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Research on the ammonia concentration in the exhaust gas of the self-ignition engines

Abstract: In the article there was reviewed the principle of operation of the SCR type catalytic reactors and explained the reason, why ammonia appears in the exhaust gas. The principles of analyzers to measure the concentrations of ammonia in the exhaust gases was reviewed. There were examined changes in EU regulations on the emissions of vehicles engines in comparison to UNECE Regulation No. 49, series 05 of amendments.

Keywords: ammonia, SCR, LDS, FTIR

Badania stężeń amoniaku w spalinach silników z zapłonem samoczynnym

Streszczenie: W artykule przedstawiono zasadę działania reaktorów katalitycznych typu SCR oraz wyjaśniono przyczynę, dla której w spalinach pojawia się amoniak. Dokonano przeglądu zasady działania analizatorów do pomiarów stężeń amoniaku w spalinach. Przeanalizowane zostały zmiany wprowadzone w rozporządzeniach UE dotyczących emisji zanieczyszczeń z układów wylotowych silników pojazdów w porównaniu z Regulaminem EKG ONZ nr 49, seria 05 poprawek.

Słowa kluczowe: amoniak, SCR, LDS, FTIR

1. Introduction

NO_x reduction systems based on the Selective Catalytic Reduction (SCR) technology are being developed for a number of mobile diesel engine applications in the EU, Japan, and the USA. The use of ammonia has been practically ruled out, due to safety concerns, and urea (in water solution) is the preferred reductant. SCR technology is approaching commercialization in Europe, where a number of heavy-duty vehicle manufacturers selected urea-SCR for meeting Euro IV (2005) and Euro V (2008) emission standards [1]. In Japan, the first commercial urea-SCR system was introduced by Nissan Diesel on its Quon heavy-duty truck launched in November 2004. [2] The 2007 emission standards for heavy-duty engines in the USA, on the other hand, will be met using EGR and other in-cylinder approaches, rather than SCR.

Historically, the introduction of ammonia/urea-SCR systems for NO_x control from mobile applications started with marine engines. Large sizes and steady-state operation of marine units, similar to stationary diesel engines, make the adaptation of stationary SCR technology straightforward. The first SCR units were installed in 1989 and 1990 on two Korean 30,000 metric ton carriers.

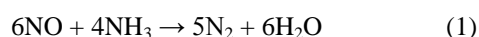
Their ship operator was seeking a permit from the Bay Area Air Quality Management District (BAAQMD) to allow the reduced-emission ships in its docks. Both ships were powered by MAN B&W 2-stroke 8 MW diesel engines. The ships were equipped with ammonia SCR system designed for 92% NO_x reduction. The SCR reactor included a

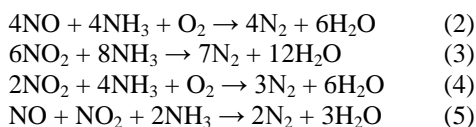
by-pass system. Exhaust gases were passed through the reactor only when the ships were sailing in waters subject to NO_x emission regulations.

2. SCR process

Two forms of ammonia may be used in SCR systems: (1) pure anhydrous ammonia, and (2) aqueous ammonia. Anhydrous ammonia is toxic, hazardous, and requires thick-shell, pressurized storage tanks and piping due to its high vapor pressure. Aqueous ammonia, NH₃·H₂O, is less hazardous and easier to handle. A typical industrial grade ammonia, containing about 27% ammonia and 73% water by weight, has nearly atmospheric vapor pressure at normal temperatures and can be safely transported on highways in the USA and other countries. [3]

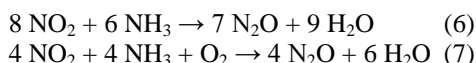
A number of chemical reactions occur in the ammonia SCR system, as expressed by equations (1) to (5). All of these processes represent desirable reactions which reduce NO_x to elemental nitrogen. Equation (2) represents the dominant reaction mechanism. Reactions given by equation (3) through (5) involve nitrogen dioxide reactant. The reaction path described by equation (5) is very fast. This reaction is responsible for the promotion of low temperature SCR by NO₂. [4] Normally, NO₂ concentrations in most flue gases, including diesel exhaust, are low. In some diesel SCR systems, NO₂ levels are purposely increased to enhance NO_x conversion at low temperatures.



