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Close-coupled SCR systems for NO_x abatement from diesel exhausts

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Abstract

The combustion of diesel fuel in an engine results in the formation of small amounts of carbon monoxide, hydrocarbons, soot and nitrogen oxides (NO_x), which form a source of environmental pollution and a threat to human health when emitted to the atmosphere. To reduce these negative effects of using diesel fuel, the exhaust gas of diesel engines is passed through a catalytic exhaust system, that reduces emissions of the harmful compounds by well over 90%. In most parts of the world, regulations dictate the maximum emission levels of the harmful compounds in diesel exhausts; in Europe the Euro VI norms dictates the allowable emissions for carbon monoxide, hydrocarbons, soot particles, and NO_x. The technology for NO_x abatement in heavy-duty diesel vehicles is the Selective Catalytic Reduction (SCR) by ammonia (NH₃), which reacts with NO_x to form nitrogen and water. Modern diesel exhaust systems contain at least an oxidation catalyst (DOC), a particle filter (DPF) an SCR catalyst, and an ammonia slip catalyst (ASC), in said sequence. The SCR catalyst can be based on V₂O₅/TiO₂ or Cu-chabazite, which are the two most commonly used SCR catalysts in diesel-exhaust systems.

To operate the SCR catalyst, a solution of urea (AdBlue[®]) is injected into the exhaust gas stream at the SCR catalyst, where the urea decomposes to form NH₃, when the catalyst has reached its operation temperature. As a consequence, the SCR catalyst can only be used at sufficiently high temperatures (180 °C). That means, that in a cold start situation, the SCR catalyst is not active as long as the catalyst has not reached the operating temperature, and in this period, NO_x is emitted to the atmosphere. A significant fraction of the current NO_x emissions from diesel engines originates from these emissions after a cold start. Improving the efficiency of SCR catalysts at operation temperatures will therefore only have a limited effect, and it becomes important to heat the SCR catalyst faster.

In conventional Euro VI exhaust systems, the SCR catalyst is placed towards the outlet of the exhaust. The concept of a close-coupled SCR (cc-SCR) is to place an SCR catalyst directly at the exhaust of the engine - the close-coupled position. At this position, the SCR catalyst is heated faster, and the conversion of NO_x can start earlier. However, a cc-SCR catalyst is exposed to a different environment, as compared to the usual position downstream. The concentrations of hydrocarbons, carbon monoxide and soot particles are higher, and these may interfere with the SCR function. Furthermore, low concentrations of SO₂, which usually are present in an exhaust gas, can lead to severe deactivation of SCR catalysts. In this project, we have investigated the performance and stability of cc-SCR systems for reduction of NO_x emissions.

To evaluate the performance of a cc-SCR exhaust system, we compare two different full-size configurations with a cc-SCR to the conventional layout of a full-size Euro VI system, by testing on a 13 L Euro VI compliant heavy-duty diesel engine using standard WHTC test cycles, combined with model calculations. In the first configuration, the entire SCR function is placed in the cc-SCR position, and in the second configuration, the SCR function is divided over a cc-SCR catalyst and a downstream SCR catalyst at the outlet of the system. For each configuration, an exhaust system with V₂O₅/TiO₂ and with Cu-chabazite based SCR catalysts were evaluated. The stability and tolerance of V₂O₅/TiO₂ and Cu-chabazite SCR catalysts for hydrocarbons, CO and SO₂ is evaluated using a laboratory reactor, using small samples of the same catalysts under controlled conditions.

Engine tests show that a system with a cc-SCR element can reduce the emission of NO_x by 10-25% in a cold start cycle, and 40-70% in a warm start cycle. The heating time to reach 180 °C at the cc-SCR is shortened from about 470 s to about 70 s. Both V₂O₅/TiO₂ and Cu-chabazite type SCR catalysts show a reduction in NO_x emissions, but the emissions of NH₃, and N₂O are different. Generally, V₂O₅/TiO₂ catalysts show higher emissions of NO_x and NH₃ and a lower emission of N₂O, as compared to Cu-chabazite SCR catalysts.

The presence of CO or hydrocarbons in the cc-SCR result in a minor decrease in NO_x conversion, but removal of these compounds from the gas phase restores the original performance. Therefore, these compounds are not critical to operate a cc-SCR. The presence of SO₂ in the exhaust gas is more problematic, as it causes a severe deactivation of Cu-chabazite catalysts in particular. Consequently, in systems containing a Cu-chabazite SCR catalyst, a periodic regeneration procedure is necessary, to maintain a sufficient performance of the system. At sufficiently low SO₂ concentrations (< ~ 1 ppm), the performance of a Cu-chabazite catalyst can be usually be restored by heating to about 500 °C. At higher concentrations (~ 6 ppm SO₂) a Cu-chabazite based catalyst can be permanently damaged. The presence of adsorbed NH₃ on a Cu-chabazite catalyst enhances the impact of SO₂ on the performance of Cu-chabazite. The performance of V₂O₅/TiO₂ based SCR catalysts is not significantly affected by the presence of SO₂.

Based on model calculations, it is found that the volume of the cc-SCR should be about 25-40% of the total SCR volume, i.e. the sum of the cc-SCR and downstream SCR. The urea dosing strategy, which controls the NH₃ concentration in the gas stream, is a critical parameter for the performance of a cc-SCR system. At the cc-SCR catalyst, the NH₃/NO_x ratio in the gas phase should be kept below 1, to avoid NH₃ slip from the cc-SCR element, which leads to unwanted emissions of N₂O. Furthermore, the use of a cut-off in urea dosing at high temperatures results in higher emissions of NO_x, and is therefore not recommended, but can be necessary for passive regeneration of the DPF. By using a V₂O₅/TiO₂ catalyst as cc-SCR and a Cu-chabazite catalyst as downstream SCR, the benefits of both types of catalysts can be combined to create systems with improved N₂O emissions and better tolerance for SO₂.

In conclusion, the cc-SCR concept, involving a rearrangement of existing catalyst elements in a diesel exhaust system, is an effective, competitive, and easy-to-implement solution that can reduce NO_x emissions by 35-50%. The first commercial application of this concept are underway, and we expect that the concept will contribute to a further reduction of NO_x emissions around the world in the near future.

Dansk resumé

Ved forbrænding af dieselolie i en motor dannes der små mængder af kulmonoxid, kulbrinter, sod, og kvælstofoxider (NO_x), som er årsag til miljøforurening, og er en fare for menneskets sundhed når de udledes i atmosfæren. For at begrænse de negative effekter ved brug af dieselolie, ledes dieseludstødningsgasser gennem et katalytisk udstødningsystem, som mindsker udledningen af de skadelige komponenter med mere end 90%. De fleste steder i verden er de maksimale niveauer for de skadelige komponenter i dieseludstødningsgasser reguleret ved lov; i Europa gælder Euro VI normerne, som dikterer de maksimalt tilladte emissionsværdier kulmonoxid, kulbrinter, sodpartikler og NO_x. Metoden, hvorved NO_x gasser fjernes fra udstødningsgassen fra store lastbiler, er ved en kemisk selektiv katalytisk reduktion (SCR), hvor ammoniak anvendes i en redox reaktion til at omdanne NO_x til N₂ og vand. Moderne dieseludstødningsystemer indeholder som minimum en oxidationskatalysator (DOC), et partikelfilter (DPF), en SCR katalysator og en katalysator til at fjerne overskydende NH₃ (ASC), i nævnte rækkefølge. SCR katalysatoren er hovedsageligt baseret på et af de aktive materialer V₂O₅/TiO₂ eller Cu-chabazite.

For at bruge SCR katalysatoren, sprøjtes en urea-opløsning (AdBlue®) ind i udstødningsgassen, hvorved urea dekomponerer til NH₃. Dette er dog kun muligt når temperaturen ved SCR katalysatoren er over 180 °C. Det betyder, at i en koldstartssituation, hvor systemet endnu ikke har opnået den nødvendige temperatur, er SCR katalysatoren ikke aktiv, og NO_x udsendes med udstødningen i denne periode. En betydelig del af de nuværende NO_x emissioner fra dieselmotorer har oprindelse fra sådanne koldstarter. Således vil en forbedring af SCR katalysatorens effektivitet ved arbejdstemperaturen kun have en mindre effekt, hvorimod SCR katalysatorens opvarmingshastighed bliver mere betydningsfuld.

I et konventionelt Euro VI udstødningsystem er SCR katalysatoren placeret i den bagerste ende af udstødningssystemet. I et "close-coupled SCR" koncept (cc-SCR), placeres SCR katalysatoren direkte efter motoren. I denne position opvarmes SCR katalysatoren hurtigere, og omdannelsen af NO_x kan derved starte tidligere. Dog er en cc-SCR katalysator eksponeret til andre betingelser end i den traditionelle position nedstrøms til DOC og DPF. Således vil koncentrationerne af kulmonoxid og kulbrinter, og mængden af sodpartikler, være højere for en cc-SCR, hvilket kan påvirke dens funktionalitet. Ydermere vil cc-SCR'en blive direkte eksponeret til al SO₂ i udstødningsgassen, hvilket kan føre til deaktivering af katalysatoren, trods de lave koncentrationer som forefindes i dieseludstødningsgasser. I dette projekt har vi undersøgt ydeevne for NO_x fjernelse, og stabilitet af cc-SCR baserede udstødningsystemer.

For at evaluere potentialet ved cc-SCR systemer sammenligner vi to forskellige cc-SCR system konfigurationer i fuld skala med et konventionelt Euro VI udstødningsystem. Sammenligningen sker på baggrund af standard WHTC test programmer kørt på en 13 L Euro VI godkendt dieselmotor, og matematiske model-baserede beregninger. I den ene cc-SCR system konfiguration er hele SCR katalysatoren flyttet til cc-positionen, og i den anden konfiguration er kun en del af SCR katalysatoren flyttet til cc-positionen, og den resterende del forbliver i sin oprindelige position. For hver konfiguration blev systemerne testet med både V₂O₅/TiO₂ og Cu-chabazite baserede SCR katalysatorer. Stabiliteten og tolerancen af hver SCR katalysator type for henholdsvis kulmonoxid, kulbrinter og SO₂, blev undersøgt ved hjælp af laboratorieeksperimenter på mindre katalysatorprøver, under kontrollerede betingelser.

Motortestene viser, at cc-SCR systemerne kan nedbringe mængden af NO_x emissioner med 10-25% i et koldstarts WHTC program, og 40-70% i et varmt WHTC program. Opvarmningstiden til 180 °C er for cc-SCR katalysatoren forkortet fra ca. 470 s til ca. 70 s, som det krævede for at opnå samme temperatur ved SCR katalysatoren i et konventionelt system. Både anven-

delsen af V_2O_5/TiO_2 og Cu-chabazite baserede SCR katalysatorer fører til lavere NO_x emissioner i cc-SCR systemerne, dog i forskellige grader og med forskellige emissioner af NH₃ og N₂O. Generelt medfører V_2O_5/TiO_2 baserede katalysatorer højere NO_x og NH₃ emissioner end Cu-chabazite baserede katalysatorer, men er mere fordelagtige med hensyn til N₂O.

Tilstedeværelsen af kulmonoxid og kulbrinter i cc-SCR katalysatoren fører til en lille reduktion af NO_x omdannelsen, men indflydelsen er momentan og forsvinder med kulmonoxid og kulbrinternes fravær. Derfor anses disse forbindelsers tilstedeværelse ikke som kritisk for cc-SCR systemer. Tilstedeværelsen af SO₂ er mere kritisk for Cu-chabazite baserede cc-SCR systemer, da SO₂ fører til en markant deaktivering af Cu-chabazite katalysatoren. En deraf afledt konsekvens for Cu-chabazite baserede cc-SCR systemer er, at cc-SCR katalysatoren bør underlægges en periodisk regenereringsprocedure, for at opretholde sin funktionalitet. Dette er muligt ved at opvarme katalysatoren til 500 °C, så længe SO₂ koncentrationen er tilstrækkelig lav (< ~ 1 ppm), som ved brug af ultra-lav svovl diesel. Derimod kan anvendelse af diesel med højere svovlindhold, som medfører SO₂ koncentrationer omkring 6 ppm, føre til permanent beskadigelse af SCR katalysatorens ydeevne. Tilstedeværelsen af adsorberet NH₃ på Cu-chabazite forstærker indflydelsen af SO₂ på katalysatorens NO_x omdannelse. I modsætning til Cu-chabazite er der ikke en markant indflydelse af SO₂ på V_2O_5/TiO_2 baserede SCR katalysatorer.

Baseret på beregninger fra matematiske modeller, blev det klargjort at andelen af cc-SCR volumen ideelt bør være 25-40% af det totale SCR volumen. Urea doseringsstrategien, som definerer NH₃ koncentrationen i udstødningsgassen, er en særlig kritisk parameter for cc-SCR systemets præstation. Ved cc-SCR katalysatoren bør NH₃/NO_x forholdet holdes mindre end 1, for at undgå at overskydende NH₃ passerer videre til DOC og DPF, hvor det uønsket omdannes til N₂O. Anvendelsen af urea doserings "cut-offs", for at tillade passiv regenerering af DPF, førte til højere NO_x emissioner, og anbefales derfor ikke. Ved brug af V_2O_5/TiO_2 som cc-SCR og Cu-chabazite som nedstrøms SCR katalysator, kan fordelene ved hver teknologi kombineres til at opnå systemer med enten lavere NO_x emission, eller lavere N₂O emission og forbedret SO₂ tolerance.

Som opsummering, cc-SCR konceptet, hvor katalysatorerne i et diesel udstødningsystem delvist omroteres, er en effektiv, konkurrencedygtig og nemt implementerbar løsning til at reducere NO_x emissioner med 35-50%. De første kommercielle cc-SCR systemer er på vej, og vi forventer at dette koncept vil bidrage til yderligere at reducere NO_x emissioner i den nære fremtid på verdensplan.

1. Introduction

1.1 Emission regulations for diesel engines

In our modern society, diesel-driven vehicles play a crucial role. For road transportation and distribution of goods, medium- and heavy-duty vehicles are used, and the vast majority of these vehicles are powered by diesel fuel. Motivated by the necessity to reduce greenhouse gas emissions, the development of non-fossil energy sources, such as hydrogen or biofuels, as well as the development of electric vehicles has gained a lot of attention in recent years. The transition to non-fossil fuel based vehicles will primarily materialize for light-duty vehicles, in particular with a noticeable growth in electric vehicles, from about 7.5 million vehicles in 2019 to an expected 135 million vehicles in 2030.¹ For heavy-duty vehicles, the transition to non-fossil fuel based vehicles will be more modest. It is estimated that by 2030, the share of electric vehicles in this class will reach about 1-3% of the total fleet, and about 1.5% of the sales.¹ It is therefore expected, that diesel powered vehicles will remain very important as a means of transportation in the coming decades, in particular for medium- and heavy-duty vehicles.

In the past 30-40 years, it has been realized that the extended use of diesel engines has a negative impact on the environment and poses a general health risk, due to the emission of unburnt fuel, carbon monoxide, soot particles, the nitrogen oxides NO and NO₂ (NO_x) and nitrous oxide (N₂O). In fact, the emission of NO_x from diesel vehicles is a major contributor to the formation of smog in urban areas. To mitigate the impact of diesel exhaust gases on the environment and public health, regulations have been put in place in many locations since the early 1990's, which have resulted in a significant reduction of the emission of harmful components in diesel exhausts. In Europe, the emission regulations are implemented on the EU level via the European emission standards Euro I-VI. At present, the Euro VI emission standard, with the emission limits for heavy-duty vehicles as summarized in TABLE 1,² is in force. Similar emission regulations exist other places in the world.

TABLE 1 Euro VI norm emission values for heavy-duty diesel engines.²

	Unit	Stationary test (WHSC)	Transient test (WHTC)
CO	g/kWh	1.5	4.0
Hydrocarbons	g/kWh	0.13	0.16
NO _x	g/kWh	0.40	0.46
Particulate Matter	g/kWh	0.01	0.01
Particulate Number	1/kWh	8.0×10 ¹¹	6.0×10 ¹¹

The historical development of the emission limits is summarized in FIGURE 1, which reflects the huge improvements in emissions from diesel engines that already have been achieved in the past decades. The current Euro VI NO_x limit is only 1/20 of that defined in Euro I; for particulate matter emission, the limit is reduced by a factor of almost 40. These improvements are the result of the technological development of engines and exhaust gas aftertreatment systems, together with timely legislation to drive the development process.

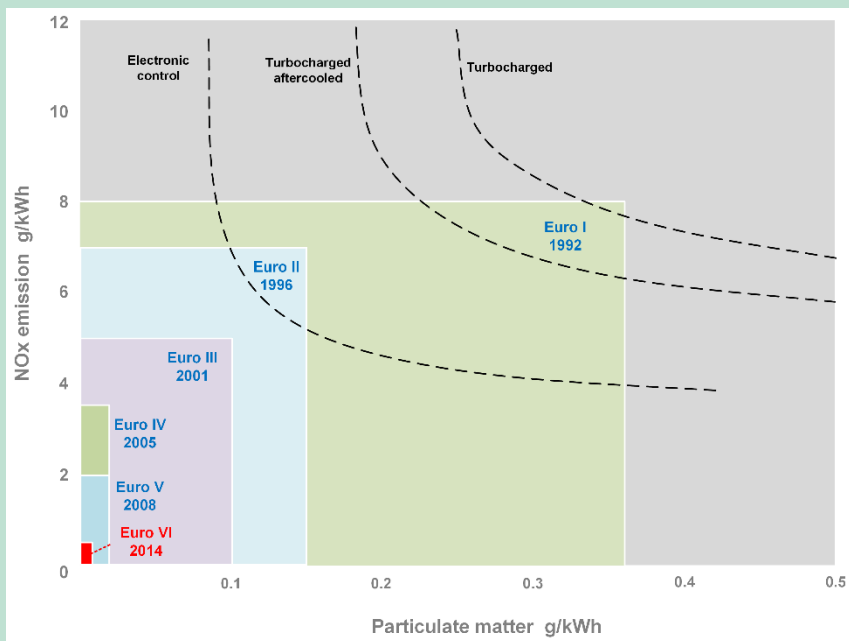


FIGURE 1. EU emission standards Euro I-VI for heavy-duty diesel engines, which have been implemented since 1992.² The dashed lines indicate the levels that can be achieved by optimizing engine technology, operation and tuning. To achieve the more recent standards, catalysts are required.

