Implementation of SCR DeNOx technology on coal-fired boilers

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Introduction

The emission of nitrogen oxides, or NOx, is a major global pollution problem. The damaging effect of nitrogen oxides on health and environment is substantial. NOx contributes to acid rain and ensuing destruction of coastal and fresh-water life, and to forest death. NOx further helps form ground-level ozone, bringing about the health-threatening yellowish smog in urban areas. Fossil-fuel combustion produces several oxides of nitrogen, most notably nitrogen oxide, NO, and nitrogen dioxide, NO$_2$. Various technologies have been developed to control emissions of nitrogen oxides, working by either reducing the initial formation or removing the produced nitrogen oxides from the flue gas.

At high temperature gaseous ammonia will react with nitrogen oxides to produce elemental nitrogen and water vapour. In the presence of a catalyst, a lower reaction temperature, typically 250°C-450°C, can be used. Both versions of the process – with and without a catalyst – are used commercially. They are known as SCR, Selective Catalytic Reduction, and SNCR, Selective Non-Catalytic Reduction, respectively. The NOx removal rates with SNCR are limited, typically around 50 per cent whereas reduction of NOx over a vanadium catalyst can yield removal rates in excess of 95 per cent.

The SCR process is by far the predominant choice of technology. It has been applied to a variety of applications since the 1970s including flue gases from boilers, refinery off-gas combustion, gas and diesel engines, gas turbines and chemical process gas streams.

Coal is an important source of fuel at power plants worldwide, also in P.R. China that has vast coal resources. With the increasing number of coal-fired power plants that results from the rapid-growing economy, flue-gas cleaning becomes increasingly important to protect the environment.
# Contents:

The Selective Catalytic Reduction process ................................................................. 3  
The SCR catalyst ........................................................................................................... 4  
Oxidation of SO₂ ........................................................................................................... 5  
Catalyst degradation .................................................................................................... 9  
Experience .................................................................................................................... 11  
Yangcheng Thermal Power Plant ................................................................................ 11  
Guangdong Guohua Yuedian, Taishan Thermal Power Plant ........................................ 12  
Fujian Huadian Kemen TPP ......................................................................................... 14  
Taiyuan Iron and Steel Co., TISCO ........................................................................... 14  
Conclusion ................................................................................................................... 16
The Selective Catalytic Reduction process

In the Selective Catalytic Reduction (SCR) process, NOx is reduced by ammonia to form harmless nitrogen and water vapour without creating any secondary pollutants.

The main components of the SCR system basically consist of a reactor with the catalyst and an ammonia storage and injection system. In coal-fired power plants, the SCR system is normally located between the boiler economiser and the air preheater to provide an optimum temperature of 350°C-400°C in the DeNOx reactor. Locating the SCR system after dust removal and flue gas desulphurisation requires costly reheating of the flue gas and is only applied when special considerations points to this solution, e.g. lack of space or high levels of catalyst poisons in the flue gas.

The NOx-reducing agent can be either anhydrous ammonia under pressure or it can be an aqueous ammonia solution at atmospheric pressure. A solution of urea can also be used if warranted by safety. The ammonia is evaporated in a heated evaporator and is subsequently diluted with air or a flue gas side stream before it is injected into the flue gas duct upstream the SCR reactor.

The SCR process requires precise control of the ammonia injection rate. Insufficient injection results in low conversion of NOx and an injection rate which is too high results in an undesirable release of unconverted ammonia to the atmosphere referred to as ammonia slip.

The injection of the ammonia-air mixture normally takes place through a grid of nozzles in order to achieve a uniform mixing of the ammonia with the flue gas. A homogeneous distribution of the ammonia in the flue gas is of crucial importance to achieve efficient NOx conversion. Uneven ammonia distribution can cause poor performance of the SCR unit because some portions of the flue gas are over-treated with ammonia, resulting in higher ammonia slip whereas other portions of the flue gas is under-treated, resulting in a lower than designed DeNOx efficiency. The requirements to mixing become increasingly important as demands to NOx removal efficiency and low ammonia slip become more stringent. Today, 90-95% NOx reduction with just 2 ppm ammonia slip is not unusual.

To ensure efficient optimum mixing, the distance from the AIG (Ammonia Injection Grid) to the catalyst should be as long as possible. Long mixing distance is costly and therefore a system of one or more static mixers may be placed in the flue gas duct to enhance the mixing. However, static mixers introduce an additional pressure loss which is not desirable.