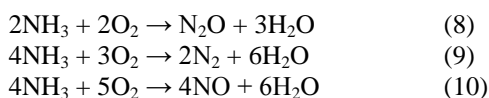


It has been found that the above reactions are inhibited by water. Moisture is always present in diesel exhaust and other flue gases.

In case the NO_2 content has been increased to exceed the NO level in the feed gas, N_2O formation pathways are also possible, as shown in equation (6) and (7). [5]



Undesirable processes occurring in SCR systems include several competitive, nonselective reactions with oxygen, which is abundant in the system. These reactions can either produce secondary emissions or, at best, unproductively consume ammonia. Partial oxidation of ammonia, given by equations (8) and (9), may produce nitrous oxide (N_2O) or elemental nitrogen, respectively. Complete oxidation of ammonia, expressed by equation (10), generates nitric oxide (NO).



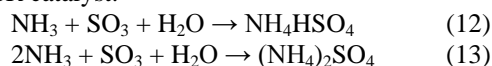
Ammonia can also react with NO_2 producing explosive ammonium nitrate (NH_4NO_3), equation (11). This reaction, due to its negative temperature coefficient, occurs at low temperatures, below about 100-200°C. Ammonium nitrate may deposit in solid or liquid form in the pores of the catalyst, leading to its temporary deactivation. [6]



Ammonium nitrate formation can be avoided by making sure that the temperature never falls below 200°C. The tendency of NH_4NO_3 formation can also be minimized by supplying into the gas stream less than the precise amount of NH_3 necessary for the stoichiometric reaction with NO_x (1 to 1 mole ratio).

When the flue gas contains sulfur, as is the case with diesel exhaust, SO_2 can be oxidized to SO_3 with the following formation of H_2SO_4 upon reaction with H_2O . These reactions are the same as those occurring in the diesel oxidation catalyst. In another reaction, NH_3 combines with SO_3 to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , equation (12) and (13), which deposit on and foul the catalyst, as well as piping and equipment. At low exhaust temperatures, generally below 250°C, the fouling by am-

monium sulfate may lead to a deactivation of the SCR catalyst.



The SCR process requires precise control of the ammonia injection rate. An insufficient injection may result in unacceptably low NO_x conversions. An injection rate which is too high results in release of undesirable ammonia to the atmosphere. These ammonia emissions from SCR systems are known as *ammonia slip*. The ammonia slip increases at higher NH_3/NO_x ratios. According to the dominant SCR reaction, equation (2), the stoichiometric NH_3/NO_x ratio in the SCR system is about 1. Ratios higher than 1 significantly increase the ammonia slip. In practice, ratios between 0.9 and 1 are used, which minimize the ammonia slip while still providing satisfactory NO_x conversions. Figure 1 presents an example relationship between the NH_3/NO_x ratio, NO_x conversion, temperature, and ammonia slip. The ammonia slip decreases with increasing temperature, while the NO_x conversion in an SCR catalyst may either increase or decrease with temperature, depending on the particular temperature range and catalyst system, as will be discussed later.

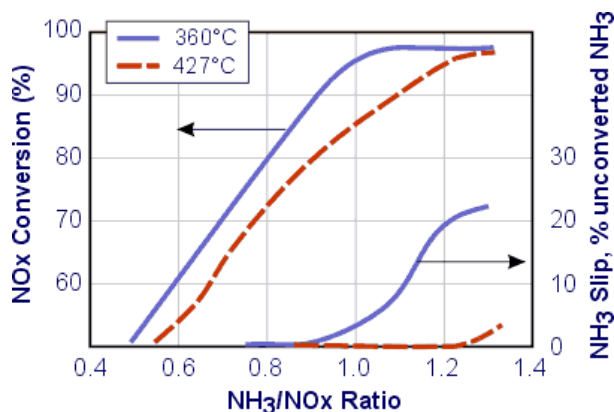


Fig. 1. NO_x Conversion and Ammonia Slip for Different NH_3/NO_x Ratios $\text{V}_2\text{O}_5/\text{TiO}_2$ SCR catalyst, 200 cpsi [3]

In stationary applications, the maximum permitted NH_3 slip is always specified, with a typical specification at 5-10 ppm NH_3 . These concentrations of ammonia are generally undetectable by the human nose. Optionally, ammonia slip can be also controlled by a guard catalyst (oxidation catalyst) installed downstream of the SCR catalyst.