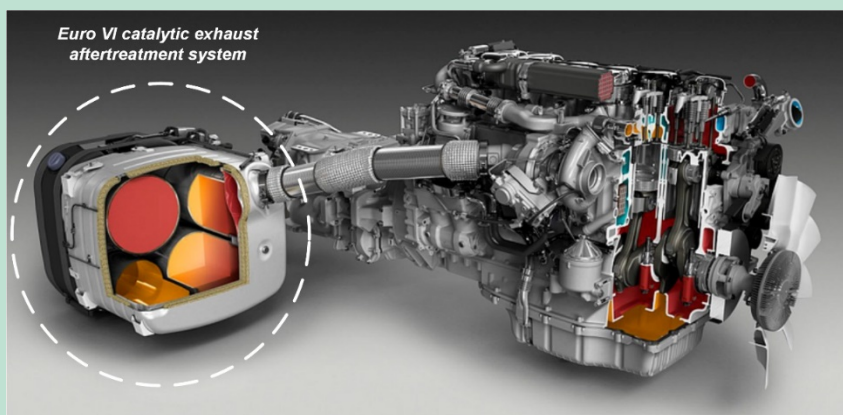


FIGURE 2. Catalytic exhaust gas aftertreatment system mounted on a heavy-duty diesel engine.

From a technical point of view, the reduction of emissions from diesel engines is achieved by optimizing engine operation, e.g. tuning, fuel injection control, turbocharging, and catalytic exhaust gas aftertreatment systems. The dashed lines in FIGURE 1 indicate the emission levels of NOx and soot particles, that can be reached by optimizing engine operation. It is clear that, since the introduction of the Euro III standard in the early 2000's, the use of catalysts in exhaust aftertreatment systems is essential to be able to comply with the emission standard. With the continued restrictions of the different emission limits with time, the catalytic aftertreatment systems have become more complicated to reach a more efficient removal of

the harmful components. An aftertreatment system for a modern Euro VI compliant vehicle consists of at least a diesel oxidation catalyst (DOC), a diesel particulate filter (DPF), an catalyst for selective catalytic reduction of NO_x (SCR), and an ammonia slip catalyst (ASC). The catalyst elements are monolithic elements, usually cylinders with a diameter of typically 25-30 cm, and 10-30 cm in height. These elements are arranged in a box mounted at the exhaust of the engine, as shown in FIGURE 2. When the engine is running, the exhaust gas passes through these catalyst elements, where the chemical reactions take place to remove the unwanted components of the exhaust gas before emission of the exhaust gas to the atmosphere.

1.2 Function and elements of diesel exhaust gas aftertreatment systems

The main components in a raw diesel exhaust gas are nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), and water (H₂O), as the result of the combustion of diesel fuel in air. The actual amounts vary, depending on the engine load and engine operation. Typical concentrations of CO₂ and H₂O in a diesel exhaust gas are in the range 2-12%, and the concentration of O₂ is in the range 3-17%, in balance (ca. 75%) N₂.³ The emission of these compounds is unproblematic as far as human health is concerned. The emission of CO₂, however, is the main cause of the climate change that we currently experience, but as a main product of the fuel combustion, its formation cannot be avoided in a combustion engine.

The total concentration of the harmful compounds regulated in the Euro VI norm, CO, hydrocarbons, NO_x, is actually very low, typically just a few tenths of a percent. Nevertheless, even at these low concentrations, they have a significant impact on the environment (e.g. smog formation, acid rain) and public health. Comparing the typical composition of a raw diesel exhaust gas with the emission limits in TABLE 1, it is clear that an exhaust gas aftertreatment system must remove the hydrocarbons, CO, soot and NO_x almost entirely. In order to comply with the Euro VI and similar regulations, about 95 % of the NO_x, and the other unwanted compounds must be removed. The challenge is that the system must achieve such conversion levels over a wide temperature range 200-550 °C, and under fast-changing flow conditions, because the conditions in the exhaust system change dynamically with the engine load and driving conditions. In a modern aftertreatment system the different elements DOC, DPF, SCR, and ASC each target specific compounds in the exhaust gas. The typical arrangement of these elements in the aftertreatment system of a Euro VI compliant heavy-duty vehicle, is shown in FIGURE 3.

The element closest to the engine is the DOC, which oxidizes the unburnt fuel (hydrocarbons) and CO to CO₂ and water, with the residual oxygen present in the exhaust gas. The catalyst consists of Pt/Pd particles on an oxidic support material, usually alumina. A second function of the DOC is to oxidize some of the NO coming from the engine to NO₂, which is needed to oxidize soot particles in the DPF further downstream. The Pt and Pd also catalyze this reaction.

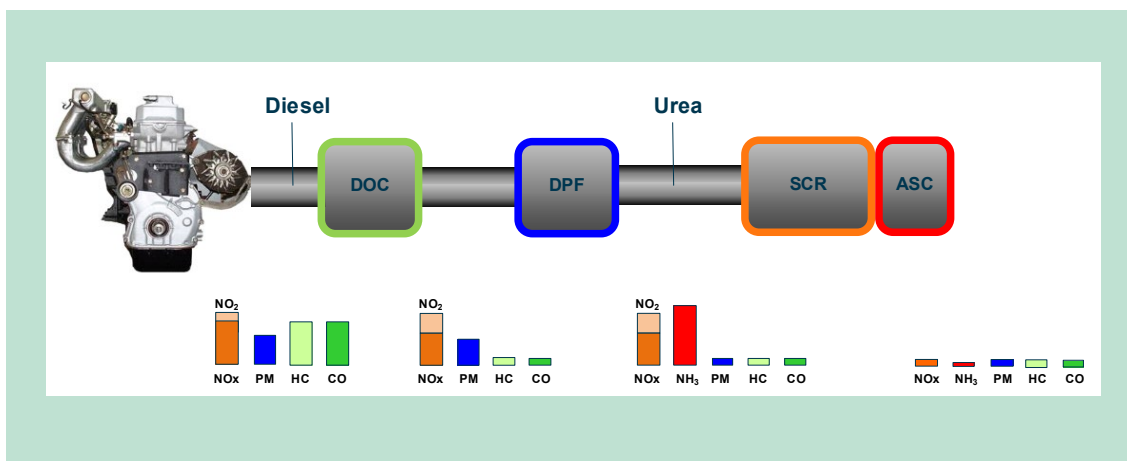


FIGURE 3. Typical arrangement of the different catalyst elements in a Euro VI compliant heavy-duty diesel vehicle. The bars give a rough indication of the contents of the NO_x, particulate matter, hydrocarbons, CO and NH₃ in the exhaust gas at the different stages in the exhaust system.

In the next step, the DPF filters out the soot particles. The DPF consists of a monolith with porous ceramic walls. The exhaust gas is pressed through these walls, and as the soot particles cannot pass through the small pores in the walls, the particles accumulate in the DPF. To remove the accumulated soot, a regular regeneration of the DPF is required. There are two procedures to do this, namely active regeneration or passive regeneration. In active regeneration, the temperature in the system is increased to up to 700 °C by a late fuel injection in the engine or a direct injection of diesel just before the DOC (see FIGURE 3). This creates a higher concentration of hydrocarbons in the DOC, resulting in an increased heat release as these are oxidized. Above ca. 550 °C, the soot particles will burn off with the residual oxygen in the exhaust gas, thus cleaning the filter. Passive regeneration relies on the oxidation of soot by NO₂, a reaction that can take place at around 400 °C, which is in the higher end of the normal operating temperature range of an exhaust system. This approach requires a balance between soot accumulation, NO₂ formation in the DOC, and temperature in the DPF. The NO₂ needed for this must be generated in the DOC, via oxidation of the NO, and this is an important reason why the DPF generally is downstream of the DOC.

In the SCR catalyst, the NO_x is removed from the exhaust gas via the selective catalytic reduction by NH₃. This reaction follows the equation:



The most common catalysts for NH₃-SCR in exhaust systems are based on Cu-chabazite (Cu-CHA) or V₂O₅ on a TiO₂ support (V₂O₅/TiO₂). The NH₃ required for this reaction is not present in the raw exhaust gas, and is therefore added to the exhaust gas stream. The most commonly used method is to inject an aqueous solution of urea, known as AdBlue® in Europe or DEF (Diesel Emission Fluid) in North America. The urea decomposes to NH₃ and CO₂ at temperatures above about 180 °C. The NH₃ released then reacts in the SCR catalyst with the NO to form N₂ and H₂O. According to Eq. 1, the NO and NH₃ react in equal amounts, and therefore, the amount of NH₃ added to the system should be equal to the amount of NO to be converted. This is often expressed as an ammonia-to-NO_x ratio (ANR) of 1. In practice, a slight excess of NH₃ (ANR=1.1-1.2) is used, as this results in a more efficient removal of the NO_x.

As a consequence of the excess of NH₃ used in the SCR, the gas leaving the SCR catalyst will contain a small amount of NH₃. This NH₃ is then removed in the ASC, which is the final stage of the exhaust system. The ASC is a bifunctional catalyst that combines an NH₃ oxidation function with an NH₃-SCR function. It usually is a combination of a supported Pt catalyst,

which provides the NH₃ oxidation function, and a Cu-zeolite for the SCR function. The Pt catalyst oxidizes the NH₃ with the residual oxygen in the exhaust gas, and this reaction usually produces NO and some N₂O. The NO formed in this reaction is taken care of by the SCR function, in which some residual NH₃ is used to form N₂ and H₂O via the SCR reaction (Eq. 1). For the ASC, it is crucial to balance the oxidation and SCR functions. Too much NH₃ oxidation will lead to a NO_x emission, since not enough NH₃ is left to convert the NO via SCR. Insufficient NH₃ oxidation will lead to an unwanted emission of NH₃. This balance is critical, as the ASC is the final stage in the exhaust system, and any deviation will result in unwanted emissions of NH₃ or NO_x at the tailpipe.

1.3 Sulfur dioxide

In addition to NO_x, hydrocarbons, soot and CO, some SO₂ is usually present as well. In contrast to NO_x, SO₂ is not a byproduct of the combustion process itself, but is a consequence of a small amount of sulfur-containing compounds in the fuel. To manage the emissions of SO₂, the sulfur content in the fuel is regulated. The sulfur compounds are removed via desulfurization of the crude oil in the refinery process, resulting in ultra-low-sulfur diesel fuels. In Europe, the ultra-low-sulfur diesel standard prescribes a maximum sulfur content of 10 wt ppm in the diesel fuel; in North America it must be lower than 15 wt ppm. Nevertheless, the exhaust gas from a ultra-low sulfur diesel fueled engine still contains about 0.5-2 ppm SO₂. Apart from a possible unwanted environmental impact, such a small amount SO₂ has a potentially severe negative effect on the efficiency of the catalyst elements in the exhaust system. Therefore, the presence of such small amounts SO₂ may cause increased emissions of NO_x and other unwanted compounds, as the function of the catalyst elements deteriorates. For this reason, the presence of SO₂ is a point of concern in a diesel exhaust aftertreatment system.

1.4 The cold-starts problem

The modern exhaust gas aftertreatment systems effectively remove the unwanted NO_x, hydrocarbons, CO and soot from the exhaust gas stream, once they have reached their operation temperature. However, the catalysts are not effective at temperatures below their normal operating temperature. Therefore, the emissions of unwanted compounds are higher in a cold-start situation, as it takes some time to reach a sufficiently high temperature. It is estimated that, with modern exhaust systems, about 60-70 % of the total NO_x emissions is due to emissions during warming up of the exhaust system.⁴⁻⁶ As a consequence, to further reduce the NO_x emissions, it is no longer sufficient to look at the 'normal' operating conditions of the exhaust system, but it is also necessary to minimize the impact of the emissions during heating the system from a cold start.

The two major reasons why the temperature is important for an effective abatement of the NO_x are (1) the ability to decompose the urea to form the necessary NH₃, and (2) the catalytic activity of the SCR catalyst below 200 °C. The decomposition of urea requires a temperature of about 180 °C, and therefore urea dosing can first start when this temperature has been reached. As long as no urea can be dosed, the SCR catalyst cannot convert any NO_x, which leads to the NO_x emission in a cold start situation. Therefore, the time needed to heat up the SCR catalyst to the operating temperature is an important factor determining the NO_x emission.

With the current systems, the exhaust system is heated by the hot exhaust gas coming from the engine without any further regulation. Therefore, the heating is faster for the upstream elements (DOC and DPF in the configuration in FIGURE 3), and becomes slower in the final part of the exhaust system. In the Euro-VI exhaust system as depicted in FIGURE 3, the SCR catalyst is placed towards the end of the system. This means that it will take some time for the SCR catalyst to reach the minimum operating temperature, and during this period, emissions

of NO_x will take place, thus leading to the significant proportion of NO_x emissions in cold starts. This means, that the rate of heating of the SCR catalyst is an important parameter that determines the overall NO_x emission, and a fast heating of the SCR catalyst will result in a more efficient removal of NO_x from diesel exhausts.

1.5 Project goal: Evaluation of close-coupled SCR systems for NO_x reduction

There are several possibilities to achieve a faster heating of the SCR catalyst. An external heating source, electric or fuel burner, can heat up the exhaust system independent of the temperature of the exhaust gas. Such a solution, however, will necessarily increase fuel consumption, which is a clear disadvantage. The approach studied in this report is to rearrange the catalytic elements in the exhaust system, with an SCR catalyst in the close-coupled position, *i.e.* mounted as the first element directly at the exhaust of the engine. In such configurations, the close-coupled SCR (cc-SCR) catalyst is heated faster, since the temperature of the exhaust gas is highest at this position. The approach with a cc-SCR element has two important advantages:

- There is no additional heating of the system, and therefore, there is no increased fuel consumption in cc-SCR systems
- A cc-SCR system is created by rearranging existing parts in a conventional exhaust system. Therefore all parts needed are already available, and no new production processes or materials have to be developed.

The goal of this project is to investigate the potential of systems with a close-coupled SCR catalyst for a further reduction of NO_x emissions from diesel engines. As explained above, in such systems, the cold-start emissions of NO_x are addressed by accelerating the heating of the SCR catalyst in a cold start situation. In order to assess the efficiency of cc-SCR catalysts, we compare two different configurations with a close-coupled SCR with that of a conventional exhaust system as shown in FIGURE 3. The basic configurations of the exhaust systems used in this study are given in FIGURE 4, indicated as aftertreatment system ATS-1, 2, and 3. The configuration in ATS-1 is the conventional Euro VI configuration also shown in FIGURE 3. The simplest way to obtain a cc-SCR system is just to swap the positions of the SCR + ASC and DOC + DPF in ATS-1. This then results in ATS-2. In ATS-3, the SCR function is split between a close-coupled SCR catalyst and a second SCR catalyst element further downstream, with a total volume of the SCR catalyst as that in ATS-1 and ATS-2.

Placing an SCR catalyst in the close-coupled position changes the conditions at which the SCR catalyst must work. In ATS-1, the exhaust gas first passes through the DOC and DPF, and therefore the SCR catalyst is not directly exposed to unburnt fuel (hydrocarbons), CO, and soot particles. In ATS-2 and ATS-3, hydrocarbons and CO are present in the SCR catalyst, and may therefore interfere with the SCR function. Removing the NO_x first via SCR also affects the ability to form NO₂ in the DOC, now further downstream, and therefore also the regeneration of the filter. These differences need to be accounted for in systems with a close coupled SCR.

In ATS-3, it is necessary to have two injection points for the urea, in order to supply the NH₃ necessary for each SCR element. In addition, the ASC function for the cc-SCR catalyst is combined with the DOC function, since the oxidation of NH₃, hydrocarbons, and CO are all catalyzed by Pt or Pt/Pd. Such a configuration has some additional degrees of freedom, as compared to ATS-2, such as the volumes of the close-coupled SCR and downstream SCR, and the independent NH₃ dosing to the two SCR elements, resulting in a different ANR in the two SCR elements. This offers some parameters that can be used to optimize a system design, or to adjust an exhaust system to a specific engine, but also adds complexity to the system.

As pointed out above, there are two common types of SCR catalyst, namely catalysts based on Cu-CHA and V_2O_5/TiO_2 . These two types of catalysts each have their own characteristic behavior and disadvantages. This means that different combinations of these types of catalyst can influence the performance of the exhaust system, which means that this choice also is important for a design of exhaust systems with a cc-SCR catalyst.

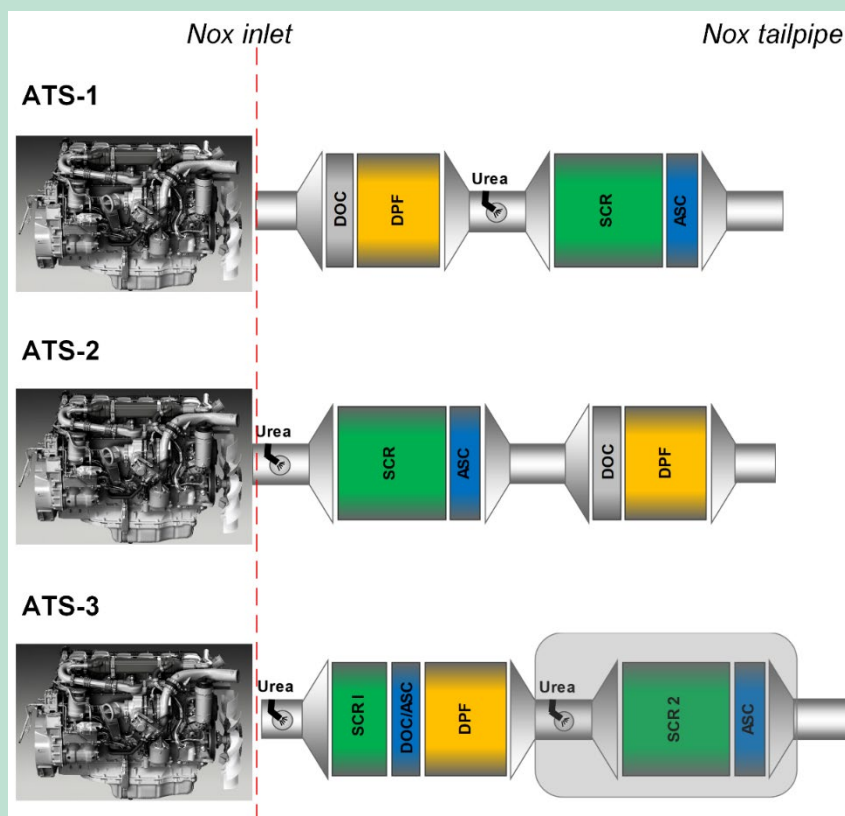


FIGURE 4. Basic configurations of a conventional exhaust system (ATS-1), without a close-coupled SCR, and systems with a close-coupled SCR catalyst (ATS-2 and ATS-3). The red dashed lines indicate the positions at the inlet and tailpipe for the evaluation of the NO_x removal.