Topsøe has developed a proprietary mixing system, the STARMIXER® (Figure 1), consisting of circular disks with four peaks forming a star. The STARMIXER® is installed angled in the flue-
gas stream which creates vortices behind the disks. This provides a close-to-perfect mixing with a minimal pressure loss.

![Figure 1: The Topsøe proprietary STARMIXER® system as seen in a flow model](image)

A prerequisite for the catalyst to perform at its best is the proper design of the SCR reactor, gas channels and the ammonia injection and mixing system. In a high-dust DeNOx unit, care must be taken to ensure an even gas flow rate and fly ash distribution across the reactor in order to avert damage to the catalyst in the form of plugging or erosion.

Use of gas-flow modelling by Computational Fluid Dynamics (CFD) or in physical scale models has proven an efficient and often necessary tool to accomplish these goals. The general objectives of the model work are to ensure a high degree of velocity uniformity upstream the ammonia injection and at the entrance to the catalyst layers and to verify proper mixing of ammonia into the flue gas. The model work further assists in optimising the layout of ducts, reactor and necessary flow control devices to minimise overall pressure loss and to ensure that formation of dust deposits is not be promoted.

The SCR catalyst

Laboratory reactor experiments have been carried out with process conditions that correspond to those prevailing in commercial units. The SCR catalyst material is based on a porous titanium-dioxide (TiO₂) carrier material in which the catalytically active components in the form of vanadium pentoxide (V₂O₅) combined with tungsten trioxide (WO₃) are dispersed. To provide a large gas contact area with a minimum pressure loss, the catalysts are provided as monolithic elements containing a large number of parallel channels. Topsøe’s DNX® catalyst is delivered in standard-sized single cassettes. The cassettes are grouped in modules on a metal frame for easy installation in the SCR reactor (Figure 2).

The catalyst is offered in a number of different models with varying channel size (often referred to as pitch), wall thickness and varying chemical composition adapted to specific operating con-
The choice of pitch and wall thickness for a given SCR installation is determined mainly by the dust content of the flue gas. For low-dust applications, channel sizes of 2-4 mm with e.g. 0.4 mm wall thickness are selected. Larger-channel catalysts (7-10 mm pitch) with minimum 0.8 mm wall thickness should be selected for operation in dust-laden gases in units on coal-fired boilers.

Figure 2 Monolithic catalyst elements are grouped in modules on a metal frame for easy installation

The required catalyst volume and thereby the size of the reactor depends on the catalyst activity, the NOx concentration in the flue gas and the desired NOx reduction efficiency, the acceptable ammonia slip and the operating temperature.

Oxidation of SO₂

Sulphur is an omnipresent component of both coal and oil and results in a significant environmental impact when combusted. At the high temperatures found in utility boilers virtually all fuel-bound sulphur is released as sulphur dioxide, SO₂ and a small fraction, generally 1-2%, of the SO₂ is further converted to sulphur trioxide, SO₃, in the combustion process.

It is a general fact that the active component in the SCR catalyst, vanadium pentoxide, is also catalysing the formation of SO₃ from SO₂. The SO₃ will react with residual ammonia to form ammonia bisulphate, ABS, which can cause fouling and corrosion of the air preheater. Also, SO₃ will react with water vapour as the flue gas cools down and forms sulphuric acid mist which
cannot be removed in common FGDs and therefore ends up in the stack as a visible, opaque plume.

Obviously, the amount of SO₃ formed over the catalyst should therefore be minimised. The choice of SCR catalyst and the selection of the operating conditions are therefore crucial to the power plant owner.

The SO₂-oxidation reaction occurs on the catalyst according to the following reaction scheme:

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \]

At the SO₂ concentrations encountered in practise, the reaction can be considered as a 1st order reaction. This means that the amount of SO₃ formed across the catalyst is directly proportional to the partial pressure of SO₂ or, in other words, that the percentage of SO₂ converted is independent of the SO₂ concentration in the flue gas. The reaction rate depends strongly on temperature, the higher temperature, the higher rate of SO₂ oxidation. The general expression can be written:

\[ -r_{\text{SO}_2} = k \cdot P \cdot c_{\text{SO}_2} \cdot \exp\left(-\frac{E}{RT}\right) \]  \hspace{1cm} (1)

in which P denotes the total pressure, k is a constant which depends on the catalyst type, \( c_{\text{SO}_2} \) is the concentration of SO₂, E is a constant (the so-called activation energy), R is a constant (“gas constant”), and T is the absolute temperature.

