How Low Can You Go?
Catalytic NO_x Reduction in Refineries

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Newly proposed NOx emissions limits in the United States for the Ohio Valley abatement area and Gulf Coast region have focused more attention on the use of catalytic reduction to meet stringent requirements. Several reduction methods have been developed, including: ultra-low NOx burners, additives, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR). For today's typical regulatory requirements of 90% - 95% NOx reduction and single-digit parts-per-million outlet levels, SCR is the only proven solution to meet these tough demands.

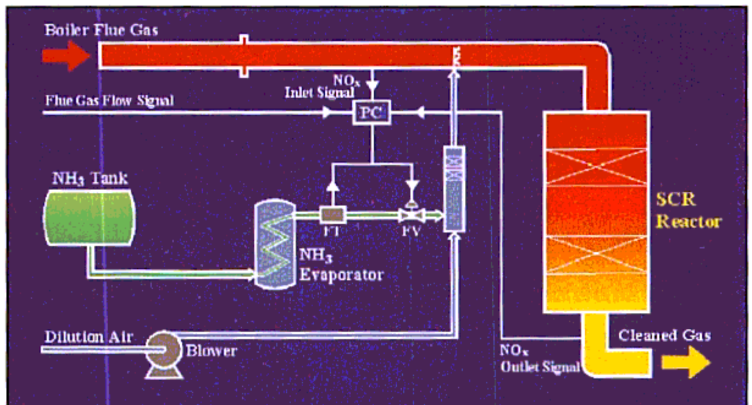


Figure 1. Topsoe SCR DeNOx process

The DeNOx Process

Topsoe's SCR system, the DeNOx process, consists of three stages: ammonia injection, mixing, and catalytic reduction. See Figure 1 for the process flow diagram. First, a reducing agent, either anhydrous/aqueous ammonia or urea, is selected. There are several factors that should be considered before deciding which ammonia source to use. What form of ammonia is already on-site? What is the safest form to handle? Furthermore, which chemical can be more easily permitted for the site?

If anhydrous ammonia is used, it must be vaporized by a heater before being mixed with air and injected into the flue gas. Aqueous ammonia is typically vaporized beforehand, but it is possible to inject it directly into the flue gas.

A urea solution can be injected directly into the duct via nozzles when the distance from the injection point to the catalyst is sufficient for the decomposition of the urea into carbon dioxide and ammonia. As an alternative, several systems are available to convert urea to ammonia and carbon dioxide.

Proper mixing is even more critical when increased NOx conversion rates are required because NH_3/NO_x misdistribution becomes more important. Optimal operating temperature also is important.

The next step is to inject the ammonia and mix it with the flue gas. The key here is to ensure the homogenous mixing of chemicals. Location is an important factor: Some gas distribution will be provided by existing heating coils in the flue gas duct, and it is often helpful to place the ammonia injection grid (AIG) upstream of the heating coils to improve the mixing.

Proper mixing is even more critical when increased NOx conversion rates are required because NH_3/NO_x misdistribution becomes more important. Injection of the reducing agent will be through a piping grid containing several nozzles. Optimal operating temperature also is important, and proper location of the SCR will prevent the flue gas from having to be cooled or heated.

In many applications, Topsoe has found that the SCR unit should be supplemented with a static mixer, turning vanes, and a flow rectifier. Flow modeling utilizing scaled physical models or computational fluid dynamics (CFD) is used to assist in the design of the ductwork and guide vanes. The mixer is the safest solution for combining the ammonia, NOx, and flue gas and will ensure that the flue gas has a uniform temperature (at the expense of a minor increase in pressure drop). In high-dust applications, the dust must be evenly distributed across the catalyst surface, and provisions for cleaning should be made. Periodic use of soot blowers or sonic horns is recommended.

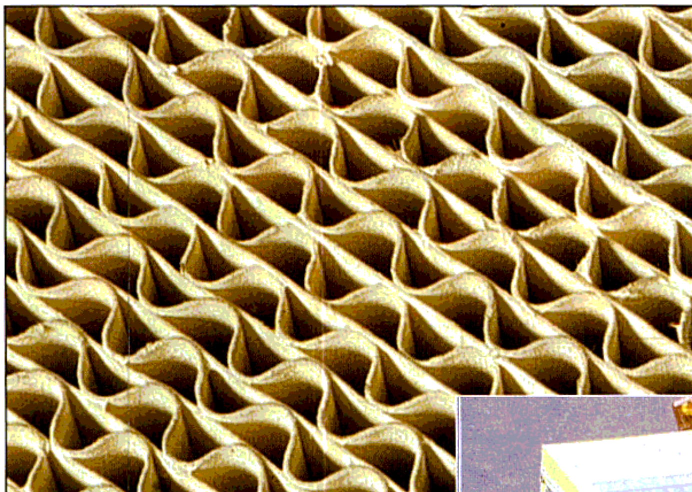


Figure 2. Close-up view of the DeNOx catalyst.