1.6 Work packages

The project has been divided in 5 work packages, which are described in more detail below.

1.6.1 WP1: Proof of principle

The goal of this work package is to show that systems with a cc-SCR catalyst actually improve the NO_x emission in diesel exhaust, and to get an idea on how systems with a cc-SCR catalyst behave. This is done by laboratory-engine tests, using a standard WHTC cycle. These tests have been performed at Umicore Denmark. In this work package, we have tested both Cu-chabazite and V_2O_5/TiO_2 based SCR catalysts for all three configurations ATS-1, ATS-2, and ATS-3 as shown in FIGURE 4. These experiments also show some other characteristics of cc-SCR systems, and give some insight in how the system design affects the performance. This is then used as input to WP3.

1.6.2 WP2: Effect of CO, hydrocarbons and SO₂ on performance of SCR catalysts.

The concept of cc-SCR catalysts necessarily implies that such catalysts are exposed to higher concentrations of SO₂, hydrocarbons, and CO, compared to the conventional SCR catalysts. This means that the standard SCR catalysts, as we intend to use them in cc-SCR systems, are exposed to gas atmospheres that these were not designed for. In this work package, the effect of the presence of SO₂, hydrocarbons, and CO on both Cu-chabazite and V₂O₅/TiO₂ based SCR catalysts is investigated. The results are then used to assess the possibility how these compounds affect the performance of the cc-SCR catalyst, and how to handle cc-SCR systems with respect to the presence of these gases. The effect of SO₂ on Cu-CHA, which is a known issue for such SCR catalysts, require a larger research effort, and are therefore studied in more detail in WP3. The experiments have been performed on a smaller laboratory reactor at DTU Kemiteknik, in which different laboratory catalysts can be arranged in a similar way as in real exhaust systems, while having a better control of the composition of the gas atmosphere and temperature at the individual catalyst elements.

1.6.3 WP3: Optimization of cc-SCR systems

Based on the input from WP1 and WP2, some ways to improve the cc-SCR systems have been investigated. The specific points studied are:

1. The general design of cc-SCR systems, in particular the size of close-coupled SCR and the downstream SCR catalyst, and how to adjust the urea dosing strategy in these situations. This work has been performed by combining a model calculations with engine tests, all performed at Umicore AG, Hanau, Germany.
2. The possibility of how Cu-chabazite based catalysts can be combined with V₂O₅/TiO₂ based catalysts in order to exploit the characteristics of these systems best. This part involves additional engine testing done at Umicore AG, Hanau, Germany.
3. The effect of repeated SO₂-poisoning and regeneration cycles on the performance of SCR catalysts, with focus on Cu-chabazite based catalysts. This study has been done by additional laboratory tests as in WP2, and further engine tests performed at Umicore Denmark, and Umicore AG, Hanau, Germany

The results of this WP have been used to design the demonstration test described in WP4.

1.6.4 WP4: Demonstration of a cc-SCR system

In this work package, an exhaust system containing a close-coupled SCR catalyst is selected, based on the results obtained in the other parts of the project, and the performance is evaluated on the basis of engine tests using WHTC test cycles. The performance of this system is then compared to the performance of a conventional exhaust system, in order to determine the improvement obtained by the cc-SCR concept. These engine tests have been done at Umicore AG, Hanau, Germany. Furthermore, a Design Failure Mode and Effect Analysis (DFMEA) is given, to find possible flaws or critical problems in the system design, and to identify how to mitigate the consequences of these points. A DFMEA document is a standard part of quality systems in the automotive industry.

1.6.5 WP5: Administration

In this work package, resources for project meetings, reporting and project management have been defined.

2. Proof of principle: cc-SCR systems

2.1 Setup of the measurements

In this part, we investigate whether a rearrangement of catalyst elements to a cc-SCR configuration actually results in an improved NO_x removal in a diesel exhaust. To this end, the performance of a conventional exhaust system (ATS-1, FIGURE 4) was compared with two different configurations with a cc-SCR element. In one configuration, ATS-2, the entire SCR catalyst and ASC catalyst were placed at the inlet end of the exhaust system. In ATS-3, 40% of the total SCR volume, as compared to ATS-1, is placed at the close-coupled position at the inlet of the exhaust system, while the remaining 60% is kept at the downstream position towards the outlet. In that configuration, an element working both as ASC and DOC is replacing the pure DOC as well. It is noted that the total volume of SCR catalyst is kept constant, so any effects due to a change in catalyst volume can be directly eliminated.

The tests were conducted on a Euro VI compliant engine with a cylinder volume of 13 L. engine, using a World Harmonized Transient Cycle.⁷ This is a normalized test of 30 min. duration, in which the engine is run with a predefined engine load (torque) and speed to represent the typical driving conditions in cities, highways, and motorways in Europe, North America, Japan and Australia. During the test, the composition of the exhaust gas was monitored by Fourier-transform Infrared Spectrometry (FTIR) at the inlet and outlet of the exhaust system, as well as the temperature at various locations in the exhaust system. Immediately before each SCR element, urea was dosed, and dedicated NO_x sensors at these locations were placed, in order to regulate the amount of urea to the amount of NO_x entering the SCR catalysts.

Each of the configurations ATS-1, ATS-2 and ATS-3 (FIGURE 4) were tested for both Cu-chabazite and V₂O₅/TiO₂ based catalysts, in both cold start and warm start conditions. In all tests with ATS-1 and ATS-2, the amount of urea used corresponded to an ANR of 1.1, which is a typical value used in exhaust systems. In the tests with ATS-3, an ANR of 0.6 was used for the cc-SCR catalyst, and an ANR of 1.1 for the downstream SCR. We chose to operate the cc-SCR catalyst in these tests with an understoichiometric amount of NH₃, to avoid an NH₃-slip from the cc-SCR. Since the following ASC/DOC catalyst contains Pt, we anticipated that such an NH₃-slip could result in some unwanted emission of N₂O. Furthermore, in all tests, the dosing of the urea was started when the temperature at the SCR catalysts had reached 180 °C, and was then kept running, also when the temperature would decrease again to below 180 °C. Finally, to monitor the effect of the ANR at the cc-SCR catalyst in ATS-3, a few additional warm tests with variable ANR values between 0.3 and 1.1 were performed as well.

An overview of the catalyst elements in the exhaust systems used in this part of the project is given in TABLE 2.

TABLE 2 Specification of the catalysts in configurations ATS-1, ATS-2, and ATS-3.

Configuration		Position 1	Position 2	Position 3	Position 4	Position 5
ATS-1	Type	DOC	DPF	SCR	ASC	
	Catalyst	10 g/ft ³ Pt/cordierite 400/4		SCR catalyst*	Cu-CHA SCR 2 g/ft ³ Pt cordierite 400/4	
	Dimension	12.5 × 3"	12.5 × 9"	12.5 × (6+3+6)"	12.5 × 3"	
	Volume (L)	6	18	30	6	
ATS-2	Type	SCR	ASC	DOC	DPF	
	Catalyst	SCR catalyst*	Cu-CHA SCR 2 g/ft ³ Pt cordierite 400/4	10 g/ft ³ Pt/cordierite 400/4		
	Dimension	12.5 × (6+3+6)"	12.5 × 3"	12.5 × 3"		12.5 × 9"
	Volume (L)	30	6	6		18
ATS-3	Type	SCR	ASC/DOC	DPF	SCR	ASC
	Catalyst	SCR catalyst*	Cu-CHA SCR 8 g/ft ³ Pt cordierite 400/4		SCR catalyst*	Cu-CHA SCR 2 g/ft ³ Pt cordierite 400/4
	Dimension	12.5 × 6"	12.5 × 3"	12.5 × 9"	12.5 × (3+6)"	12.5 × 3"
	Volume (L)	12	6	18	18	6

* SCR-catalysts: V₂O₅/TiO₂ on corrugated substrate 260 cpsi - Cu-chabazite on cordierite 400 cpsi.

2.2 Cold start performance

To assess the performance of the cc-SCR exhaust systems, we compare the measured conversions of NO_x, and emissions of NO_x, N₂O, and NH₃ in cold and warm WHTC cycles. FIGURE 5 summarizes the cumulative emission of NO_x during the cold-start and warm-start test cycles for systems with Cu-chabazite based catalysts and systems with V₂O₅/TiO₂ based catalysts. It is immediately clear, that the NO_x emissions in a cold-start test cycle is 2-5 times higher than in the warm cycle. This clearly indicates that cold-starts indeed contribute significantly to the total NO_x emissions, which is the premise of this project.

A comparison of the NO_x emissions from a standard exhaust system (configuration ATS-1) with those of systems with a cc-SCR catalyst (configurations ATS-2 and ATS-3) reveals the effect of a cc-SCR catalyst on the NO_x reduction. In FIGURE 5, this is indicated by the blue and orange dashed lines, which indicates the performance of a standard system. The cc-SCR shows a clear improvement in the NO_x conversion in all cases, in both the cold-start and warm-start test cycles, except the cold-cycle test with ATS-3, where a higher NO_x emission is found, as compared to the standard system. The higher NO_x emission with ATS-3 will be explained below. The reduction in NO_x emission is 10-25% in the cold-start cycles, and 40-70% in the warm-start cycles. These results indicate that the systems with a cc-SCR result in a more efficient NO_x conversion, and therefore, systems with a cc-SCR catalyst have a good potential for further improvement of NO_x emissions from diesel engines.

TABLE 3 summarizes the NO_x emissions, total NO_x conversions, and the measured time to reach 180 °C at the SCR elements in the different exhaust systems for the tests shown in FIGURE 5. In the cold start cycles, the times to reach 180 °C the cc-SCR are in the range 65-68 s, while these are in the range 450-470 s for downstream SCR elements (ATS-1, and ATS-

3 downstream) and 569 s in one cold-start test cycle with ATS-3. This means that the heating time of the cc-SCR is reduced by about 7 minutes, as compared to downstream SCR elements.

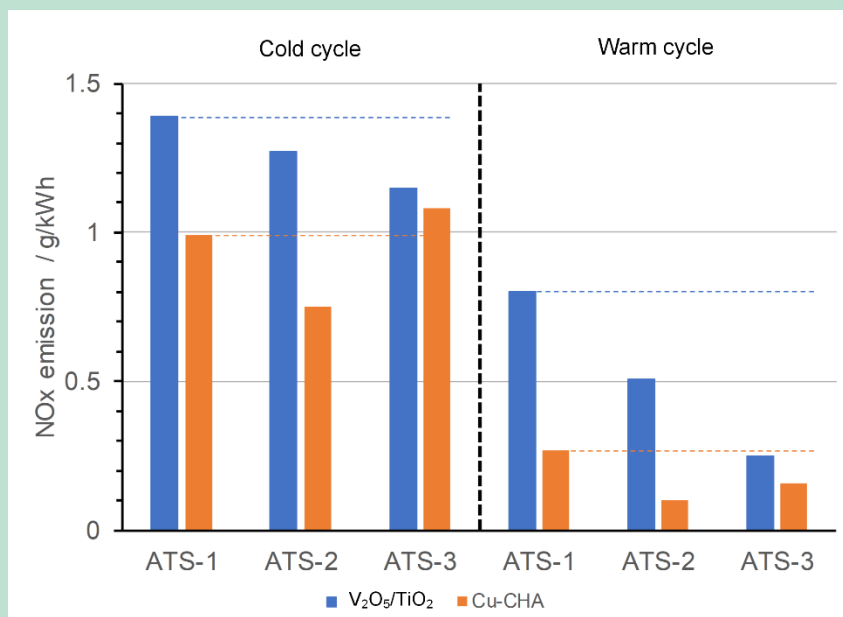


FIGURE 5 Cumulative NOx emissions at the tailpipe during a WHTC test cycle with a cold start, and two consecutive warm starts for configurations ATS-1, ATS-2, and ATS-3.

TABLE 3 Total emissions of NOx, NOx conversion and time needed to reach 180 °C at the SCR catalysts in the cold-start and warm-start WHTC cycles with V₂O₅/TiO₂ and Cu-chabazite SCR catalysts.

	ATS-1		ATS-2		ATS-3		
	V ₂ O ₅ /TiO ₂	Cu CHA	V ₂ O ₅ /TiO ₂	Cu CHA	V ₂ O ₅ /TiO ₂	Cu CHA	
Cold cycle	NOx emiss. (g/kWh)	1.39	0.99	1.27	0.75	1.15	1.08
	NOx conv (%)	85.7	90.2	87.2	92.9	88.1	89.4
	Heating time (s)	453	475	68	67	68	68
	<i>downstream</i>					471	569
Warm cycle	NOx emiss. (g/kWh)	0.80	0.27	0.51	0.10	0.25	0.16
	NOx conv (%)	92.0	97.4	95.0	99.1	97.4	98.5
	Heating time (s)	0	0	65	65	66	65
	<i>downstream</i>					8	8

In the cold-start test cycle with Cu-chabazite catalysts, the heating time of the downstream SCR catalyst is about 100 s longer, compared to the downstream SCR catalysts in the other test cycles. This is regarded as an incidental occurrence, but it immediately leads to a higher NOx emission at the tailpipe, as shown in the higher NOx emission observed in this particular test. This further demonstrates the importance of fast heating of the SCR catalysts. A comparison of the measured temperatures at the downstream SCR elements in FIGURE 6 shows that in both test cycles, the temperature follows largely the same trends, but at the point where the 180 °C point was reached with ATS-1, the temperature stayed just - by less than 1 °C - below that value in the cycle with ATS-3. As a consequence of the chosen NH₃-dosing strategy, the NH₃ dosing started about 100 s later compared to the run with ATS-1. During this

period, the downstream SCR does not remove the NO_x, leading to the increased NO_x emission. This is nicely illustrated by the measured NO_x emissions shown in the bottom panel of FIGURE 6, which shows that the ATS-3 configuration actually performs better up to the point where the NH₃-dosing at the downstream SCR starts.

Even though the higher NO_x slip in the cold-start cycle with Cu-chabazite in ATS-3 is not a representative result, it leads to two important conclusions. First, the choice of an appropriate urea-dosing strategy and timing of the NH₃ dosing can lead to large deviations in NO_x emissions, dependent on system design and operation. Secondly, if we correct for the estimated NO_x emission during this delay of the urea dosing, as indicated in FIGURE 6, we estimate that the NO_x emissions in the ATS-3 system is about 10-15 % less, compared to the standard system. This indicates that a cc-SCR configuration as in ATS-3 also has a good potential for a further reduction of NO_x emissions.

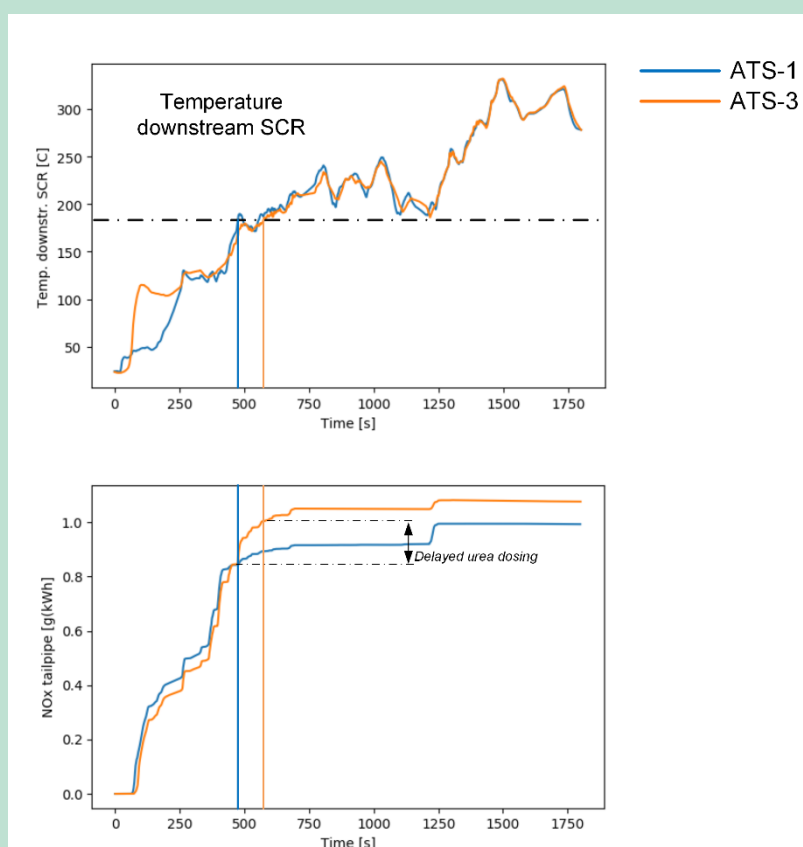


FIGURE 6 Measured temperature at the downstream SCR catalyst in ATS-1 and ATS-3 with Cu-chabazite SCR elements and NO_x tailpipe emissions.

2.3 V₂O₅/TiO₂ and Cu-chabazite SCR systems

FIGURE 5 also provides a direct comparison between systems with a V₂O₅/TiO₂ based and a Cu-chabazite based catalyst. In general, systems with Cu-chabazite based SCR catalysts are more effective. It is well known, that Cu-chabazite based catalysts are more active than V₂O₅/TiO₂ in the low temperature range.⁸ The temperature in the test cycles remained between 200 and 300 °C in the first 20 min, and reached 350-400 °C in the final part, as the load on the engine is increased. This means, that the total NO_x emission in the test cycles is to a high degree determined by the SCR performance in the range 200-300 °C, thus leading to the observed more efficient NO_x reduction with Cu-chabazite based SCR catalysts.

