Control refinery NO\textsubscript{x} with SCRs

Installing new technology provided this refiner with more flexibility with fuel gas and reduced total plant emissions

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New national environmental rules required the Preem Raffinaderi AB in Göteborg, Sweden, to limit and reduce nitrogen oxide (NO\textsubscript{x}) emissions that are present in the exhaust of furnaces and reactors. Upgrading the isomerization capacity of this refinery required raising energy requirements. The installation of a new boiler increased steam generation capability and added another NO\textsubscript{x} source. This project also raised fuel gas consumption. Increasing natural gas consumption for the boiler was not an economical option. Likewise, the extra boiler also increased NO\textsubscript{x} emissions.

This refiner elected to install a selective catalytic reduction (SCR) unit on the crude oil furnace to reduce plant-wide NO\textsubscript{x} emissions and enable burning fuel oil in place of natural gas. This case history describes how the processing goals of the revamp project were cost-effectively achieved while improving the environmental condition for the entire refinery.

Environment vs. economics. As part of an isomerization revamp project, Preem Raffinaderi AB developed a revised concept for NO\textsubscript{x} emission control. Before this revamp, several attempts were applied to reduce NO\textsubscript{x} emission, including primary and secondary approaches. One main option was changing fuel with externally supplied natural gas. However, during high demand periods (especially winter), the natural gas supply was limited and prices were higher. To limit natural gas consumption and reduce the dependency on fluctuating natural gas prices, refinery engineers proposed substituting residue fuel oil and refinery fuel gas for natural gas. This change was possible by installing a new SCR unit in connection with the existing crude oil furnace 2F-1.

Environmental situation at Preem refinery. The Preem refinery in Göteborg, Sweden, is subject to two different regulations on NO\textsubscript{x} emission. NO\textsubscript{x} emission for boilers is regulated by the Swedish Act (1990:613) “on Environmental Charges on Emissions of Nitrogen Oxides in Energy Production”). Conversely, Preem refinery also has to meet the guidance value annual cap of 365 tons of NO\textsubscript{x} emitted.

On several occasions, Preem refinery had already taken action, such as installing low-NO\textsubscript{x} burners on the fired heaters and boil-ers, water injection system in the gas turbine and installing an SCR unit on the catalytic reformer unit heaters and purchasing natural gas as additional fuel.

The isomerization unit revamp included installing a new molecular sieve unit for separating and recycling normal paraffins and retrofitting an existing catalytic isomerization unit. Both units raised steam consumption for heating purposes. Thus, a new steam boiler was installed. The annual NO\textsubscript{x} emission cap was not negotiable; the facility’s total NO\textsubscript{x} emission issue had to be treated separately.

The additional NO\textsubscript{x} emission from new steam boiler, fired with refinery fuel gas and natural gas, was abated with an existing five-year old SCR reactor. However, NO\textsubscript{x} emission from the crude oil furnace is not covered by the Swedish Act (1990:613). Hence, no secondary abatement equipment existed. The refiner awarded a turnkey project to install an SCR reactor. The goals of this project were to obtain a more flexible handling on fuel types (mainly a mixture of residue fuel oil and refinery fuel gas) and achieve more independence from using natural gas.
This project entailed the engineering, delivery and installation of the new SCR unit, including the ammonia injection system from an existing ammonia storage tank, new flue gas fan, as well as the instrumentation (including analyzers). To ensure high NOx removal efficiency at low ammonia slip, the environment contractor provided their expert knowledge in fluid dynamics and a new proprietary mixing system. The installation of the SCR unit, including civil works, was completed in 14 weeks, and the catalyst was installed in 3 days. The erection work was scheduled to minimize required downtime for the heater. All necessary tie-in work was done during the ordinary I&T turnaround in May 2003 (Fig. 1).

**The SCR unit.** The new SCR reactor is installed in series between the crude charge heater (2F-1) and downstream economizer (ECO-2). The SCR reactor is designed with a total of four layers at two different levels. Each catalyst layer has an effective height of 0.5 m. Subsequently, space for 1 m of catalyst in total at each level is available. Steam soot blowing is frequently executed once per week to remove dust and soot. Two layers at one level (in total 1 m of catalyst) were initially installed. Catalyst addition of one 0.5 m layer is foreseen at the second level after 24,000 operation hours. Since the unit is designed for installing additional layers, this work can be performed within a very short period and without any extraordinary heater shutdown.

The guaranteed NOx reduction is at least 90% with aqueous ammonia and an ammonia slip of maximum 5 ppm. The operational experience since the commissioning shows even better performance. The NOx reduction is normally controlled to 95% with an ammonia slip less than 1 ppm. In August, the plant has been operating continuously for more than 10,000 hrs since the June 2003 startup.

