Combating NOx from refinery sources using SCR

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1   Summary

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 resulting in deforestation and destruction of coastal and fresh-water life. NOx further reacts in the atmosphere to form ground-level ozone, bringing about the health-threatening yellowish smog in urban areas.

Various technologies have been developed to control emissions of nitrogen oxides. The SCR process is by far the predominant choice of technology. The SCR process works by reacting the NOx with gaseous ammonia over a vanadium catalyst to produce elemental nitrogen and water vapour. 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. In general the SCR is the technology which gives the highest possible NOx removal rates, in excess of 95%. In case of demand of Best Available Control Technology SCR will be the chosen technology.

In recent years, environmental authorities in the USA and Europe as well as in the Middle East have given reduction of NOx emissions from various sources top priority with ever-more-strict environmental regulations that control NOx emissions. The SCR technology is well able to handle such tighter regulations in the future. Today it is possible to achieve NOx removal rates higher than 98% with an ammonia slip lower than 2 ppm.

NOx emissions from petrochemical plants primarily originate from utility boilers, co-generation units, process heaters, steam methane reformers, ethylene cracking furnaces and FCC regeneration units. Topsøe is a supplier of catalyst and technology for environmental processes and has catalysts for NOx reduction in operation in such units in several refineries in the USA and Europe. The paper will deal with design and operational issues for NOx reduction units and will present actual operating experience from a number of plants.

In the past there has been reluctance from the plant operators to install SCR's because of risk of up-set in the units caused by the SCR's. The results from SCR's installed in the process industry are that they are very reliable and actually have very low running and maintenance costs. By selecting SCR, plant operators are getting a very forgiving system. E.g. the burners in furnaces will not have to be tuned to low NOx but can instead be tuned to optimum combustion and stable flames which gives a safer and more reliable operation of the furnaces.

SCR is the best proven technology to achieve maximum NOx reduction in ethylene cracking furnaces. As ethylene furnaces cycle between olefin production and decoking, the SCR system is able to smoothly accommodate the transition. This back-end technology offers 95%+ NOx reduction across a wide operating range requiring little or no maintenance while essentially remaining transparent to the rest of the furnace operation.

Deactivation of the catalyst has to be taken into account in the SCR design. High metal temperature in ethylene cracking furnaces and steam methane reformers release chromium that results in masking of the catalyst by chromium accumulation at the surface and in the pores of the catalyst. The deactivation can be minimised by applying a catalyst with a pore structure that reduces this effect. The Topsøe DNX$^®$ SCR catalyst is developed with a tri-modal, highly porous pore structure which enables the catalyst to tolerate high levels of chromium.

A further advantage of a high-porosity catalyst is that this assists in providing a very low SO_2 oxidation, an undesired side reaction of the SCR catalyst. When using high-sulphur heavy fuel oil, minimising the formation of SO_3 is of crucial importance. Operational experiences show that with the use of a properly designed SCR reactor and catalyst, very low NOx emissions are possible in FCC units that have high NOx, SOx and particulates in the flue gas. Several years of uninterrupted, trouble-free operation has been achieved even with the catalyst in a high-particulate atmosphere without an ESP upstream the SCR.

In other refineries installation of SCR's on the highest NOx-producing units serve as a buffer to the overall NOx-emission balance of the refinery, allowing for compensation of higher NOx emissions of other sources, without exceeding the refinery's cap of total NOx emission.

The present paper compiles and updates earlier papers and publications by Haldor Topsøe[1,2,3].

2   Introduction

NOx is the generic term for nitrogen monoxide, NO, and nitrogen dioxide, NO_2. 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

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removal rates with SNCR are limited, typically around 50% whereas reduction of NOx over a vanadia-titania catalyst can yield removal rates in excess of 95%.

The SCR process is by far the predominant choice of technology. It is widely used in 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.
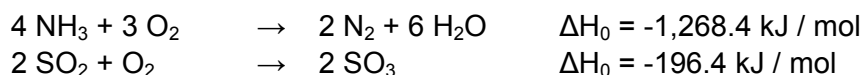
Nitrogen oxides are primarily reduced according to the following stoichiometry:

$$4\ NO + 4\ NH_3 + O_2 \quad \rightarrow \quad 4\ N_2 + 6\ H_2O \qquad \Delta H_0 = -1{,}627.7\ kJ\ /\ mol$$
$$NO + NO_2 + 2\ NH_3 \quad \rightarrow \quad 2\ N_2 + 3\ H_2O \qquad \Delta H_0 = -757.9\ kJ\ /\ mol$$
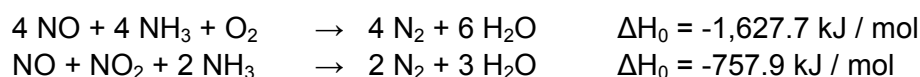
Nitrogen monoxide, NO, is the primary component in flue gases, meaning that the first reaction is the more significant one. As seen, NOx and ammonia react in a 1:1 atomic ratio.

A minor amount of NH_3 and SO_2 is oxidised in accordance with the following reaction schemes:

$$4\ NH_3 + 3\ O_2 \quad \rightarrow \quad 2\ N_2 + 6\ H_2O \qquad \Delta H_0 = -1{,}268.4\ kJ\ /\ mol$$
$$2\ SO_2 + O_2 \quad \rightarrow \quad 2\ SO_3 \qquad \Delta H_0 = -196.4\ kJ\ /\ mol$$

The reactions are exothermal, resulting in a small temperature rise of the flue gas having passed the DeNOx catalyst.

3   The SCR DeNOx process and catalyst

3.1   The SCR process

The main components of the SCR system basically are composed of a reactor with the catalyst, an ammonia storage and injection system and a control system. Figure 1 shows the typical Process Flow Diagram of an SCR system. The abatement of nitrogen oxides results from injection of ammonia into the gas and subsequent passage through the catalyst, forming elemental nitrogen and water. Ammonia is injected into the gas at slightly above the molar equivalent ratio as its NOx concentration. The ammonia injection rate is automatically controlled by combining feed-forward control based on amount of NOx to the SCR DeNOx unit and feedback control measuring outlet NOx downstream of the catalyst.
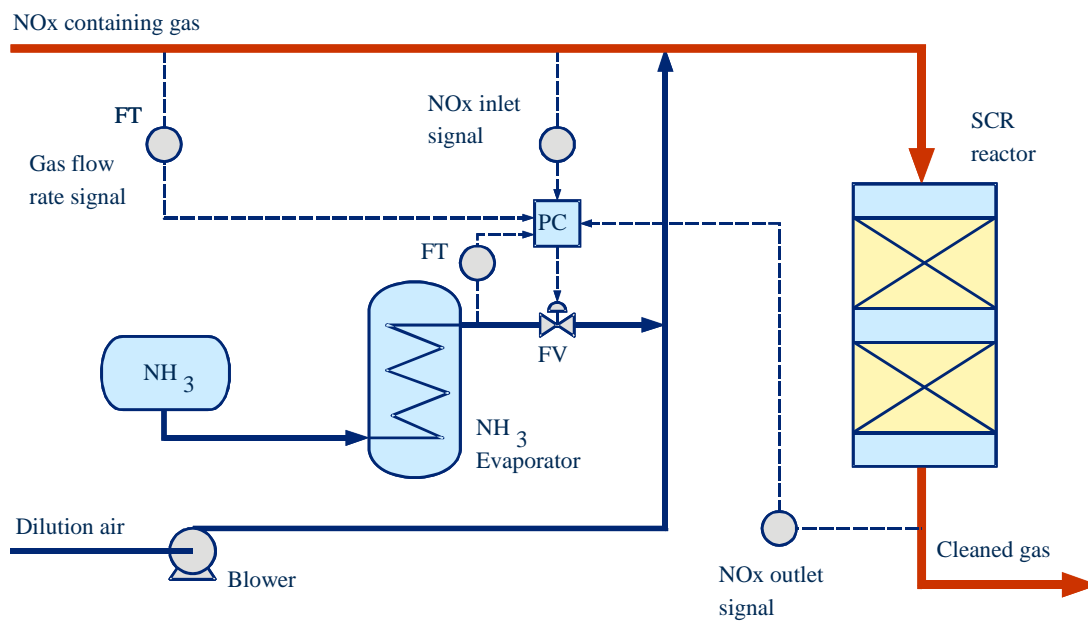
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Figure 1   Basic flow diagram for an SCR DeNOx System

The ammonia reducing agent can be either anhydrous ammonia under pressure or it can be an aqueous ammonia solution (typically 25% by weight) at atmospheric pressure. A 30-40% solution of urea which decomposes into ammonia and CO_2 at high temperature can also be used if warranted by safety. The ammonia is evaporated in a heated evaporator and is subsequently diluted with air 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. In the flue gas duct, before the reactor, the NOx mass flow rate will vary across the cross section area. A homogeneous distribution of the ammonia in the flue gas is of crucial importance to achieve efficient NOx conversion. The injection of the ammonia-air mixture therefore may take place through a grid of nozzles in order to achieve a uniform mixing of the ammonia with the flue gas or via a set of injection lances located in the turbulent zones immediately downstream vortex creating discs such as Topsøe's patented STARMIXER® system placed in the flue gas duct (see section Design considerations on page 27).

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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 the goals of optimum design of a mixing system for completeness of the chemical reactions, as well as minimum ducting and an attractive plant layout. 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 lay-out of ducts, reactor and necessary flow control devices to minimise overall pressure loss.