In addition to some differences in NO_x emission, the type of SCR catalyst also affects the emissions of N₂O and NH₃ in a different way. Even though these compounds are not part of the Euro VI regulation, car manufacturers also focus on minimizing these emissions. The fact that a standard Euro VI system includes an NH₃-slip catalyst bears witness to that. Emission of N₂O, a strong greenhouse gas (greenhouse factor = 270), is expected to become regulated in the near future.

TABLE 4 Emissions of NH₃ and N₂O from configurations ATS-1, ATS-2, and ATS-3 with V₂O₅/TiO₂ and Cu-chabazite catalysts.

		ATS-1		ATS-2		ATS-3	
		V ₂ O ₅ /TiO ₂	Cu CHA	V ₂ O ₅ /TiO ₂	Cu CHA	V ₂ O ₅ /TiO ₂	Cu CHA
Cold cycle	NH ₃ emiss. (mg/kWh)	20	1	3	1	38	1
	N ₂ O emiss. (mg/kWh)	48	142	62	89	51	74
Warm cycle	NH ₃ emiss. (mg/kWh)	18	1	1	0	48	4
	N ₂ O emiss. (mg/kWh)	45	171	100	93	64	91

The emissions of NH₃ and N₂O for the different exhaust systems are listed in TABLE 4. There is a distinct difference in the emissions from the V₂O₅/TiO₂ and Cu-chabazite based systems. In the test cycles with Cu-chabazite SCR catalysts, the emission of NH₃ is essentially eliminated, but there is a noticeable emission of N₂O. The V₂O₅ tend to emit less N₂O, compared to Cu-chabazite, but also show some emission of NH₃. This is in line with the known formation of N₂O over Cu-chabazite and lower NH₃-adsorption capacity for V₂O₅/TiO₂.

2.4 Importance of urea dosing

In configuration ATS-3, the urea is added to the system at two points, namely immediately before the cc-SCR and the downstream SCR element. This opens the possibility to operate the two SCR elements with different ANR. This is particularly relevant for the operation of the cc-SCR, because a partial NO_x conversion at this stage can be necessary for the function of other downstream elements. For example, a regeneration of the DPF may require NO₂, which then is produced by oxidation of NO on the DOC. To explore how the system reacts to different ANRs in the cc-SCR and downstream SCR, a series of warm-start WHTC cycles was performed with configuration ATS-3, in which the ANR was varied from 0.3 to 1.1 in the cc-SCR element, while keeping the ANR in the downstream SCR at 1.1.

TABLE 5 Emissions of NO_x, NH₃ and N₂O in warm-start WHTC cycles with configuration ATS-3 and variable ANR in the cc-SCR element.

	ANR	NO _x (g/kWh)		NH ₃ (mg/kWh)		N ₂ O (mg/kWh)	
		V ₂ O ₅ /TiO ₂	Cu CHA	V ₂ O ₅ /TiO ₂	Cu CHA	V ₂ O ₅ /TiO ₂	Cu CHA
ATS-1	1.1	0.45	0.41	23	0	58	183
ATS-2	1.1	0.51	0.05	1	0	65	90
ATS-3	0.3/1.1	0.44	0.28	33	2	46	124
	0.6/1.1	0.26	0.18	21	2	38	91
	1.1/1.1	0.13	0.03	11	2	150	143

The data in TABLE 5 shows that the NO_x emissions decrease with higher ANRs for the cc-SCR, and also reflect the NH₃ and N₂O emissions with V₂O₅/TiO₂ and Cu-chabazite SCR catalysts, as discussed in the previous section. However, at an ANR of 1.1 in the cc-SCR, the emission of N₂O increases significantly. This emission of N₂O is most probably due to the oxidation of the excess NH₃ leaving the cc-SCR on the Pt-based DOC. Therefore, it seems beneficial to keep the ANR below 1 in systems containing a cc-SCR and a downstream SCR

element (ATS-3). This is another example that the urea dosing strategy must be adjusted to a specific system design, in order to obtain a satisfactory overall performance.

2.5 Considerations for cc-SCR systems

Based on the data presented in this chapter, we can conclude that exhaust systems with a close-coupled SCR element are more effective in reducing NO_x emissions, with a confirmed 10-25% improvement in cold-start cycles, and 40-70% improvement in the warm-start cycles. The initial duration of heating the SCR catalyst is reduced from about 460 s to about 70 s. This indicates that systems with a cc-SCR element have a potential for a further reduction of NO_x emissions.

There are, however, some considerations to be made on the system design and operation. First, moving the entire SCR function to the inlet end of the exhaust system (ATS-2) removes essentially all the NO_x at the inlet end, leaving no NO_x further downstream. This is not necessarily an advantage, because it affects the ability for passive regeneration of the DPF further downstream, and, in case there is some NH₃-slip from the cc-SCR element, some NO_x may be formed on the DOC, which then cannot be removed any more.

To avoid a situation with little or no NO_x at the DOC and DPF in a system with a cc-SCR, it is possible to split the SCR function in a cc-SCR part and a downstream SCR part (ATS-3). This also requires that there are two points where urea is added, also allowing for different operation conditions at the two SCR elements. This gives some possibilities of controlling the system. However, the NO_x emissions can vary significantly, dependent on the way the urea is dosed. It is therefore important to adapt the urea dosing strategy to the system design.

Taking the unwanted emissions of N₂O and NH₃ into account, it is desirable to run the cc-SCR catalyst at an ANR below 1, in order to avoid a NH₃-slip from the cc-SCR, which leads to formation of N₂O on the DOC further downstream. An additional advantage of operating with an ANR below 1, is the more efficient use of urea. The downstream SCR is then used to remove the remaining part of the NO_x at the outlet end of the system.

The two most important types of SCR catalyst, V₂O₅/TiO₂ and Cu-chabazite, behave differently. In general, Cu-chabazite is more active, but produces more unwanted N₂O. V₂O₅/TiO₂ results in a slightly higher emissions of NO_x and NH₃. This behavior can also be exploited in the design of cc-SCR systems.

3. Influence of CO, hydrocarbons and SO₂

The concept of placing a part of the SCR function in a diesel exhaust after treatment system to a close-coupled position is beneficial for the overall system reduction of NO_x emissions. In this position the SCR catalyst will be exposed to conditions that were not considered in the development of a conventional SCRT (ATS-2) system. In particular, the levels of CO and hydrocarbons will be much higher, as well as all SO_x in the exhaust gas is passed directly through the SCR. Furthermore, the upper temperature limit is lowered to below 500 °C, which can affect the efficiency of removing SO_x from the SCR. In this section, the impact of the “new” conditions of the close-coupled position on the SCR performance is investigated.

3.1 Experimental

3.1.1 Bench scale setup

To study the impacts of CO, hydrocarbons, and SO_x on the SCR performance, monolith samples with a diameter of 50 mm were drilled out of full-size V₂O₅/TiO₂ (260 cpsi) and Cu-chabazite (400 cpsi) SCR elements as used in the initial engine tests for the proof-of-concept. The total volume of the catalyst samples was 50 ml.



FIGURE 7 The bench-scale setup for small monolith samples at the Technical University of Denmark.

For the measurements, the samples were mounted in a bench scale setup at the Technical University of Denmark (see FIGURE 7), in which the temperature, flow and gas composition at the SCR catalyst can be controlled. The feed gas flow was controlled by Bronkhorst mass flow controllers. The feed gas compositions were obtained by mixing the appropriate flow rates of bottled gases with known concentrations of NO, NH₃, and SO₂ with air and water vapor. Before entering the reactor section, the feed gas was heated by a Tutco-Farnam Heat torch pre-heater. The gas concentrations at the inlet and outlet of the catalyst samples were measured

online, using an MKS Multigas 2030 Fourier Transform Infrared (FTIR) spectrometer, which was connected to sample points at different locations in the reactor system.

To get a reference for the stability studies, the steady state NO_x conversions of the fresh V₂O₅/TiO₂ and Cu-chabazite catalysts were measured, which are shown in FIGURE 8. In these measurements, we used a feed gas composition of 500 ppm NO, 550 ppm NH₃, 5% H₂O and 11% O₂ in N₂ at a total flow rate of 160 N l/min (space velocity 192000 h⁻¹).

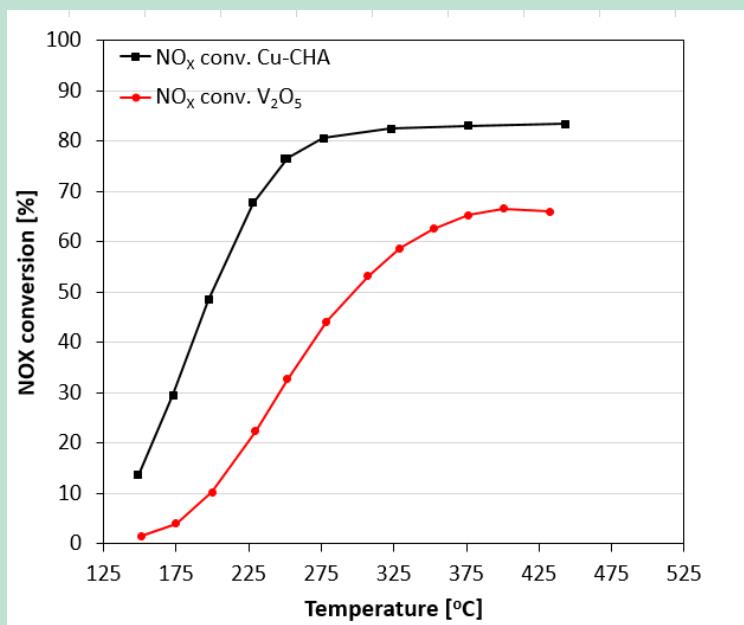


FIGURE 8 NO_x conversion in SCR gas for Cu-CHA, and V₂O₅-WO₃/TiO₂ monolith samples, diameter 50 mm, volume 50 ml, 160 Nl/min SCR gas: 500 ppm NO, 550 ppm NH₃, 5% H₂O and 11% O₂

To measure the effect of the presence of CO or hydrocarbons on the SCR performance, separate measurements were performed with 950 ppm CO, 450 ppm C₃H₈ or 450 ppm C₃H₆ added to a standard SCR feed gas as used for the measurements in FIGURE 8, also using a constant total flow rate of 160 Nl/min. C₃H₆ and C₃H₈ were chosen, because these are often used to represent hydrocarbon chemistry in exhaust gas catalysis, and these gases are easy to handle in our test system. The exposure temperature and duration of the exposure to CO or hydrocarbons were varied and are indicated in the presentation of the results.

The exposure of the catalysts to SO₂, was done by adding 2 ppm SO₂ to a base feed gas of 11% O₂, 5% H₂O, with varying concentrations of NO and NH₃ in the range 0-550 ppm, at a total flow of 160 Nl/min. The SO₂ exposures were done at 225 °C with varying durations. The concentration of 2 ppm SO₂ was chosen as a compromise between being in a relevant concentration range for application, and the time needed in laboratory tests to achieve relevant SO₂/catalyst exposures. The exposure temperature of 225 °C was chosen for two reasons, namely 1) this temperature is close to the average SCR inlet temperature in a WHTC cycle (225-250 °C, see page 35), and 2) because the measured NO_x conversion remains below 80%, which is necessary to monitor the impact of SO₂ on the catalytic activity.

After exposure of the SCR catalysts to SO₂, a regeneration of the catalysts can be done by heating to 500 °C for 20 min (18 °C/min) at 53 Nl/min feed gas with 11% O₂, 5% H₂O, 0-500 ppm NO and 0-550 ppm NH₃, similar to known methods to restore catalytic activity after SO₂

exposure.⁹ In this project, we have paid special attention to the effects of repeated SO₂ exposure and regeneration cycles, in order to obtain information about the long-time stability of the cc-SCR catalysts. For the repeated SO₂ exposure and regenerations, the exposure time was 3 h, in order to reach a target total SO₂ exposure of 1.5 gs/L_{catalyst}. Based on feedback from heavy-duty vehicle manufacturers, this exposure represents a typical sulfur exposure between regeneration events in the final application. The regeneration procedure of 20 min at 500 °C is also a typical procedure in the final application on heavy-duty vehicles.

3.1.2 Dynamic engine bench test

The effect of hydrocarbons was also studied in dynamic engine tests at Umicore. In these tests, the catalyst is exposed to a diesel exhaust gas while idling, which generates a higher concentration of hydrocarbons in the exhaust gas, followed by some regeneration steps. For these tests, a Euro VI engine with a displacement volume of 12.7 L was used. Because the tests are focused on the impact on the cc-SCR, only the first part of an ATS-3 system was installed. FIGURE 9 shows the tested exhaust system with indicated temperature and gas measurement positions.

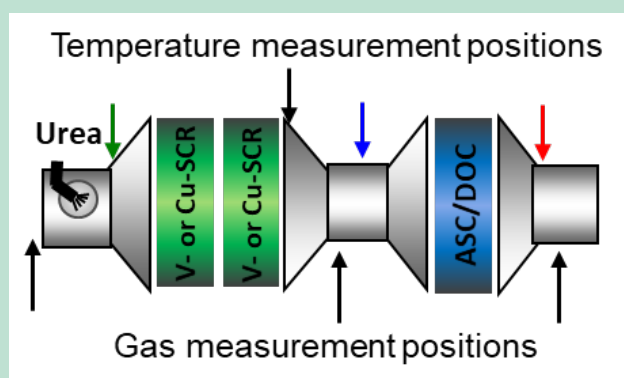


FIGURE 9 Layout of the exhaust system used in engine tests to study the effect of hydrocarbons.

The dimensions of the SCR catalysts were 12.5"x3" each (6" total SCR length of the system) and the VSCR had a cpsi of 260 while it was 400 for the CuSCR. The same ASC/DOC of 12.5"x3" and with a cpsi of 400, was used for tests with VSCR and CuSCR.

The experimental procedure consisted of several steps as follows:

1. Performance measurements:
 - 1.1. for VSCR: Steady state measurements with ANR 1.1 at 200 °C and 250 °C and a GHSV of 30 kh⁻¹ (based on SCR volume) yielding 550 and 750 ppm NO_x, respectively. Steady state measurements were followed by 4xWHTCs with ANR 1.1.
 - 1.2. for CuSCR: Steady state measurements with ANR1.2 at 200 °C and 250 °C and a GHSV of 30 kh⁻¹ (based on SCR volume) yielding 550 and 750 ppm NO_x, respectively. Steady state measurements were followed by 4xWHTCs with ANR 1.3.
2. Hydrocarbon deposition phase: 15 h idle with a constant inlet temperature of 130 °C and 70 ppm raw hydrocarbons.
3. Performance measurements (same as in point 1, except for 9xWHTCs instead of 4xWHTCs).
4. Regeneration: 15 min with 400 °C at SCR inlet
5. Performance measurement (only steady state)

6. Regeneration: 15 min with 440 °C at SCR inlet
7. Performance measurement (only steady state)
8. Regeneration: 15 min with 480 °C at SCR inlet
9. Performance measurement (same as in point 1)

3.2 Bench scale studies

3.2.1 Stability in the presence of CO or hydrocarbons

In the close-coupled position, the absence of an upstream DOC and DPF causes an exposure of the SCR element to higher concentrations of CO and a range of unburned hydrocarbons, which does not occur in conventional exhaust systems. In order to determine the impact of CO and different groups of light hydrocarbons on the performance of the SCR elements, a monolith sample of the V_2O_5/TiO_2 and Cu-chabazite based SCR catalysts were exposed to CO, C_3H_6 and C_3H_8 (only Cu-chabazite) at temperatures ranging from 200-400 °C.

FIGURE 10 summarizes the observed effects of exposure of the SCR catalysts to CO and hydrocarbons. For CO, the impact was most pronounced at around 250 °C, and a minor decrease in NO_x conversion by about 1-2 %-points was observed for both SCR technologies. After removing the CO from the feed gas again, the original NO_x conversion is restored. This means that the presence of CO does not affect the performance of the SCR catalysts in a significant way.

For C_3H_6 a similar effect is observed, but it is more pronounced at higher temperatures. The decrease in NO_x conversion is about 4-7%-points when C_3H_6 is present at 400 °C. The presence of C_3H_8 did not have an impact on the NO_x conversion over the Cu-chabazite catalyst; corresponding data for the V_2O_5/TiO_2 catalyst are not available.

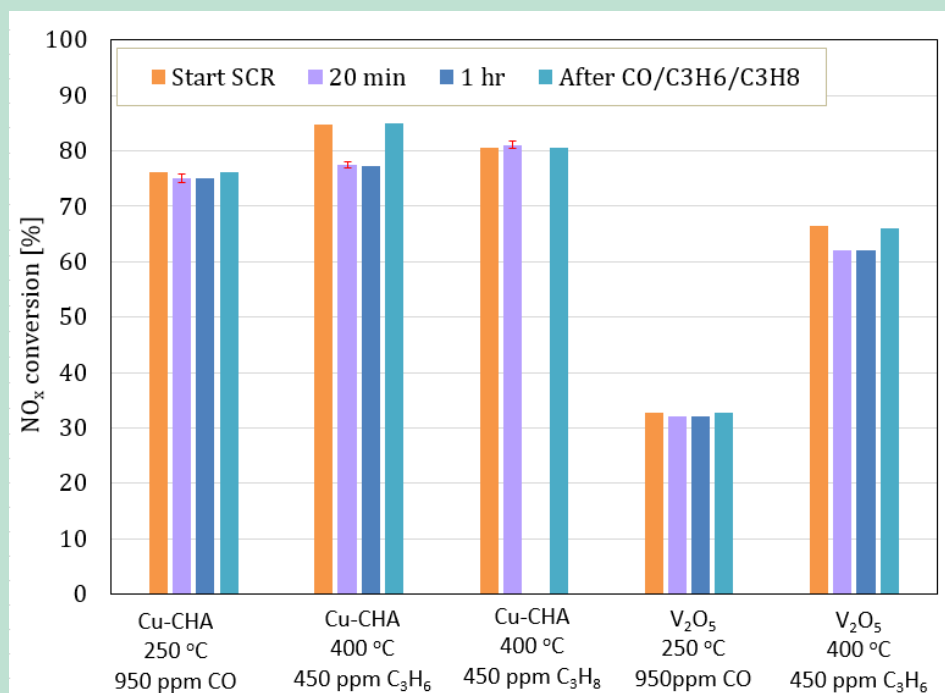


FIGURE 10 NO_x conversion in SCR for the Cu-chabazite and V_2O_5/TiO_2 based SCR catalysts before, during, and after exposure to 450 ppm C_3H_8 , 450 ppm C_3H_6 or 950 ppm CO. Monolith volume: 50 ml. Total flow: 160 Nl/min, Base feed gas composition: 500 ppm NO, 550 ppm NH₃, 5 % H₂O, and 11 % O₂.

