

Due to its longevity in the earth's atmosphere and its special absorption properties for infrared radiation, N_2O is a very potent greenhouse gas. One metric ton of nitrous oxide has the same effect in the atmosphere as 310 metric tons of CO_2. Consequently, nitric acid plants are now the largest single source of greenhouse gas emissions among industrial manufacturing facilities. Whereas limits on NO_x emissions have been in force for a long time (due to acid rain, smog etc.), N_2O was until recently allowed to be emitted into the atmosphere without restrictions. However, after nitrous oxide was recognized as a relevant greenhouse gas (and also designated as such in the Kyoto Protocol), German legislation for the first time set limits for nitrous oxide emissions from nitric acid production facilities in 2002. According to the Technische Anleitung zur Reinhaltung der Luft (Clean Air Act), such emissions may not exceed 0.80 g/m³. Because the specific impact of nitrous oxide on the greenhouse effect is many times greater than that of CO_2, the elimination of nitrous oxide from nitric acid plants can make an important contribution to protection the Earth's climate.

Development of the EnviNOx® process

In light of the above, Uhde – a world leader in nitric acid technology – set about developing a technology for removing N_2O from the nitric acid production process. The goal was not only to achieve high rates of N_2O abatement but also to ensure that the technology itself could be safely and simply integrated into the HNO_3 production process without affecting it in any way. In particular, the aim was to find a

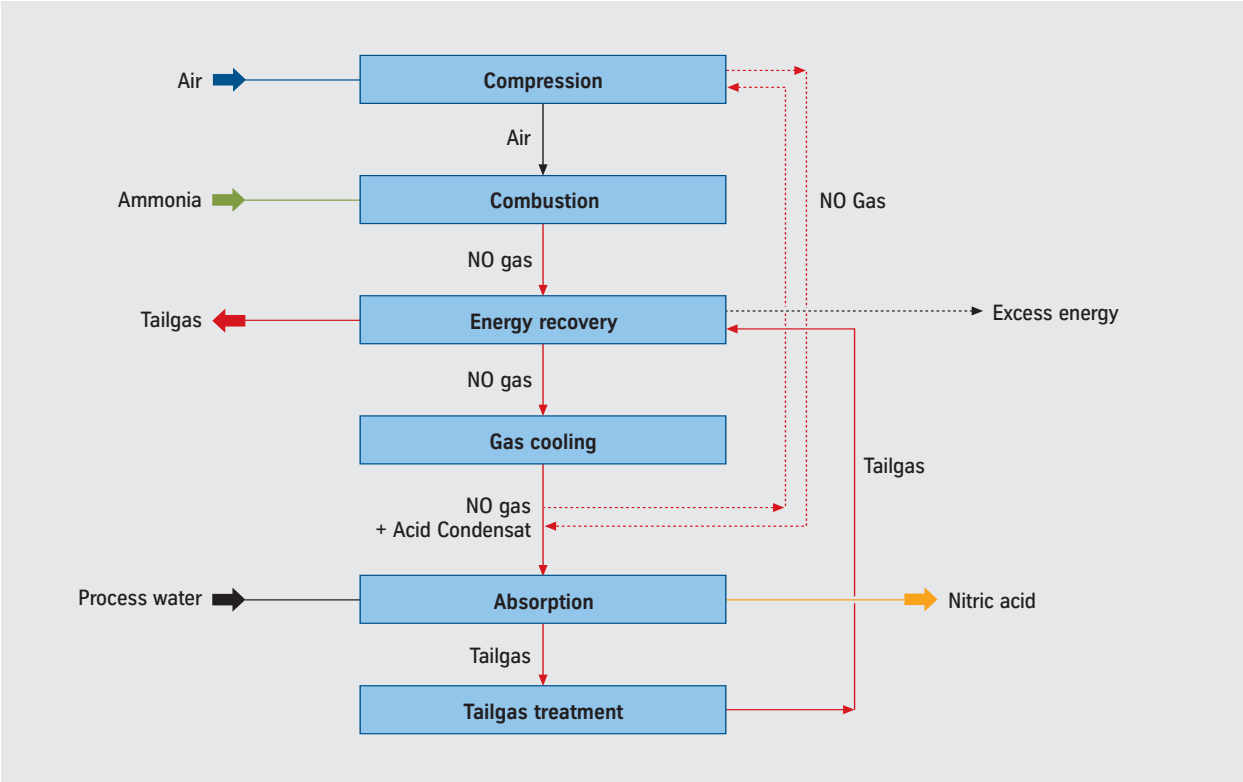

Fig. 1 | Block diagram of a nitric acid plant

Fig. 2 | Miniplant for N_2O removal

suitable way of combining the N_2O removal process with the DeNOx stage, which is also necessary for tailgas treatment. Development therefore focused on the catalytic removal of N_2O from the tailgas of HNO_3 plants (so-called tertiary measures).