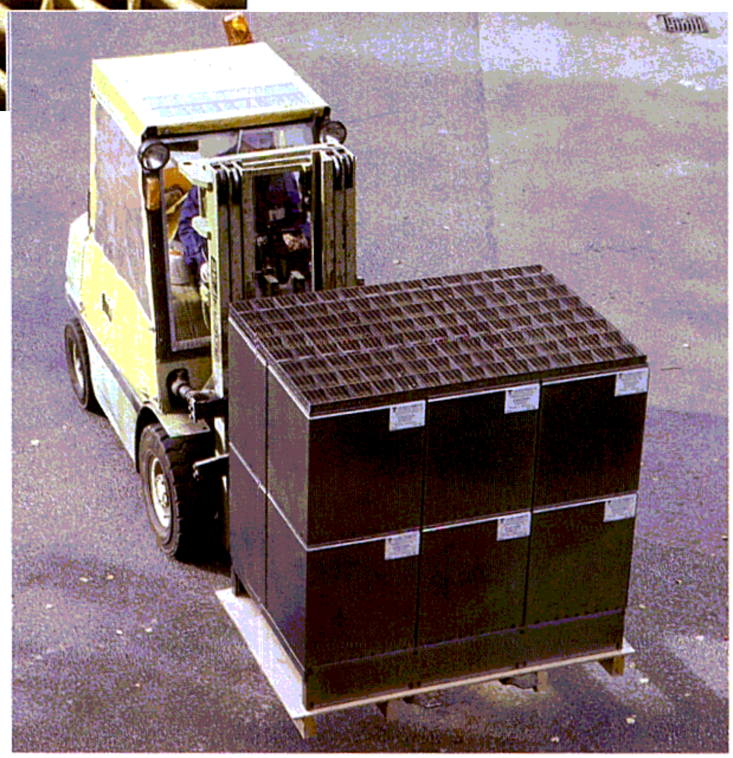


Figure 3. Assembled modules of the DeNOx catalyst are easy to handle and transport for installation.

Once the reducing agent is combined with the flue gas, the gas stream is ready for conversion. As the flue gas passes over the catalyst, nitrogen oxides and ammonia are converted to nitrogen and water.

To control the process, Topsoe and others use a forward signal from the inlet NOx concentration combined with a load signal indicating the flue gas flow. This is fine-tuned by the use of a feedback signal from the outlet NOx. This can also be supplied from the continuous emission monitoring system (CEMS) measurement in the stack. The process is fully automatic, and our experience has shown that operator intervention is rarely needed.

The DeNOx Catalyst

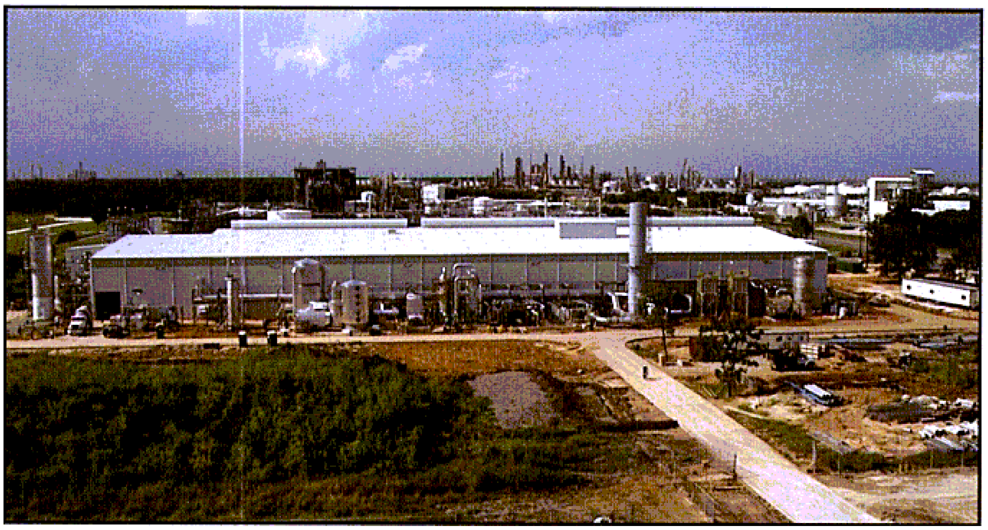
The vital part of the SCR unit is the catalyst. Topsoe has developed a monolith catalyst based on a fiber-reinforced titanium oxide (TiO_2) carrier, which is impregnated by vanadium oxide (V_2O_5) and tungsten oxide (WO_3).

These compounds are finely dispersed over the catalyst surface. The design produces a flexible, thermal shock and erosion-resistant catalyst with a high poisoning resistance, resulting in low deactivation rates and high mechanical durability. The openings in the corrugated structure are mainly determined by the particulate loading in the flue gas and, in some special cases, by limitations in the pressure drop. See Figure 2 for a close-up view of the catalyst.

Topsoe's manufacturing method results in a highly porous catalyst with a relative low content of V_2O_5, which renders a low-SO2 oxidation while maintaining a high DeNOx activity. This is important for applications in which SO_2 is present in the flue gas, as ammonium sulfates may precipitate on downstream cold surfaces, such as air preheaters and convection sections.

