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An analysis of SCR reactor deactivation impact on NO_x emissions from a compression ignition engine

Catalytic exhaust gas aftertreatment devices fitted to combustion engines are susceptible to partial deactivation as their operating time progresses. This includes selective catalytic reduction (SCR) reactors meant for NO_x emission control. There are several known deactivation mechanisms of SCR reactors already analyzed in detail in the literature. This paper, however, approaches the analysis of reactor deactivation by comparison of exhaust gas characteristics over repeatable cycle for fresh and aged samples of a SCR reactor for non-road mobile machinery. The research aims to outline which parameters describing the SCR reactor's performance are most affected by its ageing. In order to do that, fresh and aged samples of the reactor were tested under the Non Road Steady Cycle. The acquired emission results, including concentration traces of particular compounds were analyzed. The specific NO_x emission of the aged reactor was significantly higher than that of the fresh one. The NO_x conversion efficiency of both reactors was found similar at periods of steady engine operation. It was recognized that during transient conditions the NO_x conversion efficiency of the aged reactor was decreased. It was found that the main factor contributing to that phenomenon is the drop in the ammonia storage capacity of the aged SCR sample.

Key words: *SCR system, SCR deactivation, SCR ageing, nitrogen oxides emission, ammonia emission*

1. Introduction

On a global scale, the impact of internal combustion engine (ICE) operation on the natural environment is significant, as it is the most common vehicular propulsion system worldwide. The ICE exhaust gases contain both harmful and greenhouse gases. The legislation intends to limit both; however, the harmful gases have been regulated for decades while the limitation of greenhouse gases is just becoming more common. To comply with the requested emission limit of a particular harmful compound, effective exhaust aftertreatment system (ATS) is applied [1]. Nowadays, the selective catalytic reduction (SCR) of NO_x by NH_3 is recognized as the most comprehensive solution for NO_x emission control. The system is capable of reaching high overall conversion efficiency – frequently exceeding 90% [2, 3]. It is considered to be the major future deNO_x solution and considerable research is being conducted to maximize its potential [4, 5]. Nevertheless, the SCR system is susceptible to partial deactivation as its operating time progresses. There are several known reversible and irreversible SCR reactor deactivation mechanisms already analysed in detail in the literature [2, 6]. In the case of reversible phenomena, recovery of reactor functionality occurs at elevated exhaust temperature, which allows oxidation of compounds inhibiting catalytic activity. Irreversible deactivation occurs when the porous zeolite structure collapses and materials of higher density, e.g. quartz, are formed. The influence of SCR ageing on the composition of tailpipe exhaust gas is complex, as it affects the emission of NO_x, NH_3 and N_2O. This research aims to characterize which parameters describing the SCR reactor's performance are most affected by its ageing and how it influences the tailpipe emissions. For research purposes an SCR system for non-road mobile machinery applications was considered.

2. Legal requirements regarding NO_x emission

Legal regulations regarding emissions of harmful exhaust gas compounds are becoming more restrictive. The current EU emission limits for non-road mobile machinery engines (STAGE IV) have been in force since 2014. The recent tightening of this limit mainly concerned the reduction of specific NO_x emissions to 0.40 g/kWh (Table 1) [7]. This change forced engine manufacturers to apply an effective method of purifying exhaust gas from nitrogen oxides. This challenge primarily concerned CI engines operating on lean mixtures, where due to the presence of oxygen in the exhaust gas, it is not possible to reduce NO_x by a TWC reactor. In this case, it is assumed that the most efficient method of NO_x emission control is an SCR system. Such systems are now widely used in engines for non-road mobile machinery meeting the STAGE IV limits.