After preliminary tests, development concentrated on the use of special iron-zeolite catalysts. In the laboratory, these not only displayed a high level of activity in decomposing N_2O into N_2 and O_2, which was heightened significantly by the presence of NO_X in the tailgas (co-catalytic NO_X effect); they also proved to be excellent DeNOx catalysts in an unusually wide temperature window, thus allowing N_2O abatement to be ideally combined with NO_X reduction.

After optimization of the catalysts, the positive laboratory results were checked under real conditions in a miniplant installed in the bypass of an HNO_3 production plant operated by AMI Agrolinz Melamine International GmbH in Linz, Austria | Fig. 2 |.

Process concept

The design data required for implementation of the process on a commercial scale were generated in numerous test series. The diagram in | Fig. 3 | shows the process concept developed for a temperature range of approximately 400–500 °C.

The central component is a so-called combi-reactor located between the tailgas heater and the tailgas turbine. It contains two catalyst beds operated at the same pressure and temperature, and a device for the intermediate addition of NH_3. In the first stage – the so-called DeN2O® stage – N_2O decomposition takes place under full NO_X load (maximum exploitation of the NO_X effect). In the second stage, NO_X reduction is effected using NH_3 as a reduction agent, while N_2O abatement continues simultaneously.

Reactions in the DeN2O® stage:

$$2\,N_2O + 2\,NO \rightarrow 2\,N_2 + 2\,NO_2$$
$$2\,NO_2 \rightarrow 2\,NO + O_2$$
$$2\,N_2O \rightarrow 2\,N_2 + O_2$$

Reactions in the DeNO$_X$ stage:

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O$$
$$4\,NO + O_2 + 4\,NH_3 \rightarrow 4\,N_2 + 6\,H_2O$$

First commercial-scale implementation

The development of the process and the results achieved with the pilot plant were so convincing that AMI decided to implement the concept on a commercial scale at its dual-pressure HNO_3 plant in Linz, Austria, in conjunction with Uhde. The plant has a capacity of approximately 1,000 metric tons of HNO_3 per day (with 120,000 m^3/h tailgas). The contract was signed in July 2002 and the world's first commercial-scale facility for reducing N_2O and NO_X from the tailgas of an HNO_3 plant successfully came on stream in October 2003 | Fig. 4 |. | Figs 5 and 6 | show that the EnviNOx® process has achieved very high abatement levels for N_2O (>98%) in the first year of operation and NO_X (>90 %). The Linz nitric acid plant is now emitting some 2,400 metric tons less nitrous oxide per year, corresponding to a reduction of around 750,000 t/year of CO_2 equivalents. Thus AMI is making a substantial contribution to climate protection in Austria. In fact, the Linz plant alone meets approximately 50% of Austria's emissions reduction target for the industrial and manufacturing sectors (as set in the Kyoto Protocol). It is therefore the largest single emissions reduction measure to be taken in Austria. As a result AMI, received the "Climate Rescuer" award from the Province of Upper Austria in 2003.

The NO_X abatement achieved with the technology can be controlled by varying the amount of ammonia (NH_3) added. Unlike other methods of selective catalytic reduction (SCR) of NO_X based on V_2O_5/ TiO_2 catalysts, the EnviNOx® process uses an iron-zeolite catalyst that considerably reduces the risk of undesired NH_3 slip. Because excess NH_3 (within certain limits) is oxidized by the catalyst into N_2 and H_2O, the EnviNOx® process can, in principle, achieve higher rates of NO_X abatement than conventional SCR processes.