An important point is that the decrease in NO_x conversion was observed only in the presence of CO or hydrocarbons, and it disappeared instantaneously when closing for these compounds. This response to removing and adding C₃H₆ to the SCR feed is shown in FIGURE 11. This instantaneous response indicates that there is no long-term impact of the presence of these compounds. These results indicate that the presence of CO, C₃H₆, or C₃H₈ can have a minor effect on the NO_x conversion, but this can be easily handled in the system, and therefore these compounds are not expected to cause severe problems in cc-SCR catalysts.

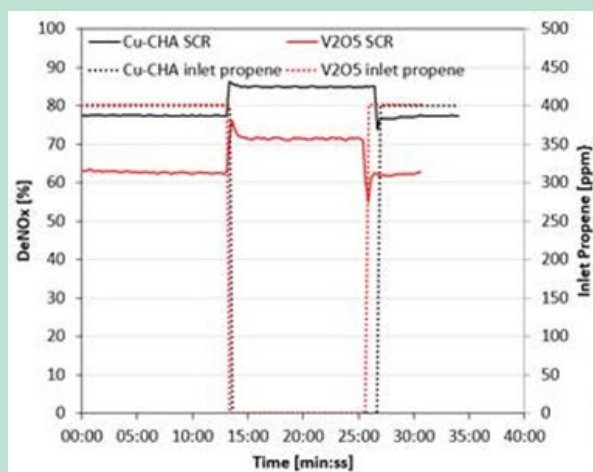


FIGURE 11 Response of the NO_x conversion over Cu-chabazite (black) and V₂O₅/TiO₂ (red) based SCR catalysts to removal and addition of C₃H₆ (propene).

3.2.2 Impact of hydrocarbon deposition on cc-SCR in engine test.

Whereas the use of C₃H₆ and C₃H₈ are useful to investigate the impact of hydrocarbons on the chemistry of the SCR reaction, these compounds tend not to form carbon deposits. However, an exhaust gas also contains heavier hydrocarbon components, which may form carbon deposits. Such deposits can block the catalytic active material leading to catalyst deactivation. Furthermore, there is also a risk of uncontrolled oxidation of these carbon deposits, which may heat the catalyst to a too high temperature that permanently damages the catalyst. To assess these risks a close-coupled setup (cc-SCR+ASC/DOC) with V₂O₅/TiO₂ and Cu-chabazite SCR elements was mounted on a test engine, and the test protocol given on p. 25 was executed. In these tests, the hydrocarbon exposure is enhanced by including a 15 h idling step, during which the exhaust gas typically contains a higher concentration of hydrocarbons.

FIGURE 12 shows the measured NO_x conversions at 200 °C before and after the idling phase, as well as after the regenerations at 400 and 480 °C, respectively. The performance of the V₂O₅/TiO₂ SCR catalyst is significantly affected by the idling, with the NO_x conversion decreasing from approx. 80% to below 10%. The Cu-chabazite SCR only shows a decrease of ca. 5% points. However, the performance is largely restored during the 9 WHTC cycles, showing a peak temperature of 370 °C (FIGURE 13 B), that were run afterwards. After heating to 400 °C, the performance is completely restored. Because the NO_x conversion can be restored by running standard WHTC cycles, it is unlikely that there will be an adverse effect of hydrocarbon exposure under normal operation conditions. Hence, an impact as a consequence of hydrocarbon deposition is only expected in rare instances, and, if these occurs, they can be easily reversed by heating to 400 °C, which is a realistic option in a vehicle.

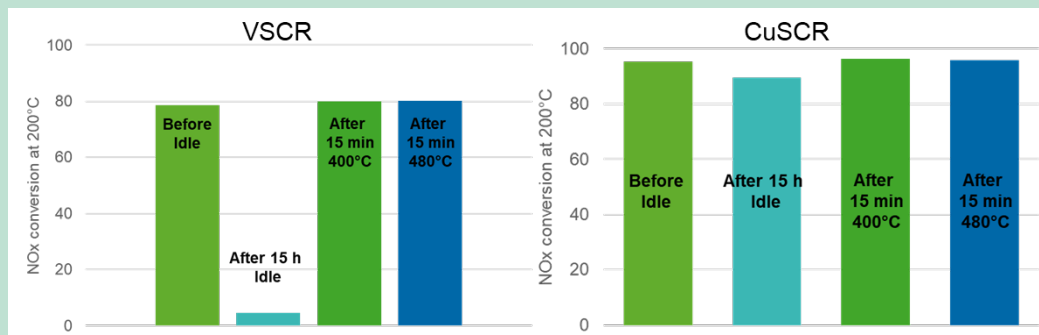


FIGURE 12 Performance of V_2O_5/TiO_2 (VSCR) and Cu-chabazite (CuSCR) SCR catalysts before and after 15 h idling and regeneration by heating to 400 and 480 °C.

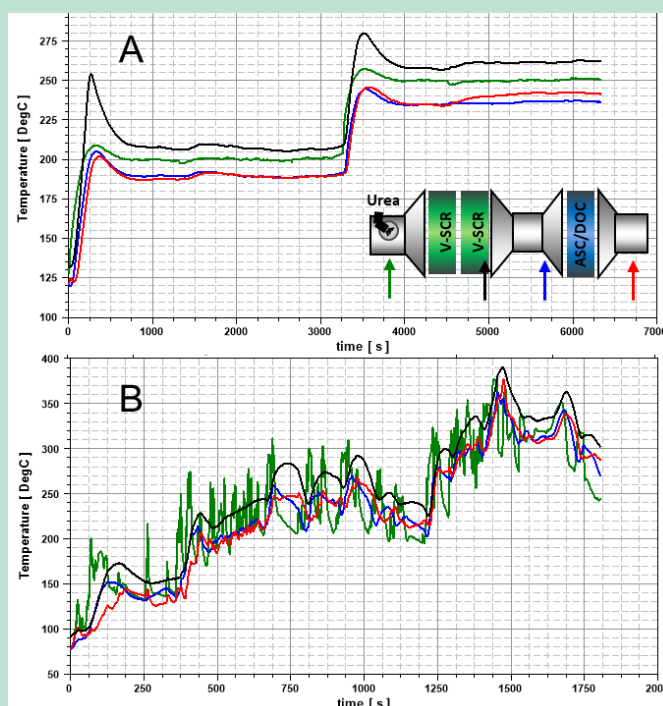


FIGURE 13 Time-dependent temperature profiles during the steady-state tests at 200 and 250 °C (A) and first WHTC cycle (B), taken after the 15 h idling period for the cc-SCR catalyst.

The presence of hydrocarbons is also reflected in the measured temperature profiles over the cc-SCR catalyst in the steady-state tests and WHTC cycles measured after idling. FIGURE 13, shows that the temperature at the outlet of the SCR element is higher than at the inlet, pointing to an exothermic process in the element. In the first WHTC cycle, the temperature increases over the SCR element as well, most clearly seen towards the end of the cycle (see FIGURE 13 B). In the subsequent WHTC cycles, this temperature difference becomes smaller and disappears eventually.

The temperature increase over the SCR element, and its decline with repeated WHTC cycles, indicates that the increase is related to oxidation of deposited hydrocarbons. The effect was only observed with the V_2O_5/TiO_2 SCR catalyst, in full agreement with the observation that the

activity of Cu-chabazite is not much affected by the idling, and thus does not accumulate carbon deposits. The highest exotherm of about 50 °C is observed in the stationary test at 200 °C, indicating that most deposited hydrocarbons already react at this temperature. The modest temperature increase of 50 °C, and the fact that it occurs at 200 °C, which is in the lower end of the normal operation temperature range, means that there is only a low risk that carbon deposits cause an uncontrolled heating of the close-coupled SCR elements.

3.2.3 Conclusion - impact of CO and hydrocarbons on cc-SCR

The monolith tests have shown that CO and hydrocarbons only cause a minor decrease in NO_x conversion, but do not show a permanent effect on the performance of V₂O₅/TiO₂ based and Cu-chabazite based SCR catalysts.

The engine tests show, that the performance of a V₂O₅/TiO₂ based cc-SCR element is more sensitive to carbon uptake and deactivation by hydrocarbons compared to a Cu-chabazite based element. However, the impact of hydrocarbon diminishes by running a standard WHTC cycle, indicating that an exhaust system will regenerate from carbon deposits on the cc-SCR under normal operating conditions. Therefore, carbon deposits are not expected to cause long-lasting damage to the exhaust system.

3.3 Impact of sulfur oxides on the cc-SCR

3.3.1 Impact of SO₂ on V₂O₅/TiO₂ and Cu-chabazite SCR catalysts

In the exhaust gas of a heavy-duty diesel vehicles using ultra-low sulfur diesel, the SO₂ concentration is typically in the range 0.5-2 ppm, depending on the operation conditions and composition of the engine oil. V₂O₅/TiO₂-based SCR catalysts are known to be robust against deactivation by SO₂, while Cu-chabazite based SCR catalysts are very sensitive to poisoning by SO₂. The different sensitivity of V₂O₅/TiO₂ and Cu-chabazite for SO₂ is illustrated in FIGURE 14, showing the NO_x conversion after exposures to 2 ppm SO₂. The NO_x conversion was measured after different exposure times.

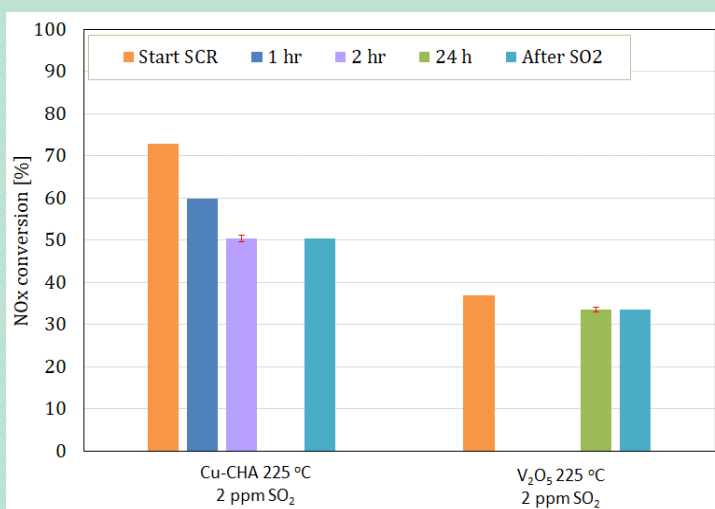


FIGURE 14 Effect of SO₂ exposure at 225 °C on the NO_x conversion over Cu-chabazite (left) and V₂O₅/TiO₂ (right) based SCR catalysts. The different bars correspond to a the indicated total exposure times.

After a 24 h exposure, the change in NO_x conversion of the V₂O₅/TiO₂ SCR catalyst is less than 10% point, while the NO_x conversion of the Cu-chabazite catalyst decreases by more

than 20% point already after 2 h of exposure. Removing the SO₂ does not restore the NO_x conversion, as was the case with CO and hydrocarbons (turquoise bars in FIGURE 14). This indicates a significant permanent impact of SO₂, in particular for Cu-chabazite, and requires special attention for application in a vehicle. Therefore, we focus on the impact of SO₂ on the performance of Cu-chabazite catalysts in the next sections.

3.3.2 Impact of SO₂ on Cu-chabazite at various ANR

Dependent on the exhaust system design, the ANR at close-coupled catalyst can vary from zero to over-stoichiometric conditions. In an ATS-3-like configuration, the targeted ANR at the cc-SCR element may very well be below 1, as a partial conversion of the NO_x at the cc-SCR can be advantageous (see also Sect. 2.4). However, in certain situations the effective NH₃ storage needs to be increased, and then an ANR above 1 is required. In other situations, such as urea cut-off events, the ANR is 0. Furthermore, the interaction of SO₂ with Cu-chabazite materials is different in the presence or absence of NH₃,¹⁰ and therefore it is important to know how the uptake and release of SO₂ is affected by the NH₃ concentration.

We conducted a set of SO₂ exposures ('sulfation') on a Cu-chabazite catalyst, followed by regenerations, in which the ANR is systematically varied between 0, 0.5, 0.6 and 1.1. In these measurements, the SO₂ exposures are done at 225 °C for typically 3 h, and the catalyst is regenerated by heating to 500 °C for 20 min. The relevant concentrations of NO and NH₃ in these sulfation and regeneration tests are given in TABLE 6. To determine the impact of SO₂ on the catalyst, the NO_x conversion was measured at 225 °C (ANR=1.1 and a total flow of 160 NL/min), before, during and after each SO₂ exposure and after regeneration.

TABLE 6 Concentrations of SO₂, NO, and NH₃ during sulfation (3 hrs at 225 °C) and regeneration (20 min at 500 °C) of Cu-chabazite catalyst.

	Sulfation (160 NL/min)			Regeneration (53 NL/min)		
	SO ₂ (ppm)	NO(ppm)	NH ₃ (ppm)	SO ₂ (ppm)	NO(ppm)	NH ₃ (ppm)
ANR 0+0	2	0	0	0	0	0
ANR 0.5+0	2	500	250	0	0	0
ANR 0.6+1.1	2	500	300	0	500	550
ANR 1.1+0	2	500	550	0	0	0
ANR 1.1+1.1	2	500	550	0	500	550

First, we focus on the effect of NH₃ on the impact of SO₂ exposure on the NO_x conversion. A complication here is, that an activity measurement implies exposure of the catalyst to NH₃ at 225 °C, and therefore, some adsorbed NH₃ is probably present when the exposure to SO₂ takes place, even though no NH₃ is present during the SO₂ exposure or regeneration (ANR 0+0) Flushing the catalyst with an NO/N₂/O₂/H₂O mixture, which corresponds to a standard SCR feed without NH₃, removes this adsorbed NH₃, because the SCR reaction will continue until all adsorbed NH₃ is consumed. The SO₂ exposure can then take place without adsorbed NH₃ present. In this way, we can control the measurement in such a way that the SO₂ exposure takes place on a catalyst with or without adsorbed NH₃.

The effect of the presence of NH₃ on the impact of SO₂ is illustrated in FIGURE 15, showing the NO_x conversion in 5 consecutive cycles of SO₂ exposure for 3 h and regeneration, in absence of NO and NH₃ (ANR 0+0), as a function of the total exposure to SO₂. In all cycles, except cycle 3, the NH₃ was removed by flushing in NO/O₂/N₂/H₂O, as explained above. When the adsorbed NH₃ is removed, the NO_x conversion decreases from about 75% to about 60%, and this seems to be reproducible in repeated sulfation-regeneration cycles.

In the 3rd cycle, the adsorbed NH₃ is not removed when the catalyst is exposed to SO₂. In this case, the NO_x conversion decreases by about 40-45% points to approximately 30%, which is

clearly a larger effect compared to the cases where NH₃ had been removed before SO₂ exposure. This indicates that the presence of NH₃ has a profound effect on the interaction of SO₂ with the catalyst, and the impact of SO₂ on the NO_x conversion.

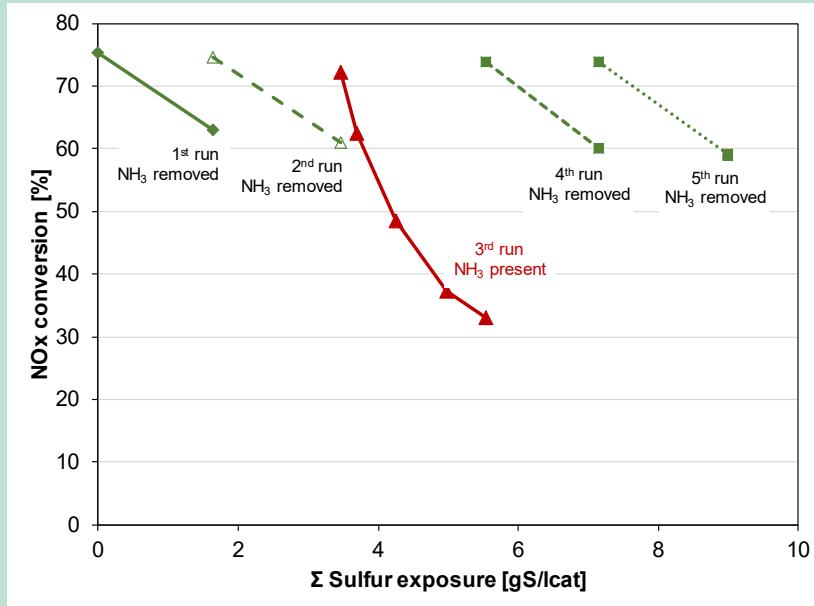


FIGURE 15 NO_x conversion at 225 °C over Cu-chabazite in consecutive cycles of exposure to SO₂ and regenerations in the absence of NH₃ and NO (see ANR 0+0 in TABLE 6) with and without removal of adsorbed NH₃.