**Technology behind the SCR process.** SCR is a widely used technology reducing NOx emissions at high reduction efficiency. To abate NOx, ammonia (NH3) is injected into the flue gas, and subsequently passes through the catalyst. The reaction byproducts are pure nitrogen and water. The SCR unit consists of ammonia handling system, flow mixing and stratification system, reactor, solid catalyst, catalyst cleaning system and a control system as shown in Fig. 2.

NOx is primarily reduced according to this stoichiometry:

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad \Delta H = -1,627.7 \text{kJ/mol} \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad \Delta H = -757.9 \text{kJ/mol}
\end{align*}
\]

Since 90% of the NOx consists of nitrogen monoxide (NO), the first reaction is the most important one. A minor amount of NH3 and SO2 is oxidized in accordance with this reaction scheme:

\[
\begin{align*}
4\text{NH}_3 + 3\text{O}_2 & \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} \quad \Delta H = -1,268.4 \text{kJ/mol} \\
2\text{SO}_2 + \text{O}_2 & \rightarrow 2\text{SO}_3 \quad \Delta H = -196.4 \text{kJ/mol}
\end{align*}
\]

These reactions are exothermal; a small temperature rise of the flue gas occurs as it passes through the SCR catalyst.

An aqueous ammonia solution is often the preferred choice, either due to location of the system or for transport reasons. Caustic ammonia typically contains 25% NH3 by weight. Due to its low vapor pressure, caustic ammonia can be stored in atmospheric pressure tanks. Caustic ammonia can be directly injected into the flue gas with special nozzles using compressed air.

Converting/removing NOx depends on the amount of NH3 injected in relation to the NOx concentration of the flue gas. This ratio is expressed as NH3/NOx ratio on a molar basis. At higher NH3/NOx ratios, a higher NOx removal efficiency is obtained by increasing the amount of unconverted ammonia (NH3 slip) in the flue gas.

In the flue-gas duct, before the reactor, the NOx mass flowrate will vary across the cross-sectional area. Thus, it is very important to inject the NH3 in direct proportion to the NOx mass flow to obtain an optimal NOx reduction at a low NH3 slip. Fluid dynamics modeling is very useful for system design. This type of modeling can streamline the design of a mixing system.
The reactor is a fluid dynamic model that is, likewise, an optimized expansion of the cross-sectional area of the flue-gas duct. The reactor needs sufficient volume to fine-tune the gas residence time with the catalyst (Fig. 3). To optimize reaction conditions and replacement strategy, the total catalyst volume necessary is distributed over several layers. Typically, an empty spare layer is included for later catalyst addition. Addition of new catalyst instead of immediate replacement offers better utilization of the remaining catalyst activity before final replacement.

The SCR NO\textsubscript{x} removal catalyst typically uses a monolithic shape, thus minimizing pressure drop through the catalyst. Most catalysts are based on a high-porous titanium oxide carrier doted with the active compounds vanadium pentoxide and tungsten trioxide. An optimum temperature range between 250°C and 400°C (up to 500°C) and optimum temperature distribution in the flue gas enhance NO\textsubscript{x} removal efficiency.

The catalyst deactivates when exposed to industrial flue gases due to catalyst poisons or fly ash. Catalyst poisons are chemical compounds in the flue gas that directly react with the active compounds of the catalyst, irreversibly inhibiting its function. Several such substances are derived from different fuels, burning equipment or chemical processes. However, fly ash compounds do deposit on the catalyst, blocking its surface or plugging its channels. To minimize deactivation and plugging by fly ash, the catalyst should be frequently cleaned. This can be done by soot blowing with superheated steam.

Minimizing NH\textsubscript{3} consumption and slip is also important. Better control of the NH\textsubscript{3} system is desired. The control principle is based on that incoming and outgoing NO\textsubscript{x} concentrations are measured; thus setting the parameter efficiency for the unit. The NH\textsubscript{3} flowrate is controlled in proportion to meet the required NO\textsubscript{x} reduction (Fig. 2).

SCR system specification. For this project, two main goals were maintaining the highest flexibility for fuel choices (refinery fuel gas, as well as fuel oil) and limiting natural gas consumption. In addition, the new SCR unit was designed for high-temperature application (up to 470°C). Table 1 summarizes the design parameters for the SCR system in this refinery.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Specification</th>
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<tbody>
<tr>
<td>Max. gas flow, Nm\textsuperscript{3}/h</td>
<td></td>
<td>100,000</td>
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<tr>
<td>Temperature, °C</td>
<td></td>
<td>350–470</td>
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<tr>
<td>NO\textsubscript{x} inlet, ppm</td>
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<td>35–160</td>
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<tr>
<td>SO\textsubscript{2} inlet, ppm</td>
<td></td>
<td>250</td>
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<tr>
<td>NO\textsubscript{x} removal efficiency, %</td>
<td></td>
<td>&gt; 90</td>
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<tr>
<td>NH\textsubscript{3} slip, ppm</td>
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<td>&lt; 5</td>
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<tr>
<td>Pressure drop, mbarg</td>
<td></td>
<td>&lt; 3.7–10.6</td>
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<tr>
<td>Lifetime guarantee, h</td>
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<td>24,000</td>
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SCR catalyst. In this application the SCR catalyst is based on a corrugated fiber-reinforced titanium-dioxide (TiO\textsubscript{2}) carrier (Fig. 4). The carrier is homogeneously impregnated with the SCR-active components, tungsten trioxide (WO\textsubscript{3}) and vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}).