3.2   The SCR catalyst

The commonly applied catalysts are all based on a porous titanium-dioxide carrier material on which the catalytically active components in the form of vanadium pentoxide combined with tungsten- and/or molybdenum oxides are dispersed. To cater for a large gas contact area with a minimum pressure loss, the catalysts are provided as corrugated or extruded elements containing a large number of parallel channels (Figure 2) or as elements with a stack of spaced, coated wire-mesh sheets.

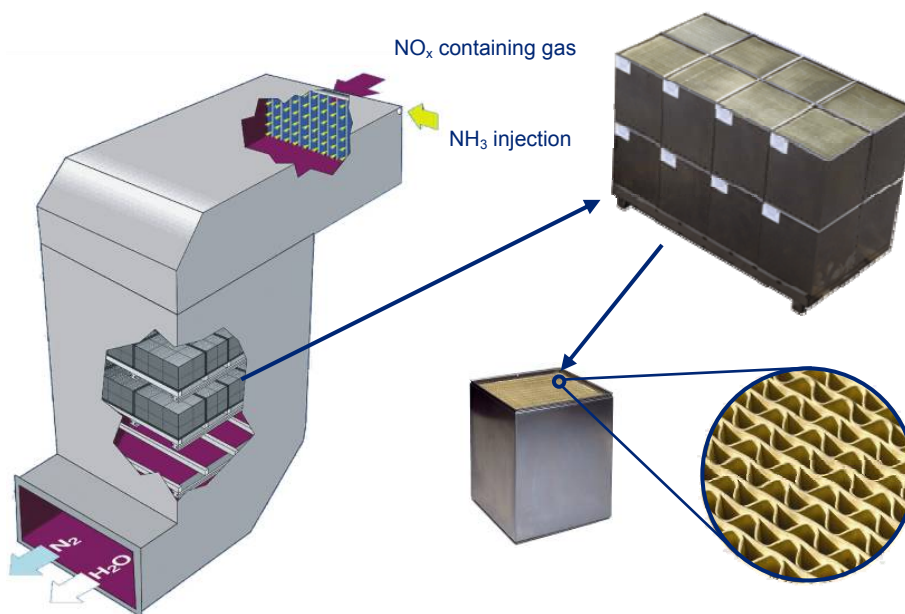
Figure 2   The SCR DeNOx reactor and catalyst
The monolithic SCR catalyst elements are assembled into modules for easy installation. Ammonia is injected in a grid in the flue gas duct upstream the catalyst

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Each type of catalyst is offered in a number of different models with varying channel size (often referred to as pitch), wall thickness and with varying chemical composition adapted to specific operating conditions. The choice of pitch and wall thickness for a given SCR installation is determined mainly by the concentration and properties of the dust in flue gas. For low-dust applications, channel sizes of up to approximately 5 mm are selected. Larger-channel catalysts (6-10 mm pitch) should be selected for operation in dust-laden gases in SCR units on e.g. Fluid Catalytic Cracking (FCC) units in which FCC catalyst fines are carried over from the regenerator.
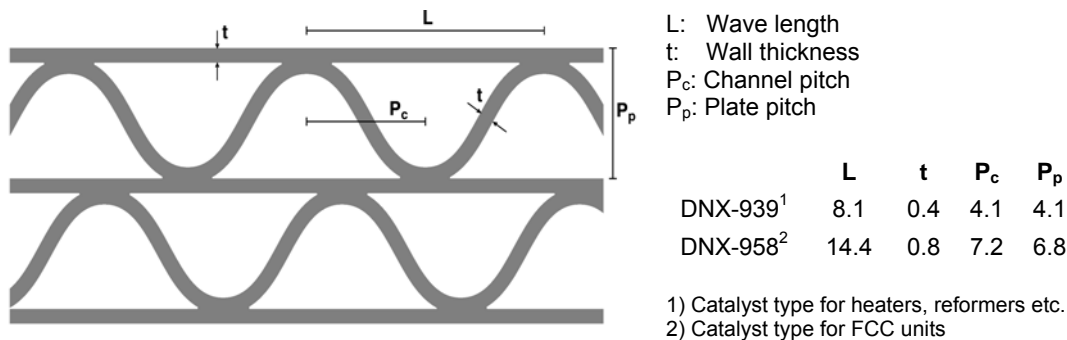

L: Wave length
t: Wall thickness
P_c: Channel pitch
P_p: Plate pitch

	L	t	P_c	P_p
DNX-939[1]	8.1	0.4	4.1	4.1
DNX-958[2]	14.4	0.8	7.2	6.8

1) Catalyst type for heaters, reformers etc.
2) Catalyst type for FCC units

Figure 3   Geometry of Topsøe corrugated DNX® catalyst

The required catalyst volume and thereby the size of the SCR reactor depends, of course, on the NOx concentration in the flue gas and the desired NOx reduction efficiency but specific operating conditions, e.g. temperature and flue gas dust content, and the selected catalyst model adapted to these conditions also have a large influence.

In order to optimise reaction conditions and catalyst replacement strategy, the total catalyst volume necessary usually is distributed on several layers. Typically, an empty spare layer is included for addition of catalyst. Addition of catalyst instead of immediate replacement results in a better utilisation of the remaining catalyst activity prior to a final replacement.

If the flue gas contains any sulphur dioxide, SO_2, the active component in the SCR catalyst, vanadium pentoxide, catalyses a typical ½-1% oxidation of SO_2 to SO_3. Downstream the SCR, SO_3 in the flue gas can react with the ammonia slip to form ammonium bisulphate (ABS, NH_4HSO_4) which can cause fouling and corrosion of equipment. Depending on SCR temperature, ABS may deposit in the catalyst, eventually blocking the access to its active sites and rendering it inactive. Furthermore,

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the formation of sulphuric acid mist from reaction of SO_3 with water vapour can give rise to the formation of a visible, blue plume in the stack.

Obviously, the amount of SO_3 formed over the catalyst should therefore be minimised. Each catalyst producer has his way of balancing the NOx-reduction and the SO_2-oxidation activities of the catalyst. A high porosity of the catalyst helps minimise the SO_2-oxidation by providing a high fraction of SCR-active surface vanadium sites. Figure 4 shows the high pore volume of Topsøe's DNX®-type SCR catalyst in comparison with extruded-types SCR catalysts. The high porosity of DNX® is achieved via a unique tri-modal pore structure, i.e. a pore structure featuring pores in three size regimes. Extruded-type catalysts typically obtain the pore volume from a micro-porous structure within a narrow size range.
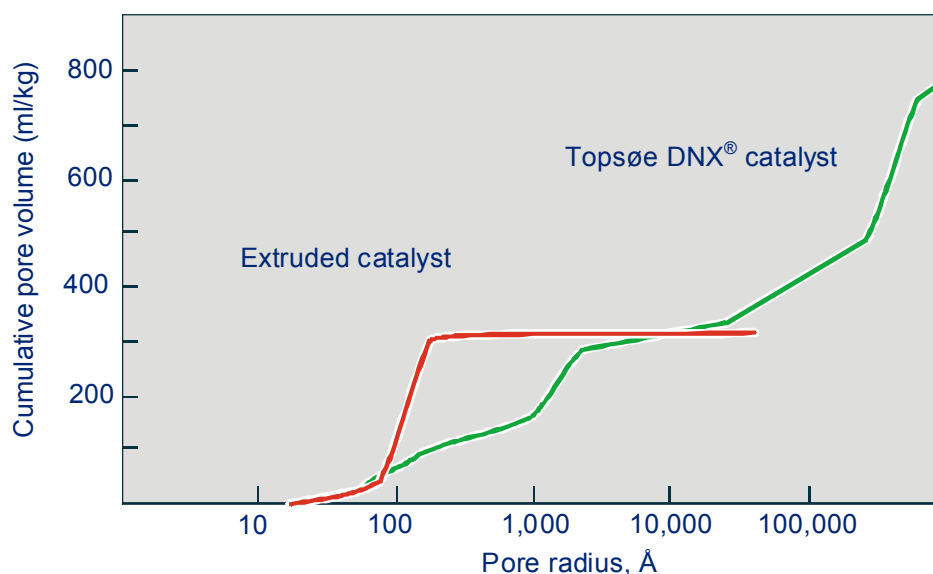

Figure 4   Pore volume in extruded SCR DeNOx catalyst and Topsøe's DNX® catalyst. The pore volume of the DNX® catalyst is roughly twice that of extruded catalyst types. The high porosity is achieved from pores in three size regimes, catering to a high resistance towards poisoning