Table 1. STAGE IIIB and STAGE IV emission limits of NO_x [7]

Limit	Power range [kW]	Date of introduction	Brake specific NO_x emission limit [g/kWh]
STAGE IIIB	$130 \le P \le 560$	2011.01	2.00
STAGE IIIB	$56 \le P < 130$	2012.01	3.30
STAGE IV	$130 \le P \le 560$	2014.01	0.40
STAGE IV	$56 \le P < 130$	2014.10	0.40

Table 2. Required period of compliance with the STAGE IV limit for non-road mobile machinery engines [8]

Limit	Power range [kW]	Limit compliance [h]
STAGE IV	< 37	5000
STAGE IV	> 37	8000

The legal provisions specify not only the maximum permissible specific emission of harmful exhaust compounds, but also the period of operation during which the limits will not be exceeded (Table 2). According to these regulations, engines – and in particular their ATS – must not only meet the emission limits in "as new" condition, but also guarantee their fulfilment throughout the required period of engine operation [8]. A key condition to meet this requirement is the lifespan of the ATS. However, such systems, including those incorporating SCR, a characterized by efficiency drops as they age. There are several known mechanisms of

SCR deactivation and they can be classified as follows [1, 3]:

- Hydrothermal deactivation: the exposition of SCR reactor to exhaust gas of temperature exceeding 600°C and humidity above 4% may lead to zeolite structure collapse.
- Hydrocarbon accumulation deactivation: the SCR reactor tends to accumulate HC, especially at exhaust temperatures below the DOC light-off point; under certain conditions the stored HC oxidizes, leading to local spots where the safety temperature of the reactor is exceeded.
- Sulphur poisoning: reduced catalytic site activity caused by the presence of sulphur compounds.
- Chemical deactivation: alkali metals may displace Cu from the exchange sites and thus reduce catalytic activity.
- Ammonia deposits deactivation: reducing catalytic sites activity by UWS-derived compounds.

3. ATS and engine setup

The unit selected for the research was a regular SCR reactor designed for a non-road mobile machinery engines. The active layer of the reactor's substrate was made of Fe-exchanged zeolite. The substrate had a cylindrical shape 18 inches (45.7 cm) long, 10 inches (25.4 cm) in diameter and thus 11.6 dm^3 of volume. The SCR reactor tested was installed in the exhaust aftertreatment system (Fig. 1), the functionality of which ensured compliance with the emission limits of STAGE IV. The system incorporated a DOC reactor, the function of which was to oxidize the CO and HC present in the exhaust gas and to oxidize a fraction of the NO present to NO_2. The right ratio of NO_2 to NO, not exceeding 50:50, ensures optimal performance of the SCR reactor [2]. Subsequently, downstream of the DOC, the UWS injector was installed in the exhaust line. In order to ensure the most uniform UWS distribution in the exhaust stream, in the close proximity of the injector, a mixing element was placed. Behind this element, at a distance of about 80 cm, the tested SCR reactor was installed. The span between the mixing element and the reactor provided time for the evaporate water from UWS and to for the thermolysis and hydrolysis reactions necessary to obtain NH_3 from urea to occur.

In addition to the active components of the ATS system, it also included a control system for the UWS rate introduced into the exhaust stream. The applied UWS dosing system worked in so-called closed loop, where the parameters determining the UWS injection rate were the mass flow of exhaust gas, the engine-out concentration of NO_x and the alpha factor regulating the composition of the obtained mixture of NH_3 and NO_x. This system consisted of an electronic controller with appropriate software and a set of sensors. At the inlet to the ATS, a NO_x concentration sensor was located in the raw engine exhaust. This sensor was of key importance for the operation of the SCR system, as its reading was a parameter directly influencing the calculated value of the UWS dosing rate. Together with the NO_x sensor, a temperature sensor was used, according to which the lower temperature threshold for the start of the UWS dosing functioned. At the end of the exhaust aftertreatment system, downstream of the SCR reactor, there was another set of sensors: an NH_3 concentration sensor, a NO_x concentration sensor and exhaust gas temperature sensor. The NH_3 concentration sensor monitored the NH_3 concentration value after the catalytic converter. Based on its readings, the UWS dosing system could reduce the amount of NH_3 introduced to minimize its emission to the atmosphere. The NO_x sensor monitored the correctness of NO_x conversions in order to diagnose the entire system functionality, e.g. to diagnose a lack of UWS. The temperature sensor could provide feedback causing the engine's performance to be limited, if the safe temperature threshold for the system was exceeded.