From the reaction rate equation follows that total pressure has a large influence on the rate of SO₂ oxidation; at 3 bar the SO₂ oxidation is three times the SO₂ oxidation at 1 bar pressure. The exponential temperature dependency corresponds roughly to a doubling of the SO₂ oxidation per each 35-40°C increase in temperature.

SO₃ in the flue gas will react with residual ammonia, forming ammonium bisulphate, ABS:

\[ \text{SO}_3 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 \]

The amount of ABS formed and thereby the ABS dew point depends on the concentrations of SO₃ and ammonia. As an approximation the ABS dew point increases by 7°C for each doubling of the concentration of either of the two components. This means that if the concentration of SO₃ increases to the double, then the ABS dew point will be maintained if the ammonia concentration is simultaneously halved.

As shown in Figure 3 there are two possible ways of controlling the SO₂ oxidation: By varying the percentage of vanadium in the catalyst or by limiting the temperature. Most often the tem-
perature is not a variable in power plants and the designer of an SCR DeNOx unit will therefore have to carefully adjust the catalyst properties to reach his goal.

Figure 3 explains the designer's dilemma: Reducing the SO$_2$ oxidation by lowering the percentage of vanadium in the catalyst also lowers the specific activity and the total catalyst volume will therefore increase and the plant become more costly.

As illustrated in Figure 4 the DeNOx reaction takes place on the internal surface in the pores of the catalyst and, by some approximation, the activity, $A_{\text{DeNOx}}$, becomes

$$A_{\text{DeNOx}} = k_1 \times A_S \times C^a \times \eta \quad (2)$$

$A_S$ denotes the active superficial area, further increased by the porosity of the titanium dioxide, $C^a$ is the percentage of vanadium in the catalysts raised to a power less than 1, expressing that the DeNOx activity is not directly proportional to the vanadium content of. $\eta$ is an effectiveness factor accounting for the resistance towards diffusion of NOx and ammonia to the catalyst's active sites.

In contrast, the oxidation of SO$_2$ is not limited by diffusion and SO$_2$ can diffuse into the clusters of primary TiO$_2$ particles which appear as islands in the catalyst, cf. Figure 4. The oxidation thus takes place in the entire catalyst mass and the SO$_2$-oxidation activity, $A_{\text{SO2}}$, can be expressed by
\[ A_{SO_2} = k_2 \times W \times C \]  

(3)

in which \( A_{SO_2} \) is the activity towards \( SO_2 \) oxidation and \( W \) is the bulk density of the catalyst. It follows from the above that the best possible SCR catalyst for a coal-fired power plant minimises the ratio \( A_{SO_2}/A_{DeNO_x} \):

\[ \frac{A_{SO_2}}{A_{DeNO_x}} = \frac{k_2}{k_1} \times \frac{W}{A_S} \times C^{1-a} \times \frac{1}{\eta} \]  

(4)

A special way of manufacturing the Topsøe DNX® catalyst allows for careful control of the pore structure within the catalyst which is optimised with a tri-modal pore-size distribution as shown in Figure 4.

By having large macro-pores in addition to the meso- and micro-pores the access to the interior of the catalyst is enhanced and the effectiveness factor \( \eta \) is thereby maximised. The elaborated pore system further increases the porosity, providing a high ratio between the active surface area and the catalyst bulk density, i.e. \( A_S/W \). The combined effect gives the lowest possible \( SO_2 \) oxidation as per equation (4).
Topsøe is capable of tailor-making catalysts for any level of sulphur in the fuel and can therefore provide the best compromise between NOx removal and SO$_2$ oxidation. Topsøe has demonstrated excellent performance together with low SO$_2$ oxidation under industrial conditions and has provided guarantees for SO$_2$ oxidation down to 0.1%.

**Catalyst degradation**

In high-dust SCR units on coal-fired boilers a gradual degradation of the catalyst with loss of activity occurs, primarily due to exposure to the fly ash. A number of factors contribute to the deterioration of the catalyst performance, determining its useful life:

- Chemical impact of fly ash components on the active sites, usually referred to as poisoning.
- Fouling of the catalyst surface by very fine ash particles, physically blocking the access to the active sites of the catalyst or reducing the active surface area
- Plugging of catalyst channels reducing the effective volume of the installed catalyst
- Erosion by abrasive components in the fly ash in case of inappropriate flue gas velocities in the SCR reactor

Obviously, an extensive knowledge of how these factors affect catalyst performance is essential in selection of the optimum catalyst type.