The conversion of NOx on the catalyst takes place on both the inner and outer surface of the catalyst. As the outer surface fouls with foreign substances deposited from the flue gas, maintaining access to the interior becomes increasingly important. Large-size pores, macro-pores, serve to ensure this access to the active interior even if large amounts of poisons have been deposited on the catalyst as illustrated in Figure 5. The macro-pores further enhance gas-phase diffusion of NOx and ammonia into the catalyst and thereby the overall activity.
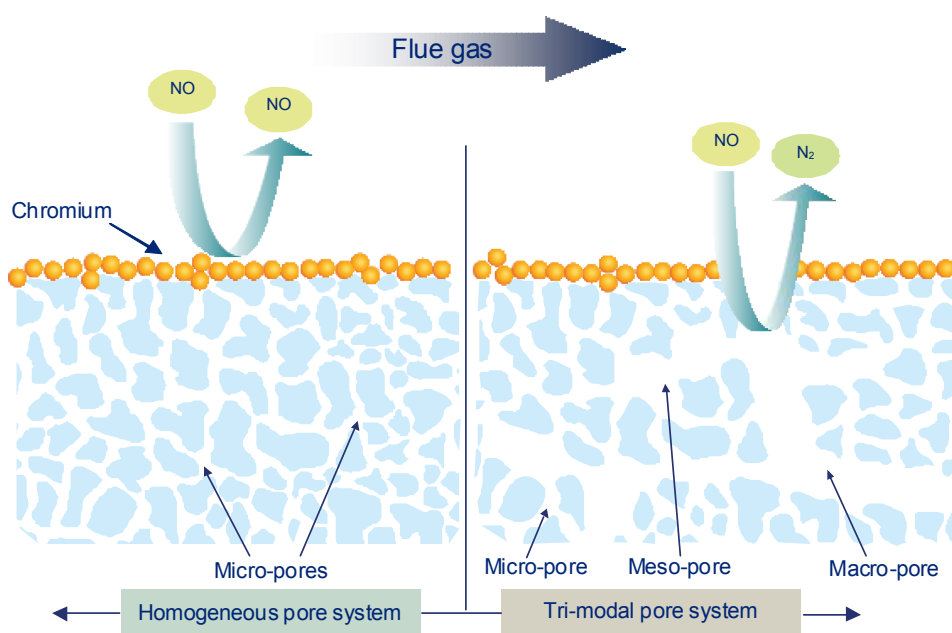
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Figure 5   The tri-modal pore system of Topsøe's DNX® catalyst (right) provides a high resistance towards poisoning from e.g. chromium as the presence of macro-and meso-pores ensures access to active sites

4 Refinery SCR applications

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.

4.1 SCR for steam cracking and reformer furnaces

Ethylene is produced by steam cracking processes where a hydrocarbon feedstock reacts with steam in a high temperature environment (700°C ~ 1,100°C; 1,300°F ~ 2,000°F). The reaction is highly endothermic and is carried out in relatively small-diameter (2-15 cm, 1-6 inches) closely arranged reaction tubes.
Steam methane reforming is used in the production of hydrogen from a hydrocarbon feed, usually natural gas by reacting methane with steam across a catalyst in heated

high-alloy tubes which operates at high temperature by direct heat exchange with the integral furnace that surrounds the reactor tubes.

The tubes in the ethylene cracker's firebox section are constructed from chromium-nickel alloys containing 25%-35% Cr and heated by gas- or oil-fired burners. At these temperatures, chromium in the radiant coil is released into the flue gas. Chromium is evaporated predominantly as chromium oxyhydroxide ($CrO_2(OH)_2$), which accumulates in downstream SCR catalyst installations and has a negative impact on catalyst lifetime. The release of chromium from furnace tubes is seen in all heated high-temperature cracking and reformer processes.

4.1.1   Chromium deactivation mechanism

Gindorf et al.[5] made experimental measurements of chromium oxide vapour pressures in humid air at high temperatures. It is likely that CrO_3 and $CrO_2(OH)_2$ are the dominant chromium vapour species in equilibrium with solid Cr_2O_3 and oxygen rich atmospheres in dry and wet gas respectively.

At wet flue gas conditions chromium is evaporated according to:

$$Cr_2O_3(s) + 2\,H_2O + 1.5\,O_2 \quad \rightarrow \quad 2\,CrO_2(OH)_2\,(g)$$
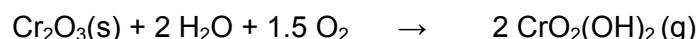
The observed Cr accumulation is 200-2,000 ppmw per 1,000 hours in the first catalyst layer and in catalyst test coupons installed above the first layer. This is in fair agreement with the prediction of Cr accumulation on the basis of the thermodynamic data: At a partial pressure of chromium at 750°C (1382°F) of 0.012 atm, the chromium uptake in the catalyst would be approximately 900 ppmw Cr per 1,000 hours at a space velocity 10,000 Nm^3/m^3 catalyst per hour, assuming 100% retention.

DNX® catalyst test coupons have been inserted in a number of ethylene cracking and steam methane reformer furnace installations in order to monitor the effect of accumulation of chromium.

The general effect of chromium on the catalyst is a decrease in activity at 350°C (662°F) that amounts to around 2.6% of the initial activity per 0.1% by weight chromium accumulated in the catalyst (Figure 6). At a US Gulf Coast ethylene cracking plant (Plant A) the effect of chromium was higher than average during a first run but was at the same level as found in the other installations during a second run. While there is a correlation between accumulated chromium and activity, there is no direct correlation between service hours and activity cf. Figure 7, which means that the chromium uptake

in the catalyst is plant specific. On average, the uptake is ~1 wt% of chromium per 10,000 hours.
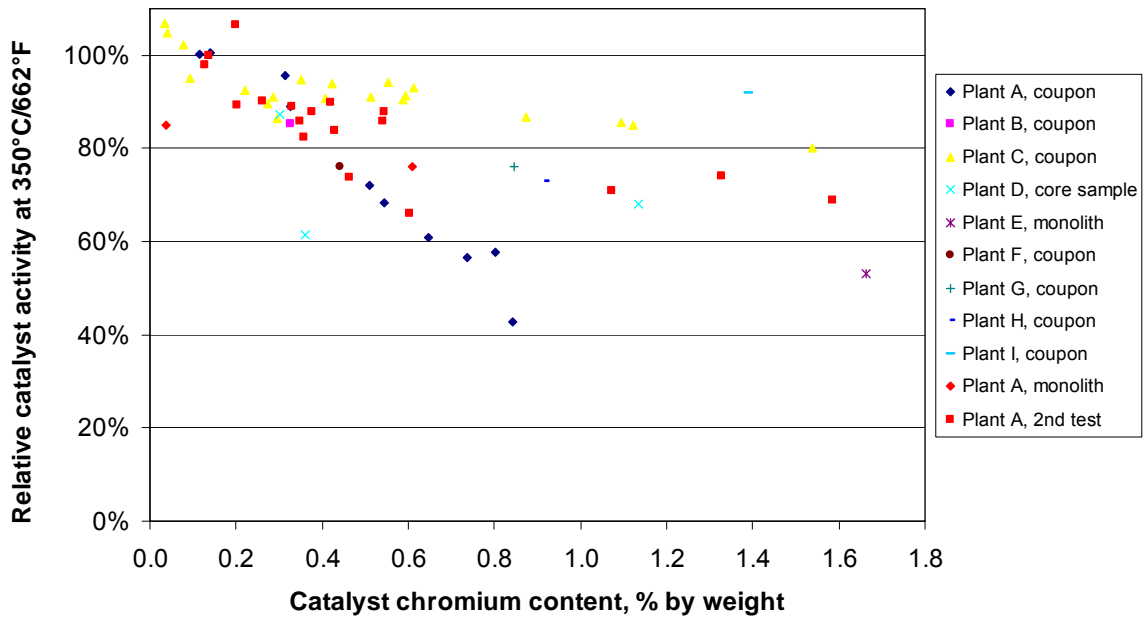

Figure 6   Catalyst activity relative to fresh catalyst activity at 350°C (662°F) versus chromium accumulation in SCRs on ethylene cracking furnaces and steam methane reformers
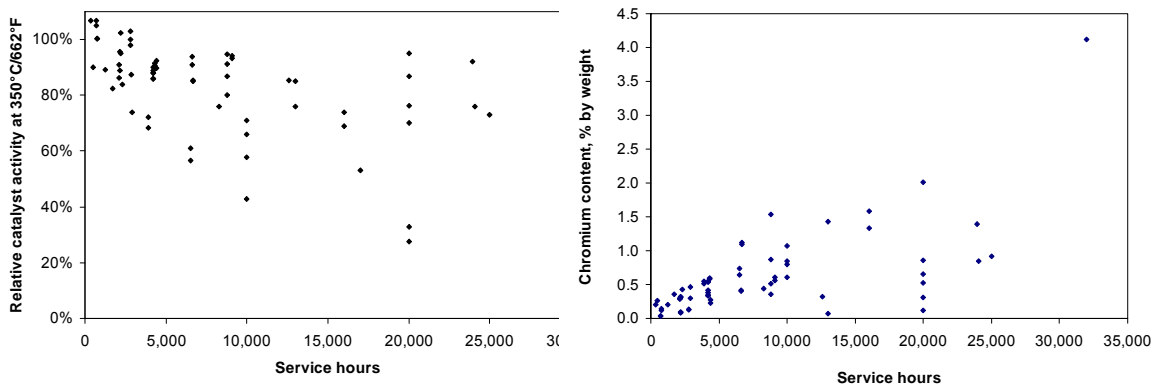

Figure 7   SCR catalyst activity relative to fresh catalyst activity versus service hours in SCRs on ethylene cracking furnaces and steam methane reformers

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Two full-size catalyst elements were taken from the same SCR unit (Plant A) after 13,000 service hours. The deactivating effect of chromium uptake on the catalyst was at the same level as found from the test coupons. In the first layer catalyst, having an average chromium content of 6,000 ppmw, a 4.0% decrease of initial activity at 350°C (662°F) per 1,000 ppmw Cr was found. Table 1 gives an overview of the results. "Position" refers to the distance from the catalyst element leading edge of the sample.