The exhaust aftertreatment system incorporating the investigated SCR reactor was built into the exhaust line of the CI internal combustion engine with the following parameters:

- displacement: 4500 cm^3,
- number of cylinders: 4,
- rated power: 103 kW,
- Common Rail fuel injection system,
- turbocharging with a waste gate,
- fuel: B7 Diesel fuel,
- engine application: non-road mobile machinery.

4. Experiment setup and ageing procedure

The engine and exhaust aftertreatment system were installed on the laboratory engine test bench. The bench was capable of executing both the emission measurements and the ageing procedure. Prior to the emission measurements,

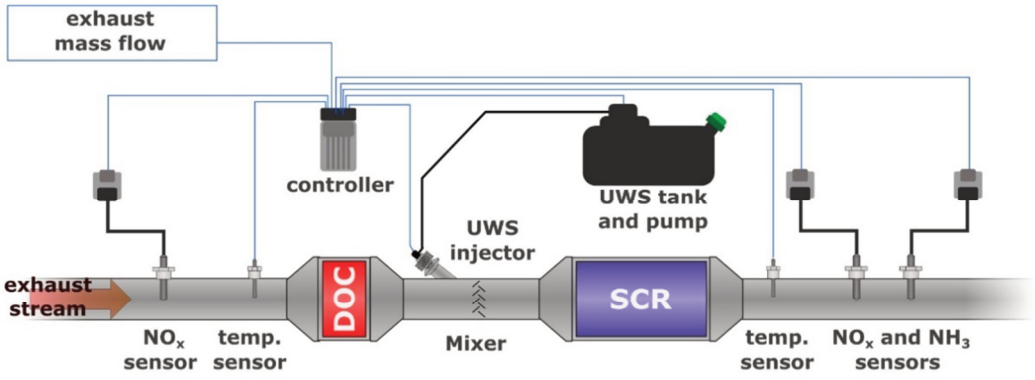

Fig. 1. Exhaust aftertreatment system including SCR reactor under test

the ATS was degreened for 5 h in a controlled manner by exposing it the exhaust stream of 350°C temperature. This operation aimed to stabilize the zeolite structure and remove any potential debris deriving from the production process. Such operation ensured the performance stability of the reactor from the very first measurement cycles.

The prepared test bench installation allowed performance of the experimental activities in the following order:

1. measurement of chosen gaseous exhaust gas compounds downstream of the ATS for the new SCR reactor,
2. controlled ageing of the SCR reactor,
3. measurement of chosen gaseous exhaust gas compounds downstream of the ATS for the aged SCR reactor.

The measurement of gaseous exhaust emissions downstream of the ATS before and after the SCR reactor ageing was done according to the same methodology. As a measurement test, the NRSC RMC (Non Road Steady Cycle Ramped Mode Cycle) stationary cycle was adopted, which is a part of the type approval procedure for engines intended for non-road mobile machinery. For the purpose of the research, the NO_x, NO and NH_3 concentrations were measured.

The test bench automation system was capable of executing the predefined cycle and acquiring measurement results at a rate of 10 Hz. Apart from exhaust gas compound concentrations, a number of channels necessary for specific emissions calculations were acquired. These included the engine speed and torque. The mass flow of air supplying the engine and the fuel consumption were also measured. On the basis of the sum of these two parameters, the mass flow of exhaust gas through the ATS was determined. In addition, the following parameters were measured: temperature and humidity of the engine intake air and atmospheric pressure. Moreover, ATS signals readings and the UWS injection rate were acquired during the test.

The test bench automation system featured data post-processing tools enabling calculation of specific emissions (g/kWh) achieved over the test. The intermediate steps of the emission calculation were the determination of the total emitted mass of each of the measured compounds and mechanical work done by the engine during the whole test.

The procedure of the controlled ageing of the SCR reactor was the following:

1. Engine operation with gradual increase of load and speed from idling up to the rated power point. Duration of the phase: 2 h 10 min, engine run time: 2 h 10 min.
2. Three repetitions of the NRSC cycle. Duration of the phase: 1 h 30 min, engine run time 1 h 30 min.
3. Two repetitions of the NRTC cycle (cold and warm test), including engine conditioning for cold tests. Duration of the phase: 6 h, engine working time 1 h 20 min.