Summary and outlook

Starting from initial laboratory experiments Uhde has developed the EnviNOx® process to a commercial-scale implementation in just three years, and it is now available to customers (i.e. operators of nitric acid plants) worldwide. The extremely high rates of N_2O and NO_X abatement that are achieved mean that current and future N_2O and NO_X emission standards can be easily met without affecting the HNO_3 production process. As a result, operating licenses for nitric acid plants can be maintained and an effective contribution can be made to lower site emissions. In addition, the technology offers numerous customers in countries with no legislation for reducing N_2O emissions

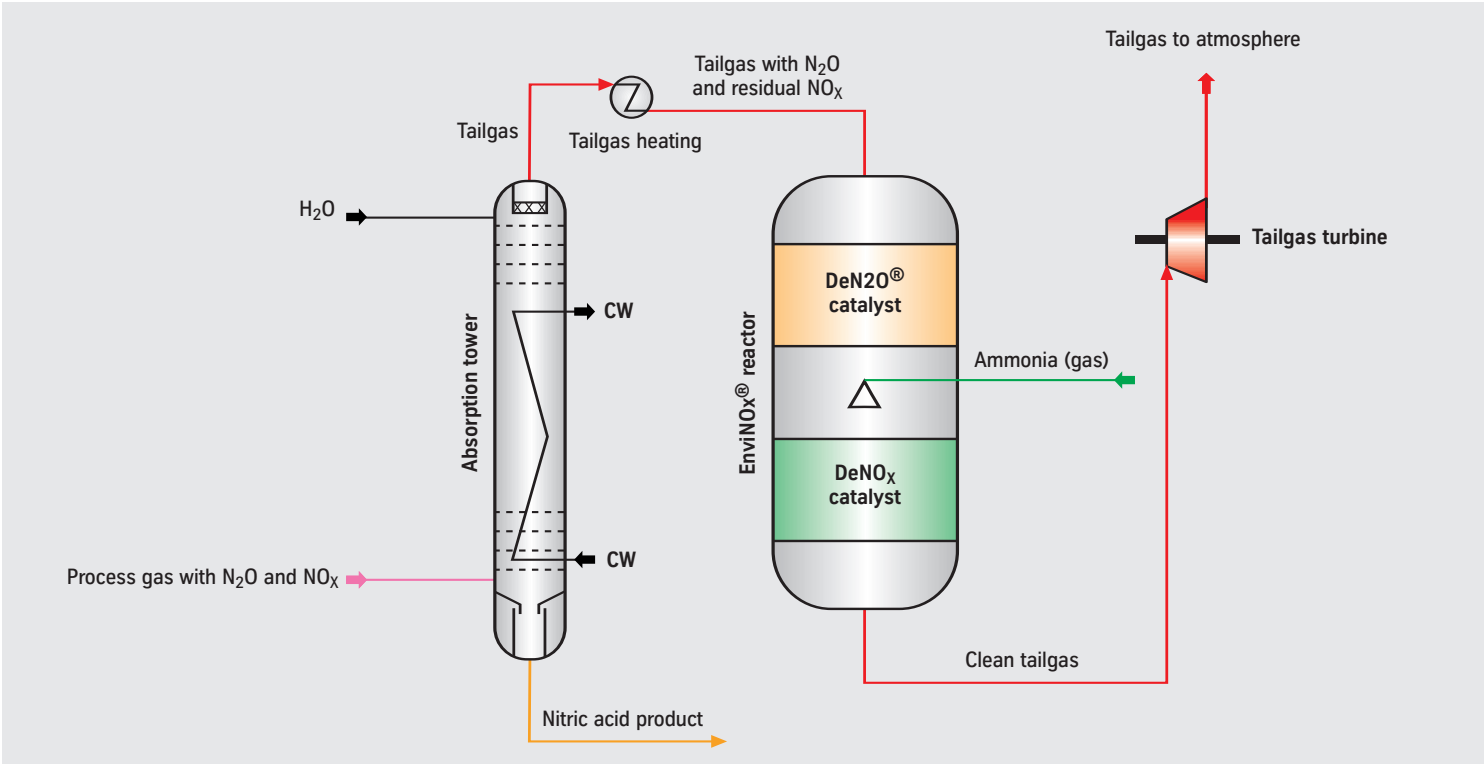

Fig. 3 | Integration of the EnviNOx® reactor into the HNO_3 process

Fig. 4 | EnviNOx® reactor in an HNO_3 plant at AMI in Linz, Austria

the possibility of being granted tradeable CO_2 certificates in accordance with the flexible mechanisms of the Kyoto Protocol.

Because all future nitric acid plants will require N_2O emission abatement technology, the Uhde EnviNOx® process is an ideal supplement to the company's proprietary HNO_3 technology and will consolidate Uhde's leading market position in the construction of nitric acid plants for the long term. Moreover, the possibility of retrofitting existing HNO_3 plants that, for technical reasons, require a tailgas temperature of more than 400°C will provide Uhde with new access to global HNO_3 customers. A modified variant of the process, which enables EnviNOx® technology to be used in HNO_3 plants with tailgas temperatures below 400°C, has also been developed to market maturity and will soon be implemented on a commercial scale for the first time.