Catalyst layer No.	Position mm	Chemical composition (ppm by weight)			k/k_0 Ratio between NH_3 and NOx reacted		
		Cr	K	Na	250°C 482°F	350°C 662°F	450°C 842°F
1	50	14,300	270	1,820	**0.49** 1.07	**0.76** 1.09	**0.25** 1.80
	250	3,100	175	1,460			
	450	815	175	1,390			
2	50	710	295	1,630	**0.63** 1.05	**0.85** 1.03	**0.69** 1.17
	250	245	230	1,390			
	450	160	230	1,340			
Reference		<100	~200	~800			

Table 1   Accumulation of poisons and activity relative to fresh catalyst activity, k/k_0, after 13,000 service hours at a US Gulf Coast ethylene cracking furnace. The activity is measured at NOx_{inlet} = 500 ppm, NH_3/NOx ratio = 1.2, 18% O_2, 3% H_2O, 500 mm catalyst element length and space velocity = 20.69 $Nm^3/m^2/h$

The gradient of chromium in the SCR reactor, showing significantly more accumulation in the first catalyst layer and especially at the inlet face of the catalyst, indicates that chromium is deposited as extremely fine aerosols with high diffusivity. This also results in significant overall capture in the SCR catalyst with more than 90% of the chromium being accumulated in the first catalyst layer. Presumably the chromium is present as sub-cooled gas-phase monomers that precipitate at the catalyst surface. The accumulation of other catalyst poisons such as sodium and potassium is very low. The effect on activity at 350°C (662°F) corresponds to a logarithmic deactivation rate of 19% and 12% per 10,000 hrs in the first and the second layer, respectively. Deactivation rates between 21% and 35% per 10,000 operating hours after three years of operation have been reported with other types of SCR DeNOx catalysts[4].

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The catalyst deactivation is lowest at 350°C (662°F) and more pronounced at lower and higher temperature. Usually blinded catalysts with an increased diffusion barrier show the highest deactivation at the medium temperature. The behaviour of the chromium-poisoned SCR catalyst is a result of the catalytic properties of chromium oxide. Chromium oxide is known to have good SCR DeNOx activity in the range of 300-350°C (572-662°F) but also with a significant ammonia oxidation activity above 250°C (662°F)[5]. The oxidation of ammonia is clearly seen from the ratio between NH_3 and NOx reacted. As appears from Table 1 the ratio is significantly higher than 1 at 450°C (842°F). At 250°C (482°F), chromium does not contribute to the DeNOx activity to an appreciable extent and observed activity is lower. The optimum temperature range for the SCR operation is therefore around 350°C (662°F) taking both initial activity and catalyst deactivation into account.

4.2 SCR DeNOx in fluid catalytic cracking units (FCCU)

One of the largest NOx emissions sources in a refinery is the regenerator of the fluid catalytic cracking (FCC) unit. FCC is the most important process in a petroleum refinery and is used to convert high-molecular weight hydrocarbons in the crude oil to high-octane gasoline and fuel oils. FCC catalysts are fine powders with crystalline zeolite being the primary active component. The FCC unit consists of the catalyst riser in which the hydrocarbons are vaporised and cracked by contact with the hot catalyst recirculated from the regenerator. The mixture of catalyst and hydrocarbon flows upward to the reactor where the hydrocarbons are separated from the catalyst, which has deactivated from depositing of carbonaceous material, coke. The catalyst is returned to the regenerator where it is regenerated by burning off the coke with air blown into the regenerator. NOx is produced in the regenerator from burning of nitrogen contained in the coke. The FCCU flue gas NOx concentration typically ranges from 50 ppmvd to 400 ppmvd with an average of approximately 200 ppmvd.

4.2.1 SCR design issues

Haldor Topsøe's design philosophy for FCCU SCR applications calls for a vertical down flow unit. This takes advantage of gravity to address the catalyst fines entrained in the flue gas. Turning vanes are required to prevent uneven stratification of the solids and ensure a uniform velocity profile leading at the inlet face of the SCR catalyst. The most economical place for an SCR installation in an FCC unit is upstream of the convection section and the design of an SCR thus presents some challenges:

- Two-phase flow as the FCC catalyst fines are entrained in the flue gas
- The flue gas contains significant amounts of sulphur oxides, SO_2 and SO_3

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The experience with SCRs in flue gas from FCC units in a "high dust" and high sulphur service is limited but the experience with SCRs from coal-fired power stations is extensive. Even though the dust level in the FCC flue gas is fairly high, it is low compared to the ash content in flue gas from coal-fired power stations. Typical dust loadings in an FCC unit are 10 to 100 kg/hr compared to 10,000 kg/hr in coal fired power stations with the same flue gas flow.

The FCC catalyst entrained in the flue gas is typically fines having an average particle size below 10 microns as well as full range catalyst with an average particle size of 70 microns during an upset. Compared to the fly ash from a coal-fired power station the FCC catalyst fines have a higher fraction of very fine particles around 1 micron but otherwise the two types of dust are comparable. Figure 8 shows the particle size distribution of FCC fines taken from an electrostatic precipitator (ESP) and two typical types of fly ash from coal-fired power stations.
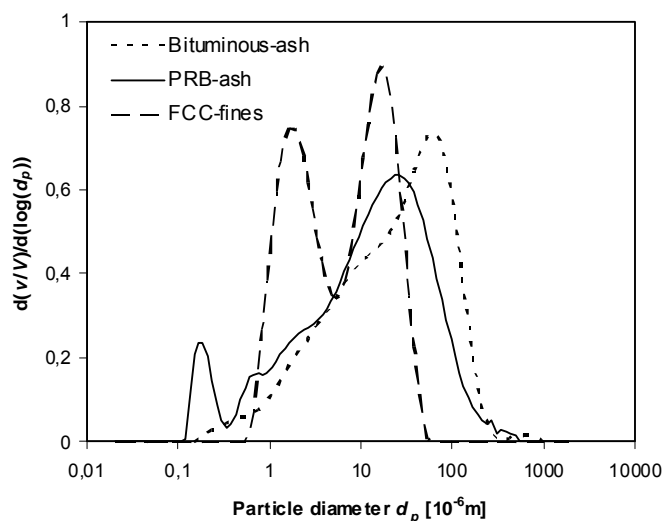

Figure 8   Particle-size distribution of FCC fines in the flue gas from an FCCU regenerator compared with two types of coal fly ash

4.2.2   ABS condensation considerations

The flue gas from the FCC regenerator contains significant amounts of sulphur dioxide and sulphur trioxide. With sulphur trioxide present in the flue gas it is necessary to operate above the temperature for formation of ammonium bisulphate (ABS, NH_4HSO_4) from reaction of the injected ammonia with sulphur trioxide:

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$$NH_3 + SO_3 + H_2O \ \rightarrow \ NH_4HSO_4 \ (l)$$

Liquid ABS formation is a function of temperature, ammonia partial pressure and SO_3 partial pressure. The bulk condensation temperature in the SCR reactor inlet is typically in the range 270-300°C (520-570°F) but the condensation will occur at a 20-30°C (35-85°F) higher temperatures in the catalyst due to capillary forces in the micro-porous structure of the catalyst. The consequence of condensation of ABS in the pores of the catalyst is that activity becomes reduced as access to the active sites becomes blocked. However, ABS is a temporary foulant as the condensation process is reversible and raising the operating temperature back above the dew point will cause the ABS to evaporate and catalyst activity be restored.

The catalyst ABS dew point temperature as a function of SO_3 concentration is shown in Figure 9 for different inlet NH_3 concentrations. The NH_3 concentration at the inlet to the SCR is around 1.25 times the NOx concentration for a desired NOx removal efficiency of 80%.
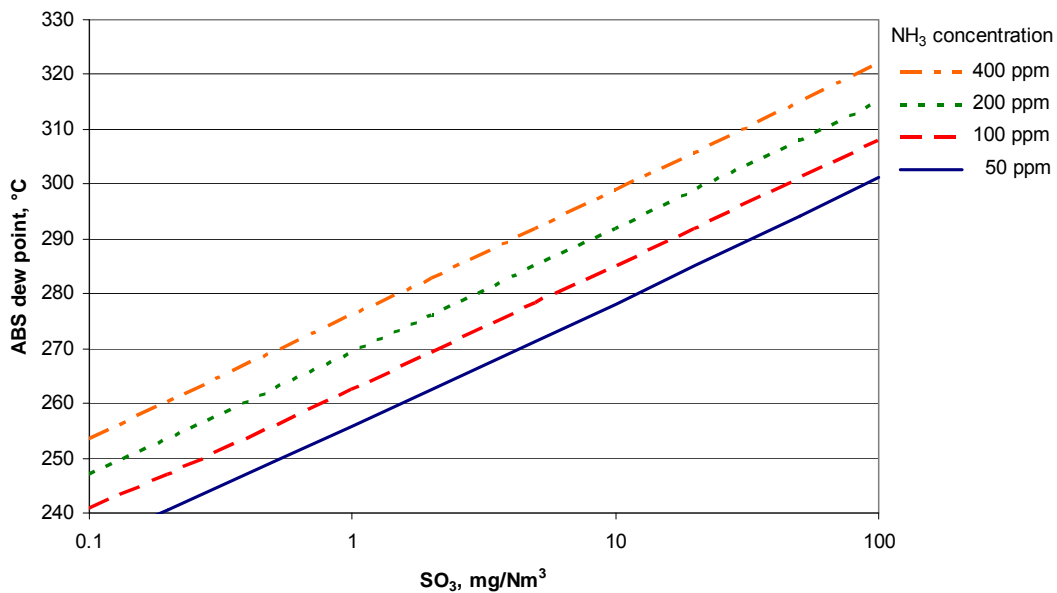

Figure 9   The temperature for ABS condensation in the catalyst as a function of SO_3 concentration for different ammonia concentrations

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4.2.3   Catalyst selection

The SCR catalyst to be selected must be designed to perform reliably in the FCC unit's erosive environment. This catalyst should have a thick robust wall and a wide pitch to avoid plugging of the catalyst channels with FCC catalyst fines entrained in the flue gas. To ensure a low pressure drop across the catalyst layers, a catalyst with an approximately 7-mm pitch and a wall thickness of minimum 0.8 mm is selected as shown in Figure 3.