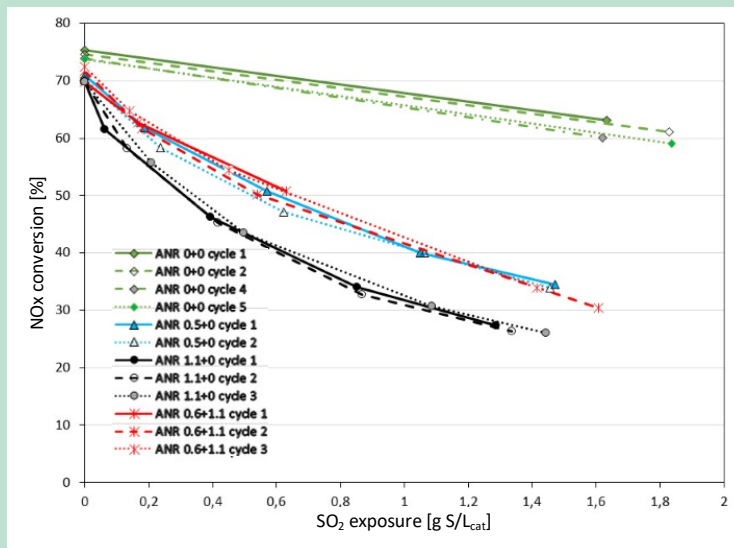


FIGURE 16 NO_x conversion over Cu-chabazite in 500 ppm NO_x and 550 ppm during 3 hrs exposure to 2 ppm SO₂ (monolith vol. 50 ml, 160 NI/min SCR gas). ANR 0+0 = 2 ppm SO₂ exposure in 0 ppm NO_x and NH₃ and regeneration at 500 °C in 0 ppm NO_x and NH₃. ANR 0.6+1.1 = 2 ppm SO₂ exposure in 500 ppm NO_x and 300 ppm NH₃ and regeneration at 500 °C in 500 ppm NO_x and 550 ppm NH₃.

Because the presence of adsorbed NH_3 enhances the impact of SO_2 on the NO_x conversion, it is important to decide how to compare the interaction of SO_2 at different ANR, as listed in TABLE 6. For the ANR 0+0 conditions, we have chosen to remove the adsorbed NH_3 , because this closely resembles a urea cut-off, which is the only situation where $\text{ANR}=0$ occurs on a vehicle; in that case, the exhaust gas still contains NO , O_2 and H_2O . The comparison of the impact on NO_x conversion after repeated SO_2 exposures with different ANRs is shown in FIGURE 16. Clearly, in the presence of NO and NH_3 , the impact of SO_2 increases, with a decrease in NO_x conversion by about 40% points at ANR 0.5-0.6, and by about 45% at ANR 1.1. It seems that the impact of SO_2 increases with NH_3 concentration. However, the impact of SO_2 due to the presence of adsorbed NH_3 , without NH_3 in the gas phase (FIGURE 15, 3rd run), is quite similar to that observed for ANR 0.5 or 0.6. This suggests that the impact of SO_2 is determined by the adsorbed NH_3 , rather than NH_3 in the gas phase.

The data in FIGURE 16 also shows that the impact of SO_2 is larger at ANR 1.1, while the impacts at ANR 0.5, 0.6, and 0 with adsorbed NH_3 , are quite similar. In particular, the initial decrease in NO_x conversion is larger at ANR 1.1. Consistent with the conclusion that the impact of SO_2 is determined by the adsorbed NH_3 , we can say that at ANR 1.1, we have an excess amount of NH_3 , and therefore, NH_3 will accumulate on the catalyst, thus further enhancing the impact of SO_2 . At lower ANR, less NH_3 is available for adsorption, and in the case of depletion of NH_3 from the gas phase, the adsorbed NH_3 can be consumed. Therefore, there will generally be less adsorbed NH_3 available at ANR below 1, resulting in a less severe impact of SO_2 on the NO_x conversion under these conditions.

The fact that the NO_x conversion is largely restored upon heating to $500\text{ }^\circ\text{C}$ indicates that it is possible to regenerate the catalyst after SO_2 exposures by heating. The NO_x conversion measured after the regeneration then also gives an indication whether repeated sulfation-regeneration cycles cause permanent damage to the catalyst. These data are collected in FIGURE 17. For ANR 1.1, there is possibly some decline of the NO_x conversion after regeneration. For ANR 0, 0.5 and 0.6, there is no significant decline. It seems that the presence or absence of NH_3 during regeneration does not have a significant impact on the regeneration. This indicates that a regeneration at $500\text{ }^\circ\text{C}$ is feasible on a vehicle, without permanent damage to the catalyst.

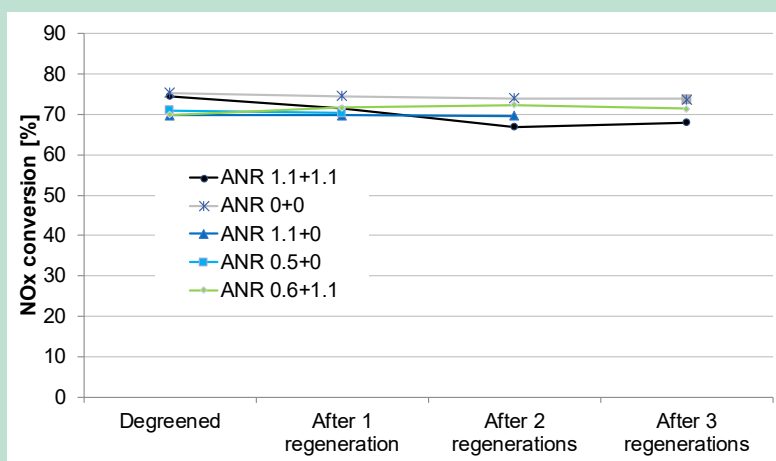


FIGURE 17 NO_x conversion over Cu-CHA at $225\text{ }^\circ\text{C}$ immediately after regeneration from SO_2 exposure by heating to $500\text{ }^\circ\text{C}$ at various ANR (flow: $53\text{ NI}/\text{min}$, base feed: $5\% \text{ H}_2\text{O}/11\% \text{ O}_2/\text{N}_2$). Parameters for activity measurement: Monolith volume: 50 ml , Flow $160\text{ NI}/\text{min}$, feed $500\text{ ppm NO}/550\text{ ppm NH}_3/5\% \text{ H}_2\text{O}/11\% \text{ O}_2/\text{N}_2$.

In conclusion, the inevitable presence of NH_3 for the NH_3 -SCR reaction also enhances the impact of SO_2 on the NO_x conversion. Furthermore, heating the catalyst after SO_2 exposure restores the NO_x conversion almost completely. This means that the impact of SO_2 on a vehicle must be managed by an appropriate combination of urea dosing strategy and effective regenerations by heating to about 500 °C.

4. System optimization

There are a number of factors that determine the performance of an exhaust system with a cc-SCR. The most important factors identified in the previous sections are a proper distribution of the SCR function over a cc-SCR and downstream SCR elements, and the operation conditions of the cc-SCR and downstream SCR. These include the urea dosing strategy and the use of a cut-off temperature for urea dosing. Furthermore, combining V_2O_5/TiO_2 and Cu-chabazite based catalysts in 'hybrid' SCR systems offers a possibility to enhance the performance of the exhaust systems, since these catalyst types differ in activity, sensitivity towards poisoning, and emissions of NH_3 and N_2O . In this chapter, we address these points to optimize the performance of cc-SCR exhaust systems.

4.1 SCR volume study – cc-SCR vs. downstream SCR

In order to investigate the optimal ratio between close-coupled SCR and downstream SCR a simulation-based approach was used. Cold and warm WHTCs were simulated, where the catalyst inlet conditions were gathered from engine bench tests. An in-house developed SCR model was used for the simulation.¹¹ The model considered surface reaction mechanisms that describe the main SCR reactions, transient effects due to nitrate storage, as well as production of side products such as N_2O .

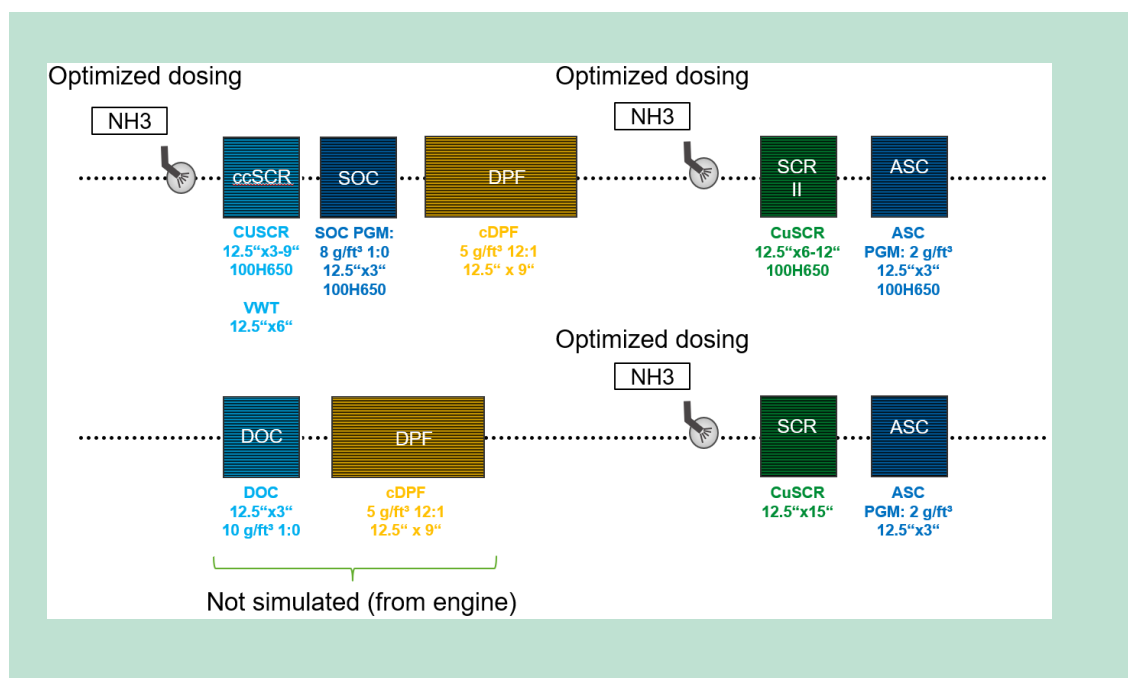


FIGURE 18 The configurations of the SCR² (top) and SCRT (bottom) systems used in the simulations.

Error! Reference source not found. The two simulated systems are shown in FIGURE 18. The top system represents the SCR² system and the bottom system the SCRT system, both with Cu-chabazite SCR catalysts. For configuration of the SCR², two NH_3 dosing positions were used and for the SCRT system one NH_3 dosing position was used. The NH_3 dosing was based on the NH_3 storage level of the SCR catalyst. Additionally, a possibility of a "cut-off" of the cc-SCR dosing was introduced, which allows for the dosing to the cc-SCR catalyst to be turned off when a certain temperature is reached, e.g. 300 °C. This can be advantageous because it allows for larger amounts of NO_x to be available for passive soot oxidation on the

DPF, if the temperature is sufficiently high. The start temperature for NH₃ dosing was set at 180°C. The dosing strategy will be described in full in Section 4.2.

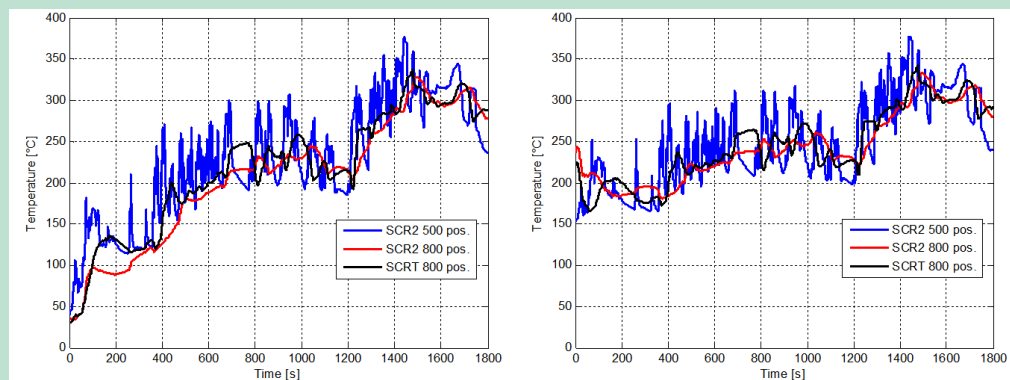


FIGURE 19 Measured temperatures at the SCR inlet positions for the SCR² and SCRT systems. Black: SCR in SCRT configuration. Blue: cc-SCR in SCR². Red: downstream SCR in SCR².

FIGURE 19 shows the measured temperatures at the SCR inlet positions during cold (left) and warm (right) WHTCs, using a SCR² system with a 6" cc-SCR. For the SCR² simulations, the system inlet temperature was chosen as the temperature at the inlet of the cc-SCR (blue lines), and the temperature changes through the system were calculated using a thermal model. For the SCRT system simulation, the inlet temperature at the SCR element (black lines) was chosen. In the cold test, the cc-SCR heats up considerably faster than the downstream SCR element, due to the closer position to the engine outlet. Compared to the SCRT system, the heating of the downstream SCR catalyst in the SCR² systems is somewhat slower. This is due to the increased thermal mass upstream of that SCR element with the introduction of the cc-SCR. The average temperatures at the inlets of the SCR are given in TABLE 7.

TABLE 7 Average temperature at the inlet of the SCR elements in the SCR² and SCRT configurations.

	SCR ² cc-SCR	SCR ² downstream SCR	SCRT
Cold start WHTC	227.9	206.5	216.4
Warm start WHTC	248.6	243.5	245.5

FIGURE 20 shows that the calculated NO_x levels at the outlet of the cc-SCR and SOC are in the range 4.8-6.0 g/kWh for the cold WHTC cycle (left) and 4.1-5.6 g/kWh for the warm WHTC cycle (right). With a raw NO_x emission of 9 g/kWh from the engine, this corresponds to NO_x conversions of 33-47% and 38-54%, respectively. The NO_x concentration at the outlet of the SOC is slightly lower, showing some contribution of the SOC to the NO_x removal. The NO_x conversions increase with the cc-SCR volume, but are generally quite low, as less than half of the NO_x is removed. This is a consequence of the chosen cut-off temperature for urea dosing at 300 °C, which in the engine tests is exceeded in particular towards the end of the cycle, see FIGURE 19. Increasing the volume of the cc-SCR catalyst gives a larger NH₃ storage capacity, allowing for a higher urea dosing, which is then the reason for the higher NO_x conversion in these cases. Consequently, with a realistic ANR below 1 for the cc-SCR, a larger volume does not necessarily result in a higher conversion of NO_x over the cc-SCR element.

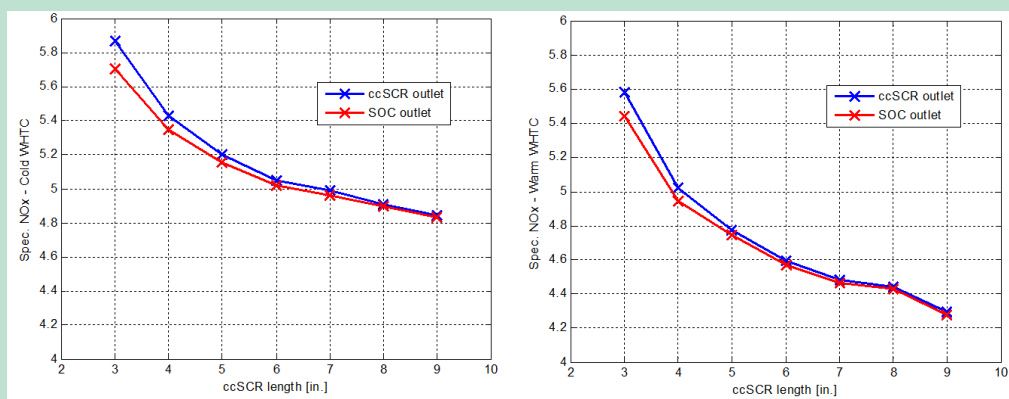


FIGURE 20 Calculated NOx levels at the outlet of the cc-SCR and SOC for the cold (left) and warm (right) WHTC simulation, for lengths of the cc-SCR elements between 3" and 9".

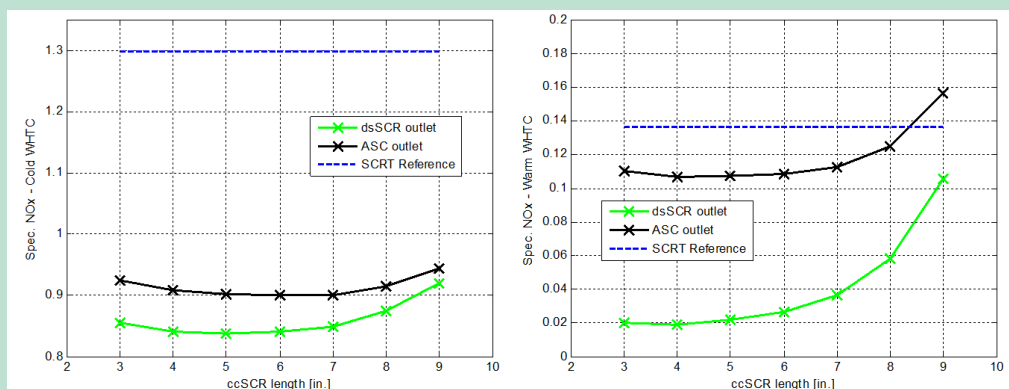


FIGURE 21 Calculated NOx levels at the outlet of the downstream SCR and ASC for the cold (left) and warm (right) WHTC. The SCRT reference shows the tailpipe values for the SCRT system.

FIGURE 21 shows the NOx levels after the downstream SCR and ASC outlet (tailpipe) for the cold (left) and warm (right) WHTC, together with the NOx tailpipe emission for the SCRT system. These calculations show that there is a clear advantage for the SCR² system in both the cold-start and warm-start WHTC cycles. The NOx emission for the SCR² system at the tailpipe (black lines) is about 30% lower than that for a standard SCRT configuration for both the cold and warm cycles. However, in the warm cycle, the NOx emission is primarily due to a re-oxidation of NH₃ to NOx in the ASC; in the cold-start cycle it is limited by the SCR activity. This means that it is important to limit the NH₃ slip from the downstream SCR when the operation temperature has been reached.