Chemical poisoning is formally chemisorption of components on the active sites of the catalyst resulting in loss of activity. Aerosols of alkali metals as sodium and potassium are of prime concern.

Fouling is a physical blockage of the catalyst pore system by aerosols or other sub-micron ash particles. Pore condensation of gaseous compounds of e.g. arsenic from the flue gas can also block the access to the active sites of the catalyst. Some Chinese coals and Powder River Basin (PRB), a US sub-bituminous coal-type, have very high contents of calcium oxide, being sulphated in the SO$_2$/SO$_3$ containing flue gas and forming fouling layers of calcium sulphate on the catalyst surface.

The ability of a catalyst to accommodate poisons without serious decline of activity strongly depends on the porosity and the pore structure of the catalyst. The catalyst should not only provide a high porosity but preferably have a broad pore-size distribution, i.e. the porosity should be made up from pores of different sizes.

Figure 5 shows how a catalyst being exposed to calcium containing fly ash has developed a dense layer of calcium sulphate which impedes diffusion of NOx in the flue gas to the active sites in the interior of the catalyst.
The conversion of NOx on a catalyst takes place on both the inner and outer surfaces of the catalyst. As the outer catalyst surface easily fouls by calcium, access to the interior becomes even more important as illustrated in Figure 6.

The ability of the Topsøe DNX® catalyst to withstand fouling with fly ash relies on a key characteristic of the catalyst: The tri-modal pore structure. The larger-sized pores, macro pores, serve to ensure access to the active interior of the catalyst even if large amounts of poisons have been deposited on the catalyst. They further enhance gas-phase diffusion of NOx and ammonia into the catalyst and thereby the overall catalyst activity.

The presence of medium-size pores, meso-pores, ensures an efficient internal distribution of the reactants to the immense network of micro-pores which provide a very high active surface area necessary for the catalyst activity. In comparison, a catalyst with a homogeneous micro-pore structure becomes effectively blocked by fouling agents whereas in a catalyst with a tri-modal pore structure, access remains available via macro- and meso-pores.

Topsøe’s DNX® catalysts have been developed to maximise the resistance of the catalyst towards calcium in fly ash. The unique pore structure is a result of selected titania raw materials combined with controlled drying and calcination processes in a fully automated catalyst manufacture.
Experience

A few examples from Haldor Topsoe’s SCR DeNOx projects on coal-fired boilers in P.R. China may illustrate some of the design issues treated above.

Yangcheng Thermal Power Plant

Yangcheng TPP Unit 8 is a 600 MWe boiler at Yangcheng, Shanxi Province. It burns anthracite from Shanxi Yangcheng Shine mine. The boiler has been equipped with SCR DeNOx and was commissioned in first half of 2007. Haldor Topsoe A/S was the supplier of the catalyst and system design including physical flow model tests for verification of design.

The design of the SCR system includes a reactor bypass and posed a challenge in the system design to avoid ash drop-out in front of the bypass dampers and in the reactor. To ensure even flow distribution in the reactor and also at the air preheater inlet to minimise the risk of ash drop-
out at low-load conditions, the model work showed it necessary to install flow conditioning devices in the reactor outlet duct.

1. ECO outlet
2. Upstream AIG
3. Downstream AIG
4. Downstream last catalyst layer
5. APH inlet flange

Figure 7: The DeNOx reactor bypass posed a challenge in system design and required careful model work.

Guangdong Guohua Yuedian, Taishan Thermal Power Plant

The Taishan TPP is a 5 × 600 MWe coal-fired power station firing domestic coals. Unit 5 includes an SCR system which was commissioned in 2006. KC Cottrell was the system supplier and Haldor Topsøe A/S was the supplier of the catalyst and system design including physical flow model tests for verification of design of critical components.

Special care was taken in the selection of catalyst due to a very high calcium content of the ash (approximately 29% CaO). As described above, a catalyst with a tri-modal pore structure has a high resistance to fouling from high calcium content in the ash. A pore structure that includes macro pores ensures access to the active sites even with a large amount of gypsum on the surface of the catalyst.

The ash content of the coal ranges from 8% to 13%. This ash content is relatively low, resulting in approximately 15 g/Nm³ fly ash in the flue gas to the SCR. However, due to the very high calcium content, a relatively larger catalyst pitch, 7.2 mm, was installed to minimise the risk of plugging.
Significant design issues had to be addressed for the reactor layout, chief among them the design of the ammonia injection grid (AIG). The design of the unit was targeted for 94% NOx reduction with just 3 ppm ammonia slip. Consequently, the distribution of the ammonia into the flue gas needed to closely match the distribution of NOx, as the reaction proceeds on a 1:1 molar basis. The use of Topsoe’s STARMIXER® system combined with careful flow modelling (Figure 8) enabled design of a system pressure loss of less than 339 Pa in spite of the high mixing efficiency required to achieve a NOx conversion of 94%.