The Haldor Topsøe DNX® catalyst utilises a tri-modal pore size distribution containing macro- pores, meso-pores and micro pores for activity retention in this dust laden environment as described in Figure 5. The fines are able to fill the macro-pores. At some point, the macro pores accept the maximum amount of catalyst dust, yet NOx and NH_3 in the flue gas can still diffuse into these pores through the remaining void space and complete the reduction reaction on the active sites of the catalyst surface.

4.2.4   Catalyst cleaning

Even though a wide-pitch catalyst is selected, provisions for regular cleaning of the catalyst must be taken. The FCC catalyst fines carried to the SCR reactor are of a sticky nature, partly because of the small particle size, and tend to build up on the top grid wire mesh covering the catalyst modules and on the leading edge of the catalyst channels (see e.g. Figure 18 on page 26).

Rake-type soot blowers using superheated steam or compressed are recommended for this cleaning purpose. They will typically have to be operated 1-3 times per day.

5   Industrial experience

5.1   Chevron Phillips, Cedar Bayou, Texas, USA (ethylene plant)

Several (13 out of 14) ethylene cracking furnaces were revamped to add SCR reactors. This project required the addition of new convection sections containing the SCR reactor. New steam super heater coils were added to the scope of the project to achieve greater thermal efficiency. Plot space is limited and forced the new equipment to be placed on top of the existing heater. This increased the overall height of the heaters by approximately 6 meters (20 feet), cf. Figure 10.

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Figure 10   Additional convection sections placed on top of the existing heater of
the ethylene plant at Chevron Phillips, Cedar Bayou, Texas, USA

The ammonia injection grid (AIG) is located less than 3 m (10 ft) from the inlet face of
the SCR catalyst. This provides only short mixing time and mixing distance for the
ammonia to blend in with the flue gas. Thus, a bank of convection coils was placed
between the AIG and the SCR catalyst to facilitate mixing and achieve optimum SCR
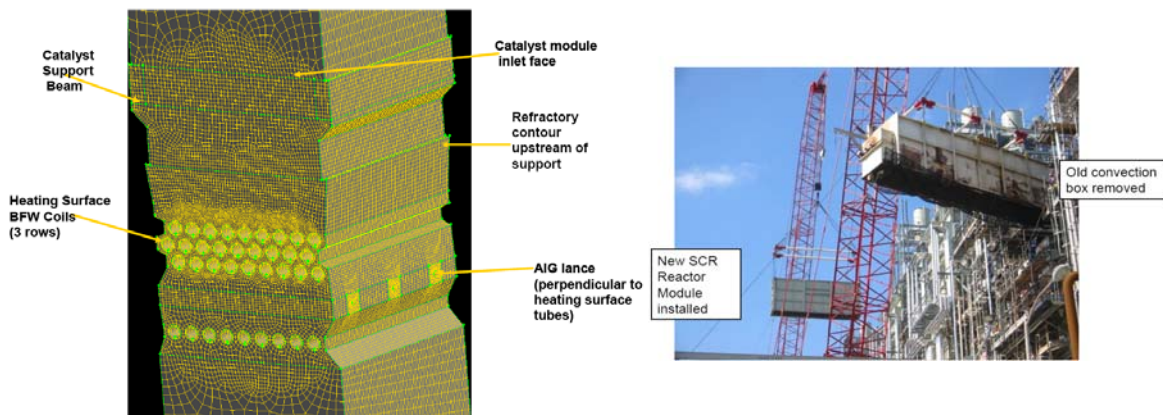reaction temperature (Figure 11).

Figure 11   Left: CFD grid of ammonia injection grid, convection section and SCR
Right: Installation of SCR

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Additional convection coils were located upstream of the stack to recover more latent heat. Prior to the turnaround project to integrate SCR into the ethylene furnaces, the outlet stack temperatures were typically around 260°C (500°F). After the revamp, the new convection sections reduced stack heat leaks and outlet stack temperatures are below 150°C (300°F).

5.1.1   NOx reduction performance

The first of the cracking furnace SCR units was placed on line in September 2003 and was given a three year service life guarantee. Figure 12 shows the catalytic performance to be excellent well beyond the service life even in this challenging application where chromium poisoning is present. The graph clearly shows that outlet NOx and NH$_3$ slip can easily be controlled below 10 ppmv more than four years after initial start-up of the SCR unit.
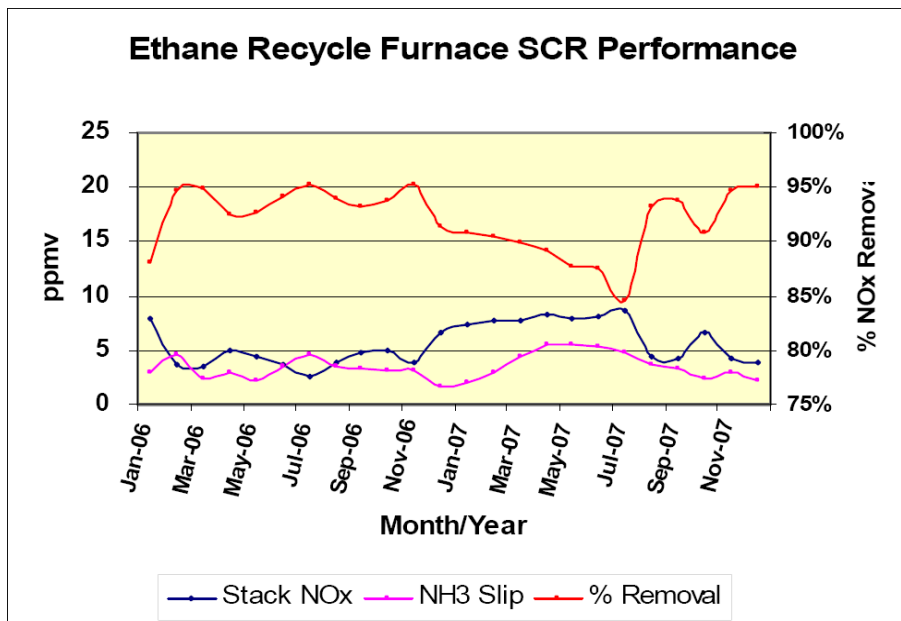

Figure 12   Ethylene cracking furnace SCR performance

5.1.2   Chromium accumulation in the catalyst

Figure 13 shows the chromium and the vanadium profile through a DNX® catalyst after 13,000 hrs in the SCR (same catalyst as the Layer 1 catalyst in Table 1 page 13). The profile is obtained by wavelength dispersive spectroscopy (WDS) in a scanning

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electron microscope (SEM). WDS provides a quantitative measurement of the element concentrations. The SEM image to the right shows where the profile was acquired. Chromium is not a traditional blinding agent but acts as a masking agent, which, as mentioned earlier, also has an effect on catalytic behaviour. The chromium has accumulated primarily at the catalyst surface with up to 9% by weight but chromium also exhibits some surface diffusion mobility and diffuses into the catalyst matrix. The thin chromium layer on the catalyst surface is visible on the wall cross section picture. Furthermore, it is seen that the deposits are visible three to four pore diameters or 50 μm into the pore mouth of the macro pores of the catalyst. This deposition pattern is typical for extremely fine aerosols or sub-cooled gas-phase monomers that diffuse into the macro pores and stick to the surface.

To maintain sufficient catalyst activity at this poison deposition pattern, the presence of a diverse pore structure is important as illustrated in Figure 5. The activity of the catalyst shown in Figure 13 is 76% of fresh catalyst activity at 350°C (662°F).
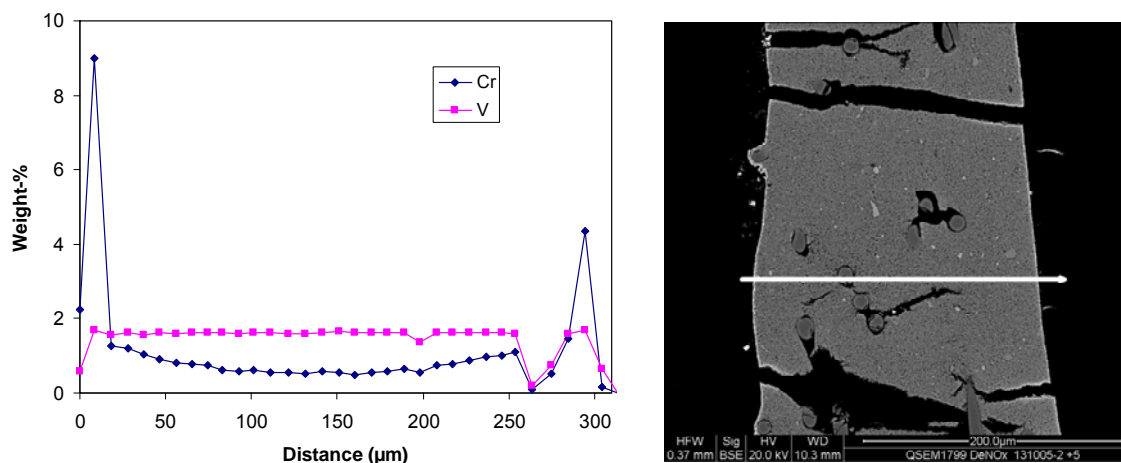

Figure 13   Vanadium and chromium profile through the catalyst wall after 13,000 service hours at Cedar Bayou layer 1. The profile is obtained by WDS in a scanning electron microscope (SEM). The SEM image to the right shows where the profile was acquired.