The calculations also show that the distribution of the SCR function between the cc-SCR and downstream SCR elements in an SCR² system affects the tailpipe emissions. There is an optimum length of the cc-SCR element, with a minimum in NOx emission at 6" cc-SCR in the cold cycle, and at 4" cc-SCR element in the warm cycle. Based on these results, we conclude that the cc-SCR volume should be between 25-40% of the total SCR volume in an SCR² system. In the proof-of-principle measurements with configuration ATS-3 described in Sect. 2, the volume of the cc-SCR element was 40%, which is close to the optimal configuration we find here.

4.2 Urea dosing strategy and use of cut-off temperature.

To determine the appropriate amount of urea needed in an exhaust system, different strategies can be used. Since the urea dosing strategy potentially affect the NO_x emissions significantly, it is an important engineering parameter. A straightforward strategy for urea dosing is to keep the ANR constant at a predefined value. The NO_x level at the inlet of the SCR is measured or estimated, and the amount of NH₃ needed is then calculated from the ANR and the corresponding amount of urea is dosed. The ANR ratio can be varied from under-stoichiometric NH₃ levels (ANR < 1), excess NH₃ levels (ANR > 1), or stoichiometric NH₃ level (ANR = 1). However, especially for Cu-zeolite based SCR catalysts, a disadvantage of this approach is that it can lead to a large NH₃ slip in situations where the temperature increases fast.

To fix the problem of unwanted NH₃ slip with fixed dosing, a more suitable way to dose urea is to keep track of the amount of NH₃ stored on the SCR catalyst. The constant-ANR and NH₃-storage based approaches for urea dosing are sketched in Figure 5. In the storage based dosing strategy, the set-point table shown in the bottom of Fig. 1, is optimized to a driving situation (for example WHTC) so that the NH₃ storage as a function of temperature is appropriate in order to reach maximum NO_x conversion while constraining the NH₃ slip. With this method, it is necessary to estimate the current NH₃ storage level on the SCR catalyst, which can limit the methods' practical use. In the calculations in the previous section, the storage based dosing strategy was used.

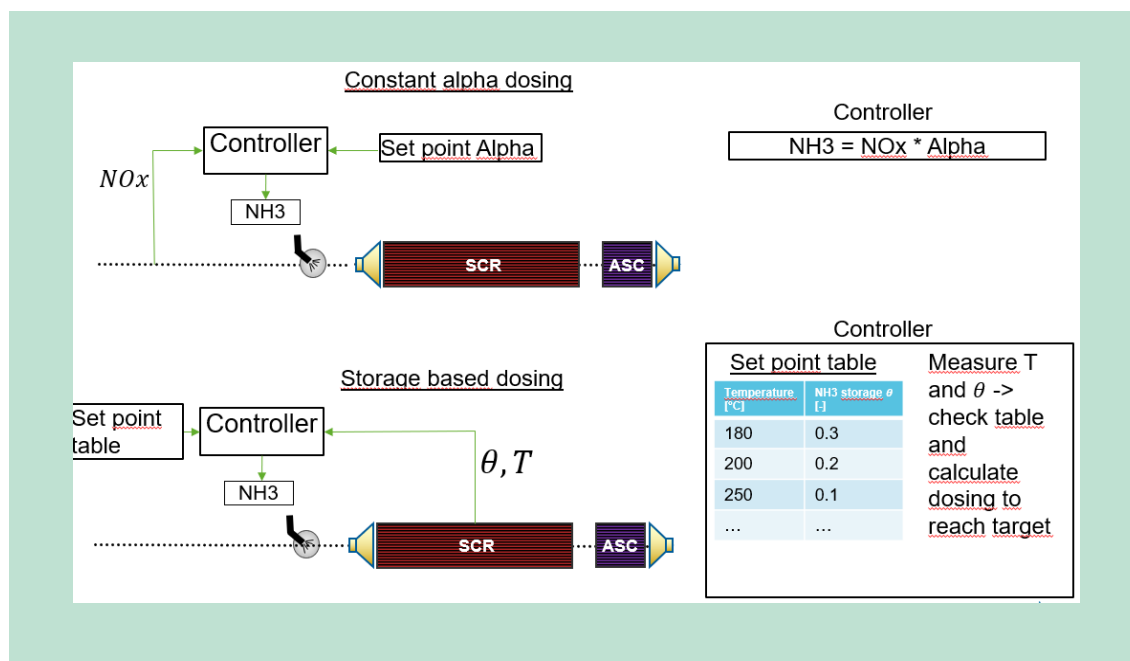


FIGURE 22 Overview of a constant alpha dosing system (top) and a NH₃ storage based dosing system (bottom)

With two dosing positions available in the SCR² system, it becomes possible to adjust dosing strategy depending on system temperature to move deNO_x activity to either the cc-SCR or the downstream SCR system. The advantage of the cc-SCR system can be utilized fully during start-up situations, when the downstream SCR is still cold. When the system has reached the normal operation temperature range, it might be advantageous to reduce the NO_x conversion on the cc-SCR to ensure sufficient NO_x levels for passive soot oxidation on the DPF. This is the basic idea of the cut-off temperature for the urea dosing at the cc-SCR catalyst, and essentially limits the use of the cc-SCR catalyst to low temperatures only; at high temperatures the SCR² system works more like a standard SCRT system.

FIGURE 23 shows a comparison between the NO_x levels at the cc-SCR and SOC outlet for an SCR² system with Cu-chabazite SCR elements operated with and without a urea-dosing cut-

off at 300 °C. When a cut-off temperature of 300 °C is used, the calculated NO_x levels at the outlets of the cc-SCR and SOC lie between 4.4 and 5.6 g/kWh, dependent on the length of the SCR catalyst. When no urea cut-off is used in the same system, the NO_x removal becomes more efficient, with calculated NO_x levels at the outlets of the cc-SCR and SOC elements between 0.4 and 2.5 g/kWh. This shows, that in this case, omitting the cut-off strategy results in a better performance of the cc-SCR catalyst, but also results in a lower NO_x concentration further downstream, which will have consequences for the ability to regenerate the DPF.

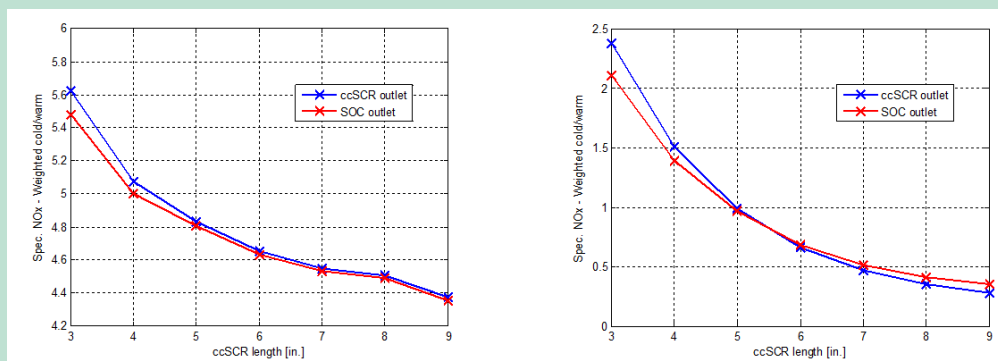


FIGURE 23 Calculated NO_x levels at the cc-SCR and SOC outlet in an SCR² system in the case with a urea dosing cut-off at 300 °C (left) and without cut-off (right).

The difference between the cases shown in FIGURE 23, however, actually show that the cut-off strategy can be very useful in regulation of the NO_x concentration at the DPF. Control systems could be designed such that the NO_x concentration is increased only at the occasions where the DPF needs regeneration, but otherwise is kept at the low level to enhance the overall performance of the exhaust system. This example illustrates again that the performance of an exhaust system, and even more so in systems with a cc-SCR element, depend to a high degree on the chosen strategy for urea dosing.

4.3 Use of V₂O₅/TiO₂ and Cu-chabazite SCR in hybrid systems

4.3.1 Hybrid cc-SCR systems

So far, the focus has been on the system optimization with respect to reduction in NO_x emissions. However, emissions of N₂O and system robustness are also important to consider in an overall evaluation of the exhaust system. N₂O is a strong greenhouse gas, with a global warming potential that is almost 300 times that of CO₂,^{12,13} and therefore N₂O emissions are a point of concern for car manufacturers as well as legislative authorities. System robustness means that performance requirements are met at the end of the expected catalyst lifetime. In this section, we assess the N₂O formation and robustness of exhaust systems, and the possibility to design hybrid systems based on both V₂O₅/TiO₂- and Cu-chabazite catalysts.

Generally, V₂O₅/TiO₂-based SCR catalysts have a lower selectivity towards N₂O than Cu-based catalysts under normal heavy-duty diesel operation conditions (see Sect. 2.3). In V₂O₅/TiO₂ based systems, N₂O emissions from a cc-SCR system are mainly due to some NH₃ slip from the cc-VSCR to the ASC/DOC+DPF, which are also effective catalysts for the oxidation of NH₃ to N₂O, in particular at low temperatures. Because V₂O₅/TiO₂ catalysts have a very low storage capacity for NH₃, NH₃ slip is likely to occur in such systems. In Cu-chabazite catalysts, N₂O is a by-product of the SCR reaction, with a selectivity of about 1-2 %, and therefore, there will always be some N₂O formation. The NH₃ storage capacity of Cu-chabazite, however, is an advantage, as it can reduce NH₃-slip. The chosen urea dosing strategy is crucial here.

To assess catalyst robustness, hydrothermal stability and poisoning are the important contributors to the deterioration of the catalysts with time. Cu-chabazite based SCR catalysts generally have a better hydrothermal stability than V_2O_5/TiO_2 -based catalysts, but both types of catalyst are sufficiently stable for application as a cc-SCR. Therefore is catalyst poisoning more critical for a cc-SCR. In that regard, V_2O_5/TiO_2 -based catalysts are generally more robust, mostly due to their known superior tolerance for SO_2 . Cu-chabazite based SCR catalysts require special management and regenerations in order to control the impact of SO_2 .

To exploit the advantages of V_2O_5/TiO_2 -catalysts and Cu-chabazite catalysts, hybrid systems containing both types of catalysts in the cc-SCR element can be designed. In the hybrid cc-SCR we propose that the inlet part is a V_2O_5/TiO_2 -based catalyst, and the outlet part a Cu-chabazite catalyst. This should result in a system with a better NO_x reduction capability than an entirely V_2O_5/TiO_2 cc-SCR, albeit not as good as a pure Cu-based system. Furthermore, the hybrid system would be expected to have an improved SO_2 sensitivity as the SCR functionality of the V-based part remains largely unaffected by SO_2 . Lastly, we expect the N_2O emissions to be significantly lower compared to a pure Cu-chabazite based system, as the V_2O_5/TiO_2 part is able to remove a large part of the NO_x with minimal N_2O formation, while the Cu-based SCR part contributes with a buffer NH_3 storage capacity to minimize the risk of N_2O formation over the ASC/DOC+DPF.

4.3.2 Performance and SO_2 sensitivity of hybrid cc-SCR.

In order to assess the potential of a hybrid cc-SCR system, dynamic engine bench tests were performed, aimed at NO_x removal and SO_2 sensitivity. For these tests, a hybrid cc-SCR element as shown in FIGURE 24 was mounted on the exhaust of a Euro VI-compliant diesel engine. Each part has the dimensions $\varnothing 10.5 \times 3$ ", with 260 cpsi for the V_2O_5/TiO_2 part and 400 cpsi for the Cu-chabazite part.

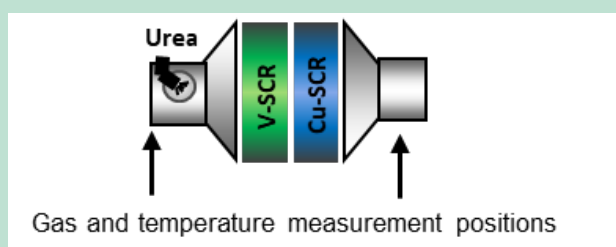


FIGURE 24 Layout of the tested hybrid cc-SCR element.

The experimental procedure for these tests was as follows:

1. Fresh performance assessment using ULSD (7 wt ppm S):
 - a. Steady state NO_x conversion at 200 and 240 °C with ANR 1.05
 - b. Hot WHTCs with ANR 0.8
2. SO_2 exposure carried out by 25 subsequent WHTC cycles with ANR 0.8 and using 250 wt ppm sulfur diesel, resulting in a total sulfur exposure of approx. 6.5 $gs/L_{catalyst}$.
3. Performance measurement (same as point 1)
4. Regeneration 30 min with 400 °C at SCR inlet, using ANR 0.8 and ULSD.
5. Performance measurement (same as point 1)
6. Regeneration 30 min with 450 °C at SCR inlet, using ANR 0.8 and ULSD.
7. Performance measurement (same as point 1)
8. Regeneration 30 min with 450 °C at SCR inlet, using ANR 0.8 and ULSD.
9. Performance measurement (same as point 1)
10. Regeneration 30 min with 480 °C at SCR inlet, using ANR 0.8 and ULSD.
11. Performance measurement (same as point 1)

The sequence described in points 1-11 was carried out 4 times in total on the same set of catalysts. In the last repetition of the test sequence, a single change was made in point 2 where a

diesel with 50 wt ppm S was used instead, and the number of WHTC cycles was increased in order to achieve the same total sulfur exposure.

FIGURE 25 summarizes the NO_x conversion, and emissions of NH₃ and N₂O at the outlet of a hybrid cc-SCR element under steady state conditions at 200 and 240 °C at different stages in the sulfation-regeneration cycle. The performance after the last regeneration event in each sulfation-regeneration cycle, is transferred to be the fresh state in the next cycle. Thus, the data point "Regen480" in the cycle "Sulf1" is the same as the data point "Fresh" in cycle "Sulf2".

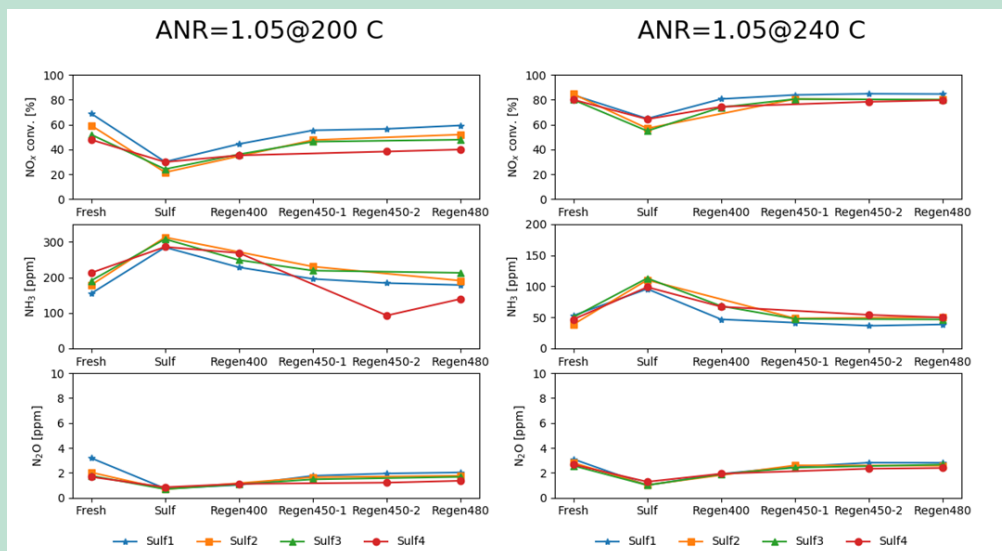


FIGURE 25 Steady-state measurements of NO_x conversion, NH₃ emission, and N₂O emission at the outlet of a hybrid cc-SCR element at 200 °C and 240 °C in repeated sulfation-regeneration cycles.

At 200 °C, the NO_x conversion decreases from 70% to 35% after the sulfur exposure, while at 240 °C the NO_x conversion decreases from 85% to 70%. As the V₂O₅/TiO₂ part remains largely unaffected upon SO₂ exposure, this means that the Cu-chabazite contributes to the conversion, and that its contribution is larger at 200 °C. Furthermore, the NO_x conversion in the initial ("fresh") stage is lower in each cycle, showing a build-up of irreversible deactivation on the Cu-chabazite part. Such a decrease is not observed at 240 °C, which means that the larger contribution of the V₂O₅/TiO₂ part at this temperature reduces the impact of SO₂ on the performance of the cc-SCR system, thus yielding a more robust system compared to a cc-SCR element entirely based on Cu-chabazite.

In the steady state measurements at 200 °C, the NO_x conversion is only partially recovered by the regeneration procedures, indicating some irreversible deactivation. The NO_x conversion after sulfur exposure is gradually restored by the regeneration 400 °C and the first 450 °C, but remains below that of the fresh state. Extending the regeneration time at 450 °C or increasing the temperature to 480 °C (the highest temperature attainable) does not further recover the NO_x conversion in this case. Such an irreversible deactivation is at odds with the results of the laboratory tests in Sect. 3.3, where we have not observed a significant irreversible deactivation by SO₂. However, there are some significant differences between this engine test and the laboratory tests. First, in the engine test, the total exposure to SO₂ is 6.5 gs/L_{catalyst}, which is significantly more than in the 1.5 gs/L_{catalyst} in the laboratory test, which allows for a larger uptake of SO₂ in the engine test. Second, the SO₂ concentration was higher in the engine tests. We do not expect that the different regeneration temperature - 480 °C in the engine test, and 500 °C in the laboratory test - affects the regeneration behavior significantly.

The static tests also show the impact of SO₂ concentration on the performance of the hybrid cc-SCR element. The actual SO₂ concentration varies, depending on the fuel consumption and intake air. With 250 wt ppm sulfur in the fuel, the average SO₂ concentration over a full WHTC cycle is calculated to be 6 ppm, assuming that all sulfur is converted to SO₂. With 50 wt ppm sulfur diesel, the average SO₂ concentration becomes about 1 ppm. The impact on the NO_x conversion after SO₂ exposure is significantly lower with 50 wt ppm sulfur in the diesel, as compared to 250 wt ppm, despite the fact that the total exposure to SO₂ has been kept constant. This suggests that using too high SO₂ concentrations can lead to an irreversible deactivation. As a consequence, the use of ultra-low sulfur diesel (ULSD) must be recommended.