The total duration of a single ageing cycle was 9 h 30 min, including engine operation time of 5 h. The total number of cycle repetitions amounted to 50, reaching 250 h of engine operation along with the ATS undergoing ageing.

5. Test results

Table 3 presents results of measurements of NO_x specific emission and maximum NH_3 concentration obtained in the NRSC RMC test on the fresh and aged SCR reactor. In the case of the fresh rector, the measured NO_x emission was 0.151 g/kWh, and for the measurement of the aged reactor, the obtained NO_x emission was 0.322 g/kWh. This increase in NO_x emissions is 218%, which clearly confirms the partial deactivation of the SCR reactor and the appropriateness of the selected ageing procedure. Despite a more than a twofold increase in post-SCR NO_x emissions, the obtained result of the aged SCR reactor is still below the STAGE IV limit of 0.4 g/kWh. A similar tendency was observed for NO emissions, where the aged sample displayed emissions 224% of the fresh sample's emissions. In line with the NO_x and NO emission trends, the fresh SCR reactor featured a lower maximum NH_3 concentration downstream of the aftertreatment system.

Table 3. Results summary of NRTC RMC test for fresh and aged sample

Reactor condition	Brake specific NO_x emission	Brake specific NO emission	NH_3 maximum concentration
	[g/kWh]	[g/kWh]	[ppm]
Fresh	0.151	0.087	13
Aged	0.329	0.195	19
Increase	218%	224%	146%

Figure 2 presents traces of selected parameters during the NRSC RMC test performed for a fresh and aged SCR reactor. The engine speed and torque lines show the selected operating points. Obtained traces in both tests are almost identical, showing very good repeatability of the test. In the NRSC RMC test, the engine operates at 9 fixed operating points, including two periods of idling: the first and the last test step.

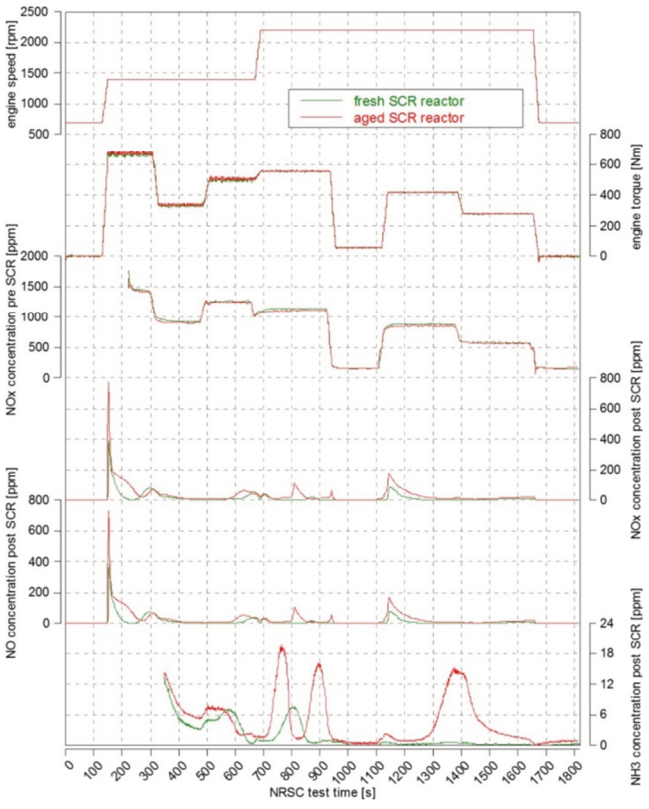

Fig. 2. Traces of chosen parameters over NRTC test

The NRSC RMC test is a hot condition test. Before starting the test, controlled warmup of the engine and exhaust aftertreatment system was performed. The engine was then stopped and immediately restarted to initiate the test without delay. The temperature of the SCR reactor at the start of the test exceeded 200°C and it was found that it was saturated with NH_3 supplied during the warm up phase.