Figure 14 shows a close up picture of the catalyst wall cross section. The thickness of the chromium deposits is just 1 - 2 μm. The surface pictures of the fouling layer show the fine chromium oxide particles. The surface is not completely closed and reactants are still allowed to diffuse into the catalyst pore system. For comparison, a surface picture of the cleaner catalyst from the second layer is presented.
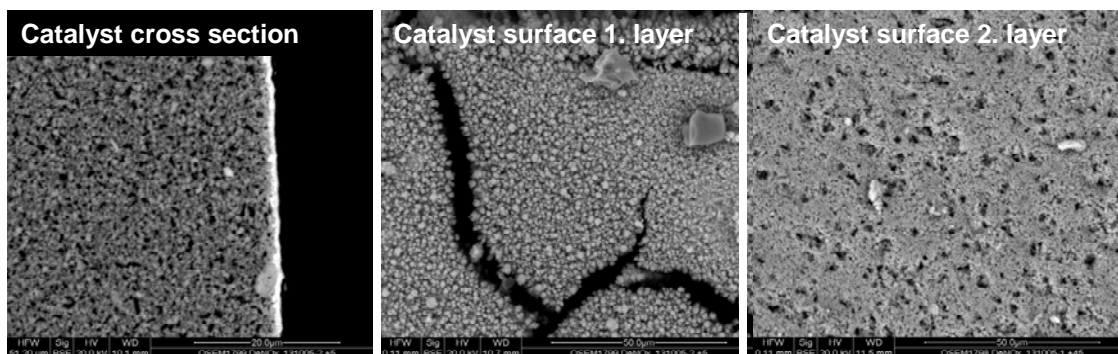
Figure 14   Wall cross section and surface pictures of chromium deposits on first and second layer catalyst at Cedar Bayou after 13,000 hrs

Extracted catalyst samples were analysed for possible presence of toxic hexavalent chromium(VI) species but none were found.

5.2   Fluid catalytic cracking units

In the following design considerations and experience from two Topsøe installations of SCR's after FCC units are presented: 1) Shell, Deer Park Refinery, Texas, USA and 2) CITGO Petroleum; Lemont Refinery, Illinois, USA. These experiences are further detailed in papers presented at National Petrochemical & Refiners Association's annual meetings in 2005[2] and 2010[3].

5.3   Shell, Deer Park Refinery, Texas, USA

In the Shell Deer Park catalytic cracker, flue gas from the catalyst regenerator first passes through a third (3rd) stage separator to knock out catalyst particles and then it flows to the expander which is used to recover power to drive the main air blower. There is no ESP in this unit. From the expander outlet, the flue gas enters the CO combustor to oxidise the CO to CO_2. Hot flue gas from the CO combustor flows to the catalytic cracker feed preheater box via four transition ducts.

Performance requirements imposed by EPA for outlet NOx were:

- 20 ppmvd on a 365-day average at 0% reference oxygen
- 40 ppmvd on a 3-hour average at 0% reference oxygen

The SCR catalyst was guaranteed to remove 90% over a 5-year run-span which put the refinery right at the maximum limit of 20 ppm outlet NOx with 200 ppm Inlet NOx.

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Based on this, the refinery decided to use both SNCR and SCR to achieve the final results.
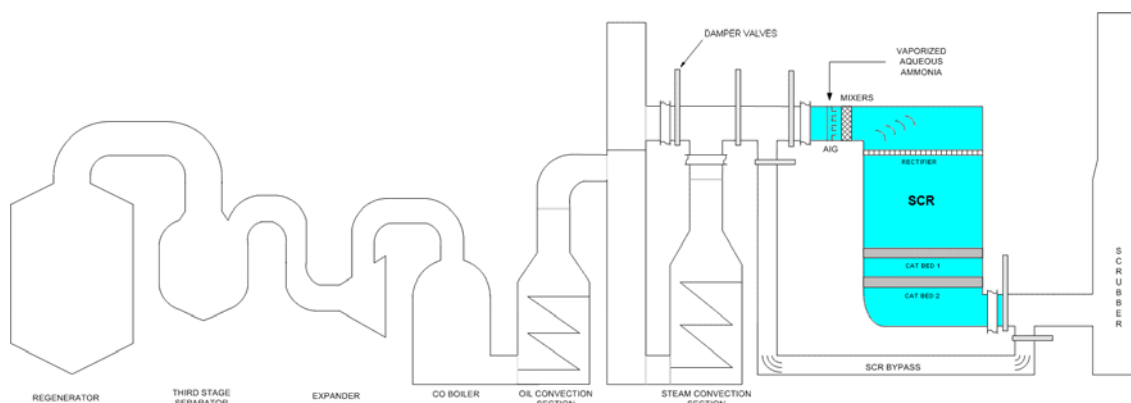

Figure 15   Catalyst cracker flue gas flow path at Shell, Deer Park Refinery, Texas, USA

Ammonia injection facilities were added to each duct to implement the SNCR technology. Flue gas from the oil box passes through another box containing coils for steam production steam superheating. Flue gas from the steam box flows to the SCR. The flue gas temperature to the SCR is controlled by bypassing BFW around the preheater coil. The SCR is designed for down flow with two catalyst layers with a provision to add a third layer. From the SCR the flue gas is routed to the caustic scrubber for desulphurisation before exiting the 60 m high stack.

Key issues in the SCR design were:

- High SO_2 content of flue gas 1000+ ppmvd
- High solids loading – 40-50 lbs/hr (18-23 kg/h) normal, 200 lbs/hr (91 kg/h) maximum as there is no ESP in front of SCR
- SO_3 content 3-12 ppmvd

Available flue gas temperature was limited to about 288°C (550°F)

All the CEMS (Continuous Emission Monitoring System) analysers are in the stack. There are NOx, SOx and opacity analysers in the duct before the SCR for checking the process performance. The SCR is also equipped with a bypass duct which is to be used in case of high pressure in the CO combustor or loss of activity of SCR catalyst. Bypass can also be used in case of excessive carryover of solids as determined by the

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opacity readings in the duct and high pressure drop in the SCR as a result of plugging with solids.

5.3.1   ABS considerations

The high SO_3 content of the flue gas, 3-13 ppmvd, 11-39 mg/Nm^3, represented a challenge to the SCR design, necessitating an operating temperature above 290-305°C (554-581°F) to avoid ABS condensation in the SCR catalyst, cf. Figure 9 on page 16. The ideal temperature for the SCR would have been above 700°F. This could have been accomplished by splitting the steam convection section; however, there was neither time nor space available to implement this idea. Another option was to place the SCR downstream of the FGD and hereby reduce the SO_3 content; however, the cost of reheating the flue gas made it prohibitive. The SCR was therefore chosen to be installed in between the steam convection section and the FGD, the advantage being that the tie-ins could be completed during the 2002 turnaround. The temperature at this point can be controlled between 260°C and 315°C (500-600°F), but there is a risk of ABS formation. The ABS formation is reversible; and in case of ABS formation on the catalyst, the inlet temperature will be elevated to 315+°C (600+°F) which is sufficient to sublime the salts. This is done with a bypass on the boiler feed water to the convection section.

5.3.2   Ammonia mixing and SCR lay-out

Shell Deer Park decided to use 19% aqueous ammonia as there are no restrictions on the quantity that can be stored. The aqueous ammonia is vaporised in kettle type electric exchangers. Ammonia dilution air is also heated using electric heaters.

For the Shell Deer Park FCC, 19% aqueous ammonia was selected as the ammonia source. The aqueous ammonia is vaporised before it is injected into the flue gas. To ensure a sufficient mixing of the ammonia and the flue gas, the point of injection of the ammonia into the flue gas must be as far away from the catalyst as possible. A proper location must be determined based on mixing and temperature. Proper mixing is even more critical when increased NOx conversion rates are required, and in a hybrid system with a combination of SNCR and SCR, there is a risk of having an uneven NH_3/NOx distribution at the entrance to the reactor. Ammonia injection is done through an injection grid containing several nozzles. For this SCR a static mixer, turning vanes, and a flow rectifier were required.

Furthermore, the plot space available made it impossible to have a more typical direct entry into the SCR reactor. After many trials, a solution was developed which required a 90° turn into the AIG and two static mixers followed by a 180° turn and drop into the main body of the SCR.