The unique manufacturing process yields a catalyst with a very porous structure. Active components are finely dispersed on the entire high-area surface, consequently having many active sites. The low specific mass of the catalyst obtained from the high-porous macro-pore structure minimizes the SO\textsubscript{2} oxidation activity. Result: A catalyst with a remarkably low SO\textsubscript{2} oxidation-to-SCR activity ratio.

The SCR catalyst is delivered in standard-sized single cassettes type A (Fig. 5). These cassettes are stackable and can easily be moved around using the lifting holes, as the weight is relatively low at approximately 50 kg.

The initial installation consists of two layers of 64 single cassettes each at one level, and was installed in three days. The hydraulic diameter of the catalyst channels was chosen to be at 4.1 mm based on the fly ash content of the flue gas of approximately 75 mg/Nm\textsuperscript{3}. The correct choice of the hydraulic diameter helps optimize the NO\textsubscript{x} removal efficiency at a moderate level of pressure drop increase over the catalyst lifetime due to fouling.

Experience with the upgraded NO\textsubscript{x} control concept. Since June 2003, the SCR NO\textsubscript{x} removal plant at Preem refinery’s 2F-1 furnace has successfully operated for more than 10,000 hrs. This new plant is a very effective tool in complying with the total NO\textsubscript{x} emission cap requirements for Preem refinery. In addition, the system enables minimizing natural gas consumption, especially during the winter period when supplies are limited and prices are high. This plant performance has exceeded the guarantee.

As shown in Fig. 6, the guaranteed NO\textsubscript{x} removal efficiency >90% can easily be met at minor NH\textsubscript{3} slip, independent of the choice of the fuel type. However, NO\textsubscript{x} removal efficiency is not the reduction criteria in any case. The main objection is the added reductions to the total NO\textsubscript{x} emissions of the refinery. This explains why the NO\textsubscript{x} removal efficiency is 80% one time and 95% at another time. NO\textsubscript{x} removal efficiency also depends on the NO\textsubscript{x} inlet value, which is defined by the fuel mixture of the furnace. In case of rich-fuel gas operation, the NO\textsubscript{x} inlet value of the SCR NO\textsubscript{x} removal plant is essentially lower, as observed in the period from June to October 2003 (Fig. 6). However, the SCR plant has proven a high flexibility in maintaining a high NO\textsubscript{x} removal efficiency at widely varying NO\textsubscript{x} inlet concentrations.

Since startup, this SCR plant has only faced some minor availability problems with the electrical motor of the flue gas...
fan and failures of one of the NH₃ injection pumps (Fig. 6: blanks in the graph of DeNOₓ efficiency and NOₓ inlet concentration). However in all cases, the SCR plant instantly met the required NOₓ removal efficiency after remedy. The pressure drop through the catalyst had been up to 3.1 mbarg, which is essentially lower than guaranteed. No increase in pressure drop had been observed.

**Overview.** Implementing the revised NOₓ emission control plan for Preem refinery, including the installation of a new SCR NOₓ removal unit, was a success. Preem refinery needed to avoid increasing the natural gas to the refinery in the wake of the isomerization plant revamp. Additionally, available fuels such as residue fuel oil and refinery fuel gas can be used in a flexible and environmentally friendly manner. For the moment, this SCR DeNOₓ unit serves as a buffer to the overall NOₓ emission balance of the refinery, compensates for higher NOₓ emissions from other sources, without exceeding Preem refinery’s total NOₓ emission cap. HP

**LITERATURE CITED**


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**Fig. 5** Schematic demonstration of a standard size cassette type A.

**Fig. 6** NOₓ removal efficiency since start-up of the SCR DeNOₓ plant in June 2003.

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**Martin Schröter** graduated as process engineer in 1987 with a M. Sc. degree from the University of Clausthal in Germany and holds a PhD degree in chemical engineering. He worked in process engineering in the chemical industry prior to occupation with SCR DeNOₓ technology in the sales and marketing division of Haldor Topsøe A/S in Denmark. Currently, he is involved in developing new business opportunities for SCR DeNOₓ applications.