The new Uhde EnviNOx® process for the combined reduction of N_2O and NO_X emissions from nitric acid plants described in this article was awarded First Prize in the 2005 ThyssenKrupp Innovation Contest.

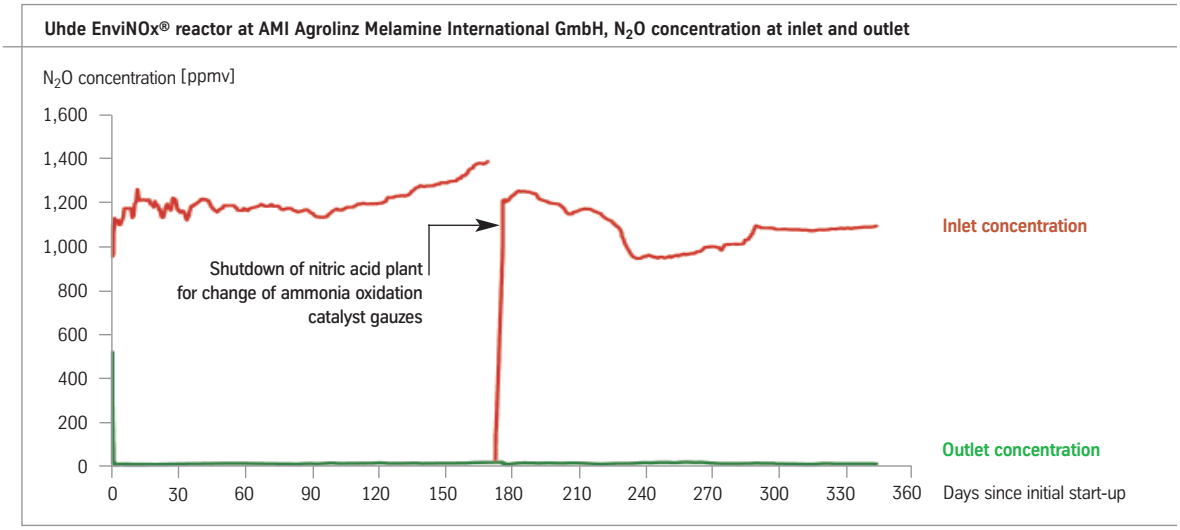

Fig. 5 | N_2O abatement in the EnviNOx® process in the first year of operation

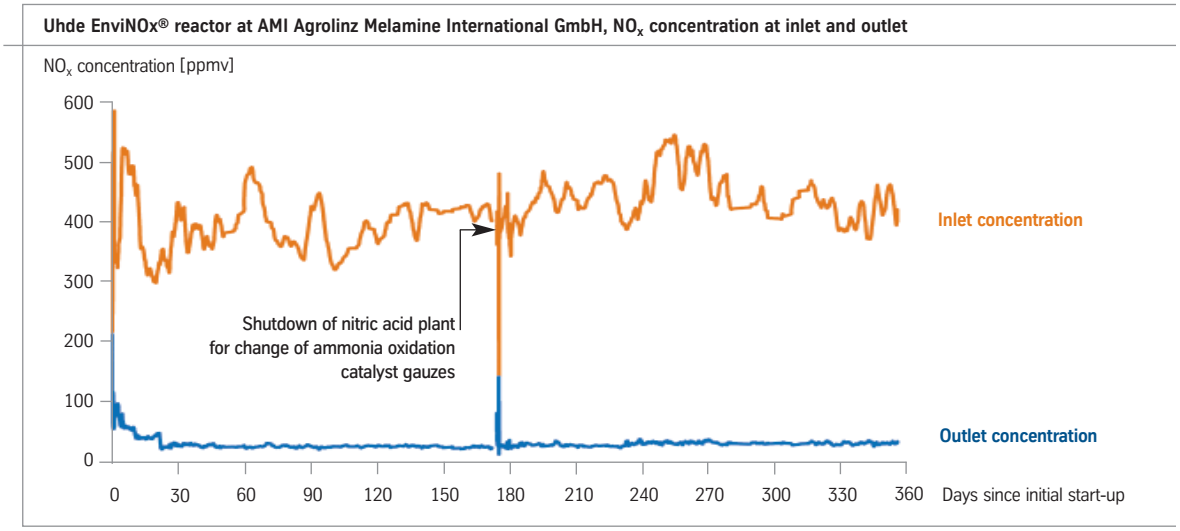

Fig. 6 | NO_x reduction in the EnviNOx® process in the first year of operation