The first step of the test was idling. In this step, lasting 120 s, a small dose of UWS was delivered to the exhaust gas stream, amounting to 0.5 g. The NO_x concentration after the SCR reactor was less than 1 ppm throughout the entire step, both for the fresh and aged reactor. Such low NO_x concentrations were possible due to the NH_3 stored in the SCR reactor and due to the appropriate exhaust temperature (approx. 200°C). A similar phenomenon occurred in the last test step, in which the engine was also idling, and the measured NO_x concentration after the SCR reactor was below 1 ppm.

At the 120th second of the NRSC test, the engine's operating point changed: from idle to the point of maximum torque. This point is characterized by the highest NO_x concentration in the raw exhaust gas, the value of which exceeds 1400 ppm. Despite the immediate response of the UWS dosing system, an increase in the NO_x concentration after the SCR reactor was noted. This tendency occurred both in the case of the fresh and the aged reactor, but the values of the concentrations obtained were different: the maximum NO_x concentration for the fresh reactor was 393 ppm, while in the case of an aged reactor it was 778 ppm. The stabilization time of the SCR system was also different for both reactors. The fresh SCR reactor revealed the minimum NO_x concentration in the analysed step 80 seconds after the beginning of the step (i.e. 145 seconds into the test) and its value was 4 ppm. In case of the aged reactor, the lowest observed NO_x concentration was 21 ppm, occurring 120 seconds after the beginning of the step (i.e. 265 seconds into the test). A significant increase in engine load also occurred at 1100 into the test. In this case, the engine load increased from 10% to 75% of the maximum torque at the engine speed for its rated power value. The SCR system response to an immediate increase in NO_x emissions was similar to that observed in the 120th second test for both the fresh and the aged SCR reactor. The fresh reactor revealed maximum NO_x concentration of 85ppm, while in the case of the aged reactor, a maximum concentration of 178ppm was obtained.

Over the entire test, the NO concentration trace is of similar trend to NO_x. The concentration traces of NH_3 clearly indicate its lower emission downstream of the fresh reactor.

6. Conclusions

An aged SCR reactor is characterized by an increase in total NO_x and NH_3 emissions after the exhaust gas aftertreatment system. The NO_x conversion efficiency of both reactors was found similar at periods of steady engine operation. It was recognized that during transient conditions the NO_x conversion efficiency of the aged reactor was decreased. Different responses of SCR system equipped with fresh and aged SCR reactor for an immediate increase in NO_x emissions of raw exhaust gases resulted from a change in the storage capacity of NH_3. A sudden increase of the NO_x concentration forces the UWS dosing system to proportionally increase the UWS dose delivered to the exhaust stream. However, this response is delayed. Initially, due to the insufficient amount of UWS in the exhaust, nitrogen oxides reacts with NH_3 stored in the SCR reactor. During this period, the amount of NO_x leaving the SCR reactor was inversely proportional to the amount of previously absorbed NH_3. With the ageing of the SCR reactor, the storage capacity of NH_3 decreases; consequently the NO_x emission increases behind the SCR reactor in the states of sudden rise in NO_x emissions of raw exhaust gas.

A reduction of the NH_3 storage capacity of the aged SCR reactor was also noted in the plot of NH_3 concentration downstream of the reactor. For the vast majority of the test duration, the NH_3 concentration behind the aged reactor was greater than in the case of the fresh reactor. Ammonia entering the SCR reactor, which was not used to reduce NO_x, in the case of the aged SCR reactor, was stored to a lesser extent. The NO_x conversion efficiency of both reactors was found to be similar at periods of steady engine operation. The deactivation of the SCR reactor primarily affected its performance under transient conditions, when ammonia storage capacity is the most crucial parameter influencing NO_x conversion efficiency.

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Nomenclature

ATS	aftertreatment system
CI	compression ignition
CO	carbon monoxide
Cu	copper
$deNO_x$	aftertreatment device meant for nitrogen oxides
DOC	diesel oxidation catalyst
HC	hydrocarbons
ICE	internal combustion engine
N_2O	nitrous oxide
NH_3	ammonia
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
NRSC	non-road steady cycle
NRTC	non-road transient cycle
RMC	ramped mode cycle
TWC	three-way catalyst
UWS	urea-water solution
SCR	selective catalytic reduction

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