The data in FIGURE 25 show that the NH₃ slip from the hybrid cc-SCR increases when SO₂ is present, demonstrating the correlation between NH₃ slip and state of the CuSCR part. As already explained, NH₃ slip from the cc-SCR can lead to formation of N₂O further downstream, and therefore, it is important to manage urea dosing to minimize NH₃ slip.

The hybrid cc-SCR shows a clear benefit with respect to the N₂O formation, as compared to a Cu-chabazite based cc-SCR. The decrease in N₂O concentration after SO₂ exposure, indicates that some N₂O is formed over the Cu-chabazite SCR, as expected. In steady state measurements, the N₂O formation over Cu-chabazite catalysts typically increases with temperature up to 250-300 °C. With the hybrid cc-SCR, however, the concentrations of N₂O at 200 and 240 °C do not increase (see FIGURE 25). This demonstrates the benefit of a hybrid cc-SCR: the increased rate of N₂O formation on the Cu-chabazite part is counteracted by an increased SCR activity of the V₂O₅/TiO₂ part, leaving less NO and NH₃ available for N₂O on Cu-chabazite.

FIGURE 26 shows the emissions of NO_x, NH₃, and N₂O at the outlet of the hybrid cc-SCR in a dynamic WHTC test cycle, which is a more realistic representation of actual driving conditions. In these cycles the decrease in average NO_x conversion is now 10% points, which occurs in the first two cycles upon exposure of the catalyst to SO₂. This is lower than the corresponding decrease in NO_x conversion of 35 %points (200 °C) and 15% points (240 °C) in the steady-state tests, indicating that the impact of SO₂ on the NO_x conversion in a dynamic operation of the hybrid cc-SCR is smaller, suggesting a smaller contribution of the Cu-chabazite part to the NO_x conversion. It is also noteworthy that the impact of SO₂ largely disappears when using 50 wt ppm sulfur diesel. This is a good indication that in a real application with ULSD, the impact of SO₂ on the NO_x reduction over a hybrid cc-SCR system is limited.

Regarding N₂O, the average concentration in the dynamic test is about 1 ppm, which is lower than the 3 ppm measured in the steady state tests. This is consistent with a lower contribution of the Cu-chabazite part in the dynamic tests, as also indirectly inferred from the impact of SO₂ on the NO_x conversion.

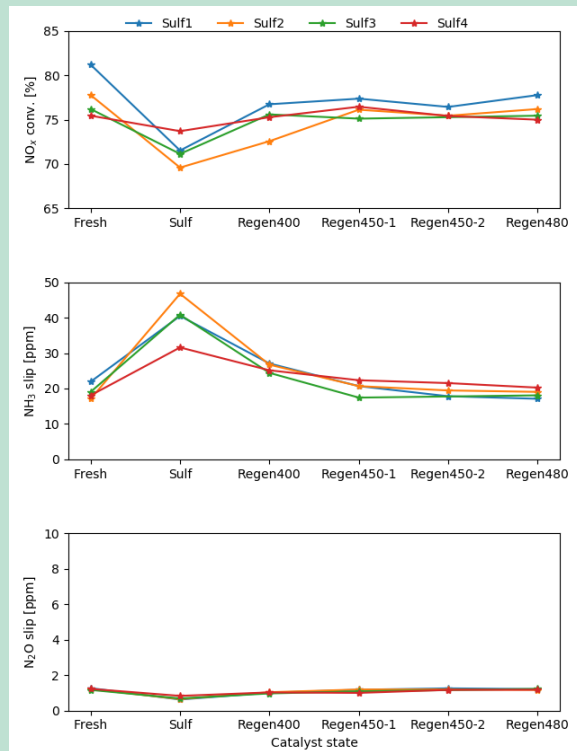


FIGURE 26 Emissions of NO_x, NH₃ and N₂O at the outlet of a hybrid cc-SCR element in a dynamic WHTC cycle.

In conclusion, there are clearly benefits in using a hybrid cc-SCR element, with a V₂O₅/TiO₂ part at the inlet end, and a Cu-chabazite part at the outlet end. In comparison to a Cu-chabazite based cc-SCR, the tolerance towards SO₂ is improved and the N₂O emission can be reduced, but the NO_x conversion is reduced, in particular at lower temperatures. Compared to a V₂O₅/TiO₂-based cc-SCR, the Cu-chabazite improves the NO_x conversion on the cost of SO₂ sensitivity and N₂O formation.

5. Failure mode analysis and final test

5.1 Design failure mode and effects analysis (DFMEA).

A Failure Mode and Effects Analysis (FMEA)¹⁴ is a risk assessment method that is commonly used in quality systems in the automotive industry. The goal of a Design-FMEA (DFMEA) analysis is to identify possible failures related to the design of an item. In TABLE 8, some risks identified in the DFMEA analysis are given, together with a recommendation based on the results and experiences obtained in this project.

TABLE 8 Risks of implementation of cc-SCR in exhaust systems in a DFMEA analysis and recommended solutions based on the results in the present study.

Risk	Solution / recommendation
High temperature due to oxidation of hydrocarbon deposits	Maintain flow in the exhaust system during regeneration
Low NOx conversion due to presence of hydrocarbons	No risk, hydrocarbons have only minor effect on NOx conversion
Low NOx conversion due to presence of CO	No risk, CO does not affect SCR performance
cc-SCR system design results in high N ₂ O emission	Consider use of V ₂ O ₅ /TiO ₂ based catalysts or hybrid cc-SCR system
cc-SCR system design results in high N ₂ O emission	Avoid NH ₃ slip from cc-SCR, use ANR < 1
Unforeseen change in NH ₃ adsorption capacity	Avoid high temperature during regeneration or removal of hydrocarbon deposits
N ₂ O or NH ₃ emission due to unforeseen change in NH ₃ adsorption capacity	Implement NH ₃ sensor, adjust urea dosing strategy
Low NOx conversion due to SO ₂ exposure	Consider V ₂ O ₅ /TiO ₂ or hybrid cc-SCR system to mitigate SO ₂ sensitivity
	Recommend use of ULSD fuel

5.2 Performance of a cc-SCR system

As a demonstration of the performance of a cc-SCR system, it was decided to compare the performance of an ATS-1 system, to represent a conventional Euro VI system, with that of an ATS-3 configuration, to represent a cc-SCR system (see FIGURE 1). The ATS-3 configuration was chosen, because the calculations in Sect. 4.1 show that an optimal performance can be expected for a cc-SCR/downstream SCR volume ratio of 2/3, and, by chance, we have used the same ratio in ATS-3 in Sect. 2. The ATS-1 system was based on Cu-chabazite SCR, in order to obtain a single reference for the performance of a conventional Euro VI system. The ATS-3 systems had either a V₂O₅/TiO₂ catalyst or a Cu-chabazite catalyst in both cc-SCR and downstream SCR positions; no hybrid systems or combinations of V₂O₅/TiO₂ and Cu-chabazite have been used here.

The performances of the ATS-3 systems were compared to that of the ATS-1 reference, based on two consecutive standard WHTC test cycles, starting the first from a cold state. In contrast to the measurements in Sect. 2, an NH₃-dosing strategy based on the NH₃-storage level on the SCR catalysts during the test cycle was used. The dosing strategy was optimized for each system layout with respect to NOx reduction and NH₃ slip. Furthermore, for the ATS-3 layouts,

a cut-off in the urea dosing was implemented when the inlet temperature of the cc-SCR was higher than 300 °C.

As the performance of the catalysts in vehicles tend to deteriorate over time, the benefit of the ATS-3 should be valid over the full life time of the catalysts. Therefore, for the demonstration tests the Cu-chabazite catalysts were hydrothermally aged at 650 °C prior to the measurements. This procedure is often used to mimic the performance of a downstream Cu-chabazite SCR catalyst to reflect a performance state close to that expected at the end of useful life. The V₂O₅/TiO₂ catalysts cannot be exposed to temperatures above 550 °C, and therefore, a short degreening at 550 °C was done before the tests.

The emissions from an aftertreatment system depend to a high degree on the interplay between the engine operation and the management of the aftertreatment system. Especially, the physical setup regarding heat insulation, flow distribution and NH₃ dosing strategy have significant impacts on the performance. Therefore, in order to provide a more general and realistic picture of the potential benefits of ATS-3 exhaust systems, we determine the relative reductions in the emissions of NO_x, NH₃ and N₂O in the ATS-3 configurations, with respect to the reference ATS-1 system.

TABLE 9 summarizes the relative reductions of the average emissions of NO_x (g/kWh), NH₃ (ppm) and N₂O (g/kWh) over the two WHTC cycles. The relative reductions are calculated as:

$$\frac{ATS1_{avg\ emission} - ATS3_{avg\ emission}}{ATS1_{avg\ emission}} \cdot 100\%$$

A relative reduction in NO_x emissions between 35 and 56% is observed for the ATS-3 system layouts in comparison to the ATS-1. This means that the rearrangement to a cc-SCR system, from a conventional Euro VI (ATS-1) system, and only using existing catalyst elements, results in a significant reduction in NO_x emissions. This is achieved without increasing the catalyst volume, and without further modifications to the exhaust system, such as external heating. We also note that we now have used an aged Cu-chabazite catalyst, indicating that we can expect a NO_x reduction on this order of magnitude over the life time of the Cu-chabazite catalyst.

TABLE 9 Relative reductions of NO_x, NH₃, and N₂O in cc-SCR systems based on Cu-chabazite or V₂O₅/TiO₂, compared to a Cu-chabazite based Euro VI system.

Aftertreatment system	Relative reduction of NO _x emissions (%)	Relative reduction of NH ₃ emissions (%)	Relative reduction of N ₂ O emissions (%)
Cu-chabazite ATS-3	55.9	98.8	16.3
V ₂ O ₅ /TiO ₂ ATS-3	35.3	52.3	37.4

The data in TABLE 9 also show that the reduction in NO_x is obtained without compromising the emissions of NH₃ and N₂O. In fact, the emission levels for NH₃ and N₂O levels are also reduced with the ATS-3 system layouts.

It is noted that these results are achieved without making changes to the existing catalysts, but only by adjusting the exhaust after treatment system layout and and management. Therefore, the cc-SCR concept can be easily implemented. As a final note, the learnings in this project have shown that there are many factors that determine the performance of cc-SCR systems, such as urea dosing strategy, combining V₂O₅/TiO₂ and Cu-chabazite SCR catalysts, volume ratio of cc-SCR with respect to downstream SCR. This offers opportunities for further tuning the cc-SCR systems than has been possible within this project.

6. Conclusions

In the project, we have shown that diesel exhaust systems with a close-coupled SCR catalyst (cc-SCR) have a potential to reduce NO_x emissions from heavy-duty vehicles by approximately 35-50 %. This reduction in NO_x emission is achieved by rearranging the catalyst elements in a Euro VI system such that a part of the SCR catalyst is placed at the inlet end of the exhaust system. Therefore, cc-SCR concept is easy to implement, as it, in principle, can be constructed from parts that already are commercially available. Furthermore, improved SCR catalysts that may be developed in the future can also immediately be applied in a cc-SCR system design. An improvement in NO_x emission can be achieved with both V₂O₅/TiO₂ based and Cu-chabazite based SCR catalysts, but V₂O₅/TiO₂ systems show a lower NO_x conversion.

The most efficient cc-SCR systems have both a cc-SCR element and a downstream SCR/ASC element at the outlet of the exhaust system. Moving the entire SCR catalyst to the close-coupled position is not recommended, since this gives complications in the regeneration of the DPF, due to the lack of NO₂. In addition, any NO_x formed on the noble-metal based oxidation catalyst (DOC) cannot be removed without a downstream SCR element. Based on calculation, the most efficient cc-SCR systems have about 30-40% of the total SCR volume as a cc-SCR, and the remaining 60-70% as a downstream SCR.

The performance of a cc-SCR system does not only depend on the design of the exhaust system, but also on the operation. In particular, the urea dosing strategy is an important factor for the performance. Delays in urea dosing due to slower heating can contribute significantly to NO_x emissions. The use of cut-off strategies for urea dosing at the cc-SCR can lead to higher NO_x emissions, and do not seem favorable. Excess amounts of NH₃ (ANR > 1) is not recommended at the cc-SCR, since this leads to NH₃ slip from the cc-SCR catalyst, which gives high emission levels of N₂O, and makes the overall use of urea less efficient.

The presence of hydrocarbons or CO in the cc-SCR catalyst, as a consequence of its placement upstream of the DOC, does not affect the SCR performance of the cc-SCR catalyst in a critical way. The presence of hydrocarbons may reduce the NO_x conversion somewhat, but the catalysts remains sufficiently active. Hydrocarbon deposits during idling can already react at around 200 °C and any lost activity is thereby restored, which means that no special actions need to be taken with regard to this.

The presence of SO₂ affects the performance of Cu-chabazite based SCR catalysts, and therefore, SO₂ must be handled carefully in systems containing Cu-chabazite. V₂O₅/TiO₂ catalysts are more tolerant for SO₂ exposure. High concentrations of sulfur in the fuel (ca. 250 wt ppm) may cause permanent damage to a Cu-chabazite catalyst. When ultra-low sulfur diesel (ULSD) is used, the SO₂ concentration remains low, and the SCR activity can be restored by regeneration. Under such conditions we have not found indications for permanent damage to a Cu-chabazite catalyst. The presence of NH₃ on the catalyst enhances the impact of SO₂ on the SCR performance, and may also affect the regeneration. This implies that the urea dosing strategy also has an influence on how a cc-SCR system reacts to the presence of SO₂.

Finally, the V₂O₅/TiO₂ based SCR catalysts tend to show a lower NO_x conversion, but also generate less N₂O, as compared to Cu-chabazite SCR catalysts. By combining a V₂O₅/TiO₂ cc-SCR catalyst with a Cu-chabazite downstream SCR catalyst, a cc-SCR system can be improved with respect to emission of NH₃, and N₂O, while reducing the sensitivity of the exhaust system for SO₂.

7. Impact of cc-SCR on employment, legislation, and technology.

As we have shown in this report, the cc-SCR concept provides a way to improve the NOx reduction from diesel engines, using already existing parts, and in principle without increasing the fuel consumption. Therefore, no new production methods or catalysts need to be developed to apply the cc-SCR concept, which makes it cheap and accessible for most car manufacturers. The cc-SCR concept is a next step in diesel-exhaust gas cleaning, and as future legislation very probably will include further restrictions in NOx emissions, car manufacturers will need a technology like cc-SCR to comply with those.

There exist other approaches to achieve lower NOx emissions from diesel engines. For example, Bosch has developed temperature management and exhaust gas recirculation systems for exhaust systems.¹⁵ This approach also targets a fast heating of the SCR catalyst, and accordingly results in a significant improvement of the NOx emissions, as well. Other technologies include a Passive NOx Adsorber (PNA), which adsorb NOx during a cold start occurs, and releases it again when the normal operating temperature has been reached.^{16,17} The competitiveness of the cc-SCR system lies in its simplicity, as it essentially works in the same way as the conventional exhaust systems we know today, without the need of implementing new technologies. In addition, future developments in SCR catalysts can be immediately applied in cc-SCR systems as well.

Umicore is the third largest supplier of catalysts to the automotive industry in the world, with about 3000 of the 11000 employees in the Catalysis BU,¹⁸ with production sites in Europe, Asia, North America, and South America.¹⁸ In Denmark, Umicore has about 115 employees. The production site in Frederikssund produces SCR catalysts for heavy duty vehicles, employing 65 people. A significant part of the production in Frederikssund until 2027 is already reserved for SCR catalyst units in cc-SCR systems. Given that the cc-SCR concept answers to the need for further reduction of NOx emissions, it is expected that the cc-SCR concept will find applications around the world, and cc-SCR systems are considered for application in North America in the near future. Discussions with car manufacturers are ongoing at the moment, showing that they are interested in the concept. At present, it is difficult to foresee how a market for cc-SCR systems will develop, but it is conceivable that the cc-SCR concept will be generally applied and becomes a new standard for diesel exhaust aftertreatment systems.

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Close-coupled SCR systems for NOx abatement from diesel exhausts

Emission af kvælstofoxider (NOx) fra dieselmotorer påvirker luftkvaliteten væsentligt verden over, fx. ved dannelse af smog. På et dieseldrøjet fjernes mere end 90% af NOx ved hjælp af en SCR katalysator, hvor NOx reagerer med ammoniak til kvælstof og vand.

SCR katalysatorer er særdeles effektive ved driftstemperatur (180-500 °C). En betydelig del af NOx emissionerne stammer dog fra koldstart af dieselmotorer, hvor SCR katalysatoren ikke endnu har opnået driftstemperaturen. Traditionelt placeres SCR katalysator mod enden af udstødningssystemet, hvor opvarmningen er langsom. I et "close-coupled SCR" system (cc-SCR), placeres SCR katalysatoren forrest, hvor den opvarmes hurtigere, og så mindsker NOx emissioner ved koldstart. I en cc-SCR vil der dog være mere kulmonoxid, kulbrinter, sod, og SO₂ tilstede, som kan påvirke SCR katalysatorens effektivitet og stabilitet. En vigtig fordel af et cc-SCR system er at de kan laves ved omrokering af eksisterende katalysatorelementer.

Projektet har vist at cc-SCR systemer giver generelt en 35-50% lavere NOx emission. Ideelt udgør cc-SCR volumen 25-40% af det totale SCR volumen. Man bør undgå at overskydende ammoniak i cc-SCR katalysatoren, da det giver uønsket N₂O på de øvrige katalysatorer i udstødningen. Ved at kombinere V₂O₅/TiO₂ som cc-SCR og Cu-chabazite som nedstrøms SCR katalysator, kan cc-SCR systemer effektiviseres yderligere for enten lavere NOx emission, eller lavere N₂O emission og forbedret SO₂ tolerance.

cc-SCR konceptet har vist sig som en effektiv, konkurrencedygtig og nemt implementerbar løsning til at reducere NOx emissioner med 35-50%. De første kommercielle cc-SCR systemer er på vej. Det forventes, at dette koncept vil bidrage til yderligere at reducere NOx emissioner på verdensplan i den nære fremtid.



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