A performance test in November 2006 demonstrated a NOx conversion at BMCR load of 93-95% with approximately 1 ppm ammonia slip, well within the guarantee performance. Inspection of the SCR after months of operation showed no signs of fly-ash deposits (see Figure 9) demonstrating that close-to-perfect flow conditions have been achieved in the reactor.
Fujian Huadian Kemen TPP

Units 3 and 4 at the coal-fired Fujian Huadian Kemen power plant are being retrofitted with SCR DeNOx, scheduled for start-up in 2008, by Shanghai Longking Environmental Protection Co., Ltd. As for the Taishan TPP, the STARMIXER® has been applied for the ammonia-flue gas mixing to achieve an efficient mixing of the ammonia into the flue gas with a minimum of pressure drop. An ammonia-to-NOx ratio distribution with less than 3% standard deviation at the inlet to the catalyst layer was demonstrated by CFD modelling as well as in a gas-flow model study.

Taiyuan Iron and Steel Co., TISCO

The Taiyuan Iron and Steel Company, TISCO, thermal power station in Shanxi Province comprises two 300 MWe coal-fired boilers. The boilers are being retrofitted with SCR DeNOx plants, scheduled for commissioning in 2008. Guangzhou Tinci Sahne Environmental Engineering Co., Ltd. supplies the system while Topsøe has been the supplier of the SCR catalyst, the basic engineering design including flow modelling by CFD as well as in a scale model, and the STARMIXER® ammonia injection mixing system.

The design coal has a high ash content resulting in very high dust content in the flue gas, up to 40 g/Nm³. This was taken into consideration in the design of the reactor and in the selection of catalyst. A high dust load in the SCR reactor implies a risk of erosion of the catalyst. However, erosion can in far most cases be ascribed to improper flow conditions in the SCR reactor, causing:
- areas high gas velocity
- areas with high ash load
- areas in which the flow angle deviates significantly from vertical

The wear of the catalyst is proportional to the gas linear velocity raised to the 3rd power. The reactor cross section was therefore designed to provide a relatively low velocity, approx. 4.0 m/s. It is not unusual to apply a velocity of 5 m/s or more in high-dust SCR's with a more modest dust content of 15-20 g/Nm³.

Because of the high amount of fly ash, Topsøe’s DNX-HD catalyst type with a 9-mm pitch and a 1.0-mm wall thickness was selected. This large-pitch catalyst has a high void fraction which minimises a risk of plugging of the catalyst channels: The high void combined also serves to minimise any risk of erosion by reducing the linear gas velocity in the catalyst channels.

The SCR system at TISCO furthermore has been designed with strict requirements to the flow conditions at the inlet to the catalyst layers, allowing a maximum ±25% deviation from average linear velocity and a maximum 20° deviation from vertical flow direction. The flow model work provided the design of flow guide vanes to achieve these goals and verified that the conditions are fulfilled. Homogenizers are inserted at the 90° bend at the top of the riser to guide the gas flow, minimize pressure losses, and retain uniformity of flow at inlet to the reactor. A 10-vane cascade was found to be necessary to obtain a sufficiently uniform velocity field at inlet to the 1st catalyst layer. A side-view drawing is shown in Figure 10.

**Figure 10:** Flow conditioning devices in the SCR system at TISCO TPP
Conclusion

NOx emission regulations become ever stricter. To achieve high DeNOx efficiencies with minimum ammonia slip in SCR DeNOx units operating in high-dust position on coal-fired boilers, careful selection of the catalyst model and proper system design is crucial.

High ash contents of the coal must be considered in selection of catalyst channel size (pitch) and wall thickness. Presence of calcium or other constituents that can chemically or physically impact the catalyst must be considered in prospected deactivation rates. A highly porous catalyst with a diverse pore structure as the Topsoe DNX® catalysts provides a high tolerance to poisoning.

Gas flow modelling is a necessary tool in verifying the proper design of high-dust SCR units. The modelling can be made by Computational Fluid Dynamics (CFD) modelling or by the use of physical scale models. The application of physical flow model study in the design phase will accomplish verification of uniform gas velocity distribution and layout of necessary flow conditioning devices and evaluation of dust precipitation and distribution.