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A 1:12 scale model, Figure 16, was constructed based on the results of the CFD modelling and interaction with the engineering design company for space availability. The advantage of the physical model is its ability to simulate two phase flow. Dust accumulation was modelled in various areas of the duct-work and the SCR using a suitable powder to represent the FCCU fines at the test conditions.
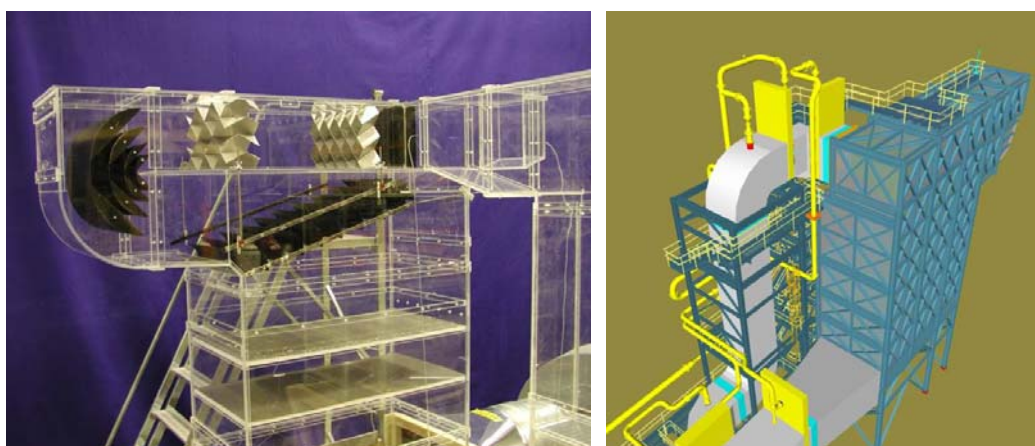

Figure 16   1:12 scale model and 3D drawing of the SCR at Shell, Deer Park Refinery

Dust accumulation tests were carried out at different dust loads corresponding to normal operation and a simulation of a major FCCU catalyst carry-over.

The use of the physical model greatly assisted in the determination of the position and shape of the turning vanes, mixers and the AIG. Sulzer supplied the scale model mixer and AIG components for the test as well as the full-sized components for the project.

5.3.3   Performance

The SCR for the Shell Deer Park FCCU was commissioned in the fall of 2004. The unit was built with the FCCU in operation and started up within schedule. When the unit came online it performed immediately; no tuning was necessary because of the way the SCR is designed. The pressure drop over the SCR is constant and lower than the guarantee. The NOx reduction has been higher than the guarantee. Since it is start of run for the catalyst It has been possible to bring the outlet NOx down to much lower numbers than the guarantee of 20 ppmvd. The outlet NOx is consistently controlled lower than 20 ppmvd, and the SNCR has therefore not been put in service. The inlet temperature to the SCR has been maintained between 525°F and 550°F (275-288°C).

There has not been any measurable ammonia slip in the stack, which is not a surprise since it is downstream of the FGD. However, we have not found any measurable ammonia increase in the waste water from the FGD.
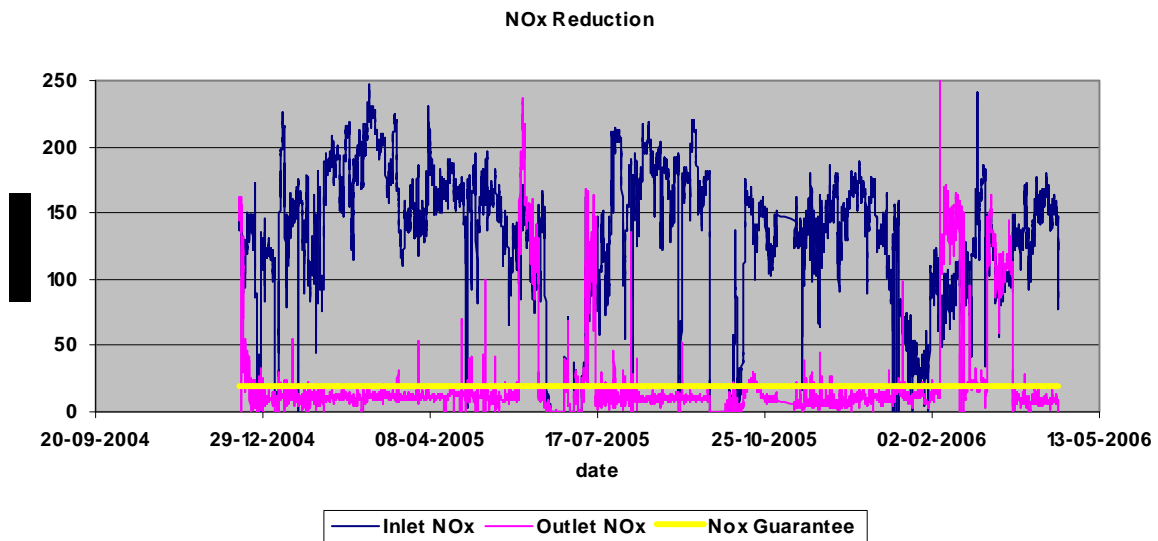

Figure 17   The outlet NOx level at the Shell Deer Park Refinery well below guarantee

5.3.4   Catalyst cleaning

Sonic horns were initially selected for this project. Sonic horns can be operated at any defined interval of time, cost less than traditional soot-blowers and are more easily maintained.

However, at several occasions an increased pressure loss across the SCR catalyst layers was experienced. Inspections revealed a significant build-up of FCC catalyst fines on the wire mesh covering the catalyst modules. After investigation of the operating data it was found that the increased pressure drop was caused by operation at temperatures lower than the ABS condensation temperature for a long period. ABS should be possible to evaporate but the combination of sticky ABS and FCC fines apparently made it impossible to evaporate the ABS. Figure 18 shows how the dust covers the catalyst layer, effectively blocking the gas passage, and the situation after vacuum cleaning. It became obvious that the sonic horns were not able to remove the dust build-ups and it was therefore decided to install steam soot blowers in 2006.

Figure 18   Typical FCC catalyst fines build-up (left) and catalyst layer after cleaning

5.3.5   Operation of the SCR

Operation of the SCR proved simple and could be included in the daily work routine of the operators. The operators have to monitor equipment status and emissions levels but no physical adjustments are required for daily unit functions. The vaporised-ammonia injection rates are controlled by stack NOx levels. Operating results from this SCR indicate that very low levels of NOx emissions are achievable, even with the SCR in a high-dust and high-sulphur service.

5.4   CITGO Petroleum, Lemont Refinery, Illinois, USA

In 2005, CITGO Petroleum entered into a Consent Decree with the U.S. Environmental Protection Agency. The refiner agreed to reduce NOx emissions from the Lemont Refinery's Fluid Catalytic Cracking Unit to 20 ppmvd on a 365-day rolling average and 40 ppmvdc on a 7-day rolling average.

In order to achieve these emission targets, CITGO installed, on the flue gas line, an SCR Unit for NOx reduction immediately upstream of a wet-gas scrubber, which removes particulates, SOx and ammonia. An existing ESP was removed from service after start-up of the new wet-gas scrubber. The ESP was no longer required because of the high-dust SCR unit offered by Haldor Topsøe and the state of the art wet-gas scrubber offered by GEA Bischoff. KTI Corporation from Houston, Texas, USA was the Engineering, Procurement and Construction firm.

5.4.1　　Design considerations

In the CITGO Lemont FCCU SCR unit, two catalyst layers are employed. A 3D drawing of the unit is shown in Figure 19. A set of the Haldor Topsøe patented STARMIXER® static mixers along with the NH_3 injection lances are located at the CO Boiler outlet, well upstream of the SCR catalyst, to provide adequate mixing time for the ammonia to blend completely with the flue gas prior to reaction on the catalyst surface.
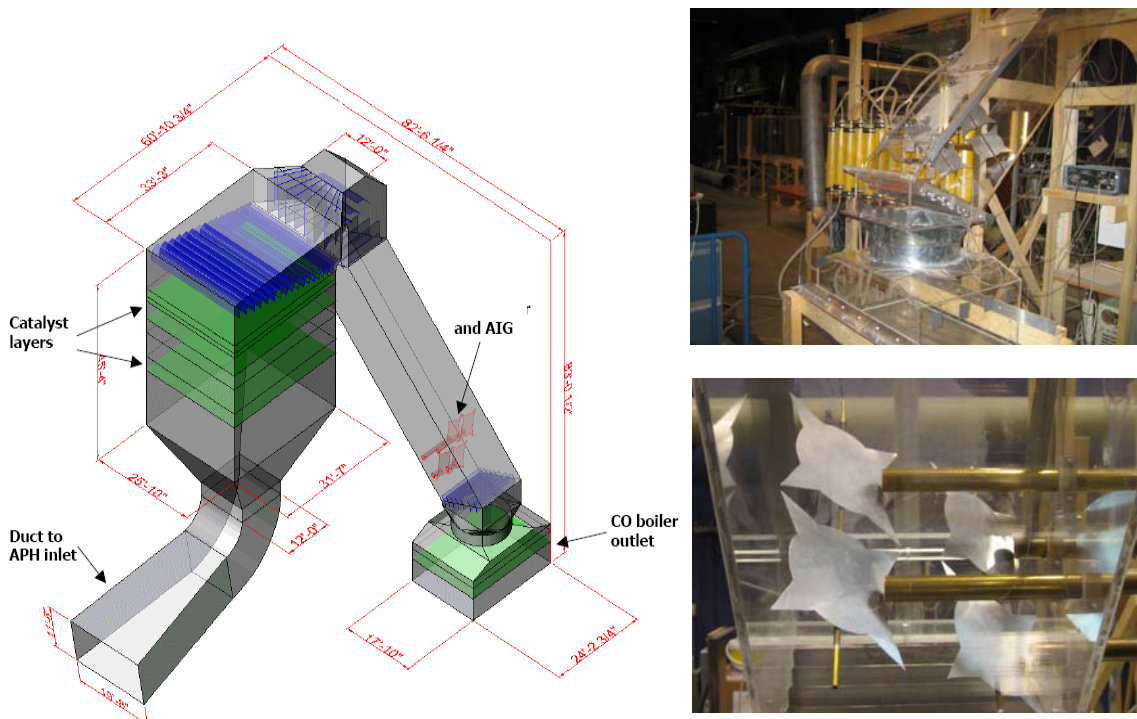

Figure 19　　SCR DeNOx unit at CITGO Petroleum, Lemont Refinery, Illinois, USA
Left: 3D drawing; Right: Details of STARMIXER® arrangement shown in scale model used for cold flow verification of the design

Flow modelling using Computational Fluid Dynamics, CFD, was used to develop the design as shown in Figure 19. The CFD modelling leads to scale modelling for cold flow verification of the design. Location and orientation of the turning vanes are discovered through repeated smoke and dust tests.