Another advantage of the catalysts' high porosity is its lower weight. The lighter catalyst allows for the SCR to be installed on top of the heater, and this results in a large reduction of structural steel and ductwork. Topose's overhead system also requires less space than a ground-level SCR that is placed beside the heater.

The operating temperature window for DeNOx catalyst is 350 °F-1,000 °F. The catalyst is active down to 300 °F, but at the lowest end of the temperature range the amount of catalyst needed increases, and if sulfur is present in the fuel, the formation of ammonium bisulfate could pose a problem. The optimal temperature is 650 °F-750 °F. At higher temperatures, the vanadia sites will start to sinter and the adsorption of ammonia to the surface will decrease.



Haldor Topsoe's newest DeNOx catalyst manufacturing facility, located in Houston, represents the company's continued dedication to leadership in catalyst development and manufacturing.

To facilitate handling, the catalyst is produced as cassettes, which are then assembled in modules (Figure 3). The modules will normally be used in large installations, where the number of cassettes in the module will be determined by the system and reactor layout.

Refinery Experience

Many refineries in the U.S. and Europe are facing large NOx emissions reductions over the next few years. After assembling a list of NOx-emitting equipment, a refiner and its contractors should review their options, taking into account the technology, catalyst availability, capital costs, and budget. Refiners have found it necessary to install SCRs in many of the large heaters, hydrotreaters, catalytic reformers, thermal crackers, fractionators, and utility boilers, cogeneration equipment, and FCC regenerators.

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Following are some examples of Topsoe's experience in refineries.

Hydrogen Plant Steam Reformer

For a U.S. West Coast refinery, Topsoe designed a 85,000 scfd hydrogen reformer equipped with a DeNOx SCR system. The addition of ammonia takes place through a number of nozzles positioned in the wasteheat section of the reformer. The catalyst is placed inside the duct. Ammonia is evaporated by use of a side stream of flue gas re-entering through the AIG. The direction of the flue gas flow is horizontal, which is a viable option when the flue gas does not contain dust. The system is operated at about 550 °F, with a NOx removal efficiency of greater than 95%, which results in NOx emissions of 1-2 ppm. Although the sulfur dioxide level is 20-40 ppm, with excursions up to 100 ppm, the unit continues to run well.

Residual Oil-Fired Boiler

An SCR unit was installed on a 205,000 Btu/h boiler in a European refinery in 1998. The boiler produces 131,000 lb/h of steam for both internal use in the refinery and the district heating system during the winter months. The boiler operates with residual fuel oil in the winter and on refinery fuel gas during the summer.

Three initial layers of catalyst were installed in two separate beds before the economizer section. Because of the dust content in the flue gas, Topsoe designed the flow direction to be downwards and installed steam-powered soot blowers above each catalyst bed. Injection of aqueous ammonia takes place through a number of nozzles, and static mixers ensure a homogeneous mixture of ammonia and NOx at the inlet of the catalyst. Since commissioning, the unit has exceeded the design NOx removal efficiency of 94% with an ammonia slip of less than 5 ppm.

Cogeneration

At an East Coast U.S. refinery, an SCR unit was installed on a 172-MWe cogeneration facility. The turbine is powered by gas, with diesel as back-up fuel. The flue gas flow direction is horizontal, and NOx emisions are lower than 1 ppm, with a maximum ammonia slip of only 2 ppm.

FCC Regenerators

One of the largest NOx emissions sources in a refinery is the FCC regenerator. The most economical place for an SCR installation in an FCC is upstream of the convection section. The main concern is that the off-gas contains FCC catalyst fines. In the worst cases, the particulate loading can be several tons per day.

Topsoe has many years of experience in the engineering and operation of DeNOx catalyst for high-dust applications, like coal-fired power stations. In these cases, it is possible to operate continuously with particulate loadings and order of magnitude higher than those encountered with an FCC. The chemical composition and particulate size distribution of the FCC fines are similar to those of the dust generated from coal-fired boilers.

Conclusion

Based on many years of experience in a wide range of applications, SCR units can be designed to meet today's stringent requirements for NOx removal and have limited impact on the rest of the process unit. Experience also has proved that SCR systems are easy to operate and require little attention from operators. NOx reduction requirements in the U.S. can be severe, but vary by location. For example, current regulations in the Houston area will require 90% reduction by 2007. There has also been increased interest from other parts of the world.

ABOUT THE AUTHORS

Marie P. Laplante joined Haldor Topsoe as technology sales manager in 2000. She represents several environmental technologies to manage sulfur and reduce NOx and VOC emissions. Laplante has more than 14 years of experience in the chemical industry in operations and project management. She holds a B.S. in chemical engineering from the University of Massachusetts.

Peter Lindenhoff joined Haldor Topsoe as DeNOx technology manager in 1999. He worked previously as a process engineer for both a Danish refinery and a Danish utility.

He has 10+ years experience with DeNOx systems. Lindenhoff holds a B.S. in physics and chemistry from the University of Aarhus, Denmark, and an M.S. in chemical engineering from the Technical University of Denmark.

Since the 1980s, Haldor Topsoe has designed and constructed SCR units around the world. By the end of 2002, Topsoe will have more than 100 SCR installations in the

United States alone.