The SCR reactor contains two identical catalyst layers. Each layer has 40 Haldor Topsøe VE422AA modules, seen in Figure 20, loaded with DNX-858 catalyst arranged 5 long by 8 wide and translate to an SCR reactor cross sectional area of 9.5 m long by 7.6 m wide (31 feet × 25 feet).

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The weight of each module approaches 900 kg (2,000 pounds). The weight of the catalyst modules is distributed across a pedestal frame which rests on structural steel supports. Grating is used to construct a floor inside the SCR reactor. The seal is made at the base of the module frame using 5-cm (2 inch) wide sealing gutters constructed from sheet metal. This creates a small space between the wall and the modules. Dust deflectors (seen in Figure 20 right) prevent FCC catalyst fines from collecting between the walls and the modules by directing all material of the flue gas to pass through the catalyst bed. Screens with wire mesh are incorporated into the design to provide additional protection during future inspections and maintenance outages.

Figure 20   Each catalyst layer has 40 Haldor Topsøe VE422AA catalyst modules (left). Dust deflectors along the reactor wall prevent FCC catalyst fines form collecting in the space between the walls and the modules

Dust removal from the SCR catalyst and re-entrainment back into the flue gas is achieved with the use of steam soot blowers. The large cross-sectional area of the SCR catalyst requires a soot blower system with retractable rakes (seen in Figure 20 left) to keep build-up of dust to a minimum. The soot blowers cycle once every 8 to 12 hours depending in the amount of particulates in the flue gas. During upset conditions, the soot blowers can sweep the catalyst bed more frequently until normal operations are re-established.

5.4.2   Operational performance

The SCR unit has performed well on every design parameter. The key design parameters are shown below:

NOx Limit
Both Consent Decree NOx requirements have been met since unit start-up. The maximum 20 ppmvdc 365-day rolling average NOx limit has been met and currently is

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12 ppm cf. Figure 21. The 40 ppmv 7-day rolling average NOx limit has also been met; however, start-up and shutdown procedures were modified because the 600°F (316°C) minimum temperature, required for ammonia injection, cannot be maintained with only the CO boiler in operation.
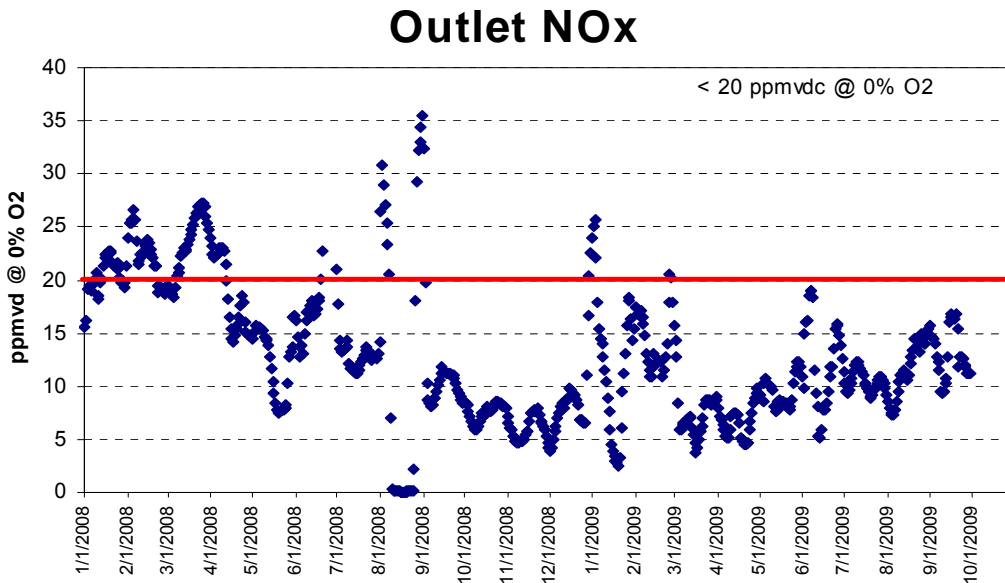
Outlet NOx

Figure 21   The maximum 20 ppmvdc 365-day rolling average NOx limit has been met

Pressure drop

The SCR has a total system design maximum pressure drop of 5 inches of H_2O (127 mm WC) and catalyst bed pressure drop of 1.5 inches H_2O (38 mm WC) per layer. The total system pressure drop, which includes the ammonia injection grid, flow rectifiers, turning vanes, soot blowers and catalyst beds, is measured at 2-2.5 inches of H_2O (50-65 mm WC), cf. Figure 22. This is well below the design value of 5 inches of H_2O. The pressure drop across each catalyst bed is measured at 0.8 inches of H_2O (20 mmm WC), which is also significantly below the design value of 1.5 inches of H_2O.
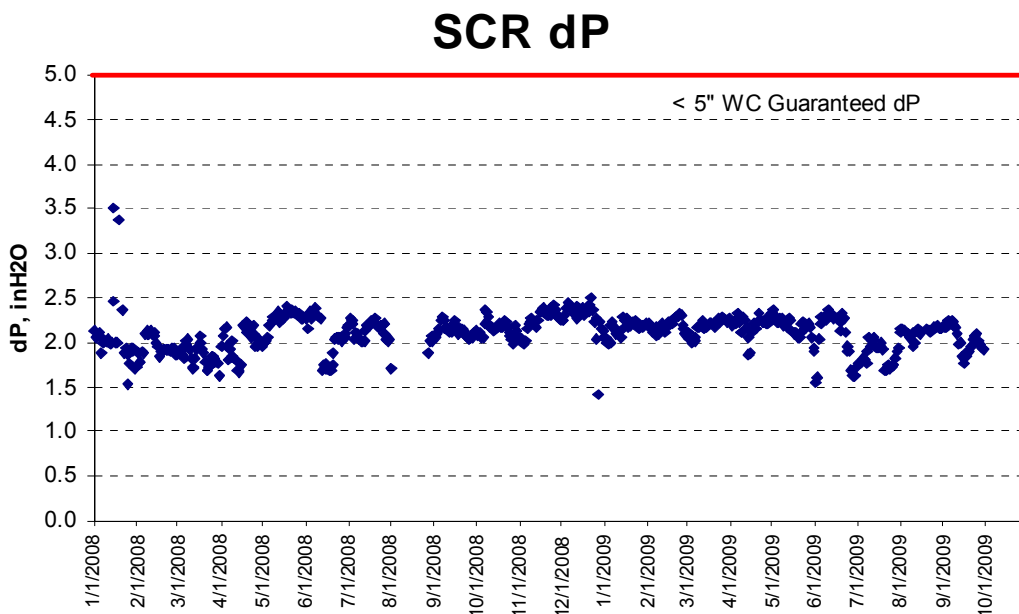
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SCR dP

Figure 22   The total system pressure drop is measured at 2-2.5 inches of H_2O (50-65 mm WC). This is well below the design value of 5 inches of H_2O

6   Conclusions

Selective catalytic reduction, SCR, is the best proven technology to achieve maximum NOx reduction and SCR units for NOx abatement can be designed to meet today's stringent requirements by offering 95%+ NOx reduction.

SCR units have successfully been installed on ethylene cracking furnaces and steam methane reformers. Deactivation of the SCR catalyst as a result of chromium accumulation has to be taken into consideration in the SCR design. The deactivation from chromium masking can be minimised by using an SCR catalyst with a high-porosity diverse pore structure which offers less susceptibility to poisoning.

One of the largest NOx emission sources in a refinery is the flue gas coming from the regenerator in the fluid catalytic cracking unit. It can be the source of 50% of the total NOx emitted from the refinery. The high sulphur oxides concentration and carry-over of FCC fines in the flue gas represent a challenge. With the use of a properly designed SCR reactor and catalyst, experience shows that very low levels of NOx emissions can be achieved from FCC units that have high NOx, SOx and particulates in the flue gas.

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Flow modelling by CFD as well as cold-flow modelling in scale models of the SCR unit are useful tools to verify proper ammonia mixing and flow conditions to the catalyst as well as to identify and eliminate areas for possible dust build-up.

The SCR operating temperature should be selected well above the temperature for formation of ammonium bisulphate, ABS, in the catalyst and the catalyst layers in the SCR reactor should be equipped with soot blowers for regular removal of possible build-up fine-particulate FCC catalyst.

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