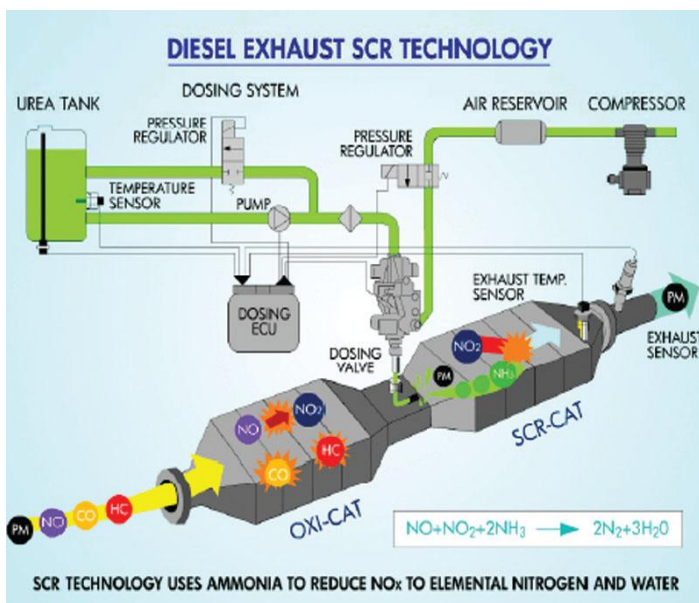


Fig. 2. Diesel exhaust SCR technology [7]

3. Catalysts

SCR catalysts are manufactured from various ceramic materials used as a carrier, such as titanium oxide, and active catalytic components are usually either oxides of base metals (such as vanadium, molybdenum and tungsten), zeolites, or various precious metals. Each catalyst component has advantages and disadvantages.

Base metal catalysts, such as the vanadium and tungsten, lack high thermal durability, but are less expensive and operate very well at the temperature ranges most commonly seen in industrial and utility boiler applications. Thermal durability is particularly important for automotive SCR applications that incorporate the use of a diesel particulate filter with forced regeneration. They also have a high catalysing potential to oxidize SO_2 into SO_3 , which can be extremely damaging due to its acidic properties. [8]

Zeolite catalysts have the potential to operate at substantially higher temperature than base metal catalysts; they can withstand prolonged operation at temperatures of 900 K and transient conditions of up to 1120 K. Zeolites also have a lower potential for potentially damaging SO_2 oxidation. [8]

Iron- and copper-exchanged zeolite urea SCR have been developed with approximately equal performance to that of vanadium-urea SCR if the fraction of the NO_2 is 20% to 50% of the total NO_x . [9] The two most common designs of SCR catalyst geometry used today are honeycomb and plate. The honeycomb form usually is an extruded ceramic applied homogeneously throughout the ceramic carrier or coated on the substrate. Like the various types of catalysts, their configuration also has advantages and disadvantages. Plate-type catalysts have lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types,

but plate configurations are much larger and more expensive. Honeycomb configurations are smaller than plate types, but have higher pressure drops and plug much more easily. A third type is corrugated, comprising only about 10% of the market in power plant applications. [10]

4. Reductants

Several reductants are currently used in SCR applications including anhydrous ammonia, aqueous ammonia or urea. All those three reductants are widely available in large quantities.

Pure anhydrous ammonia is extremely toxic and difficult to safely store, but needs no further conversion to operate within an SCR. It is typically favoured by large industrial SCR operators. Aqueous ammonia must be hydrolysed in order to be used, but it is substantially safer to store and transport than anhydrous ammonia. Urea is the safest to store, but requires conversion to ammonia through thermal decomposition in order to be used as an effective reductant.

5. Limitations

SCR systems are sensitive to contamination and plugging resulting from normal operation or abnormal events. Many SCR are given a finite life due to known amounts of contaminants in the untreated gas. The large majority of catalyst on the market is of porous construction. A clay planting pot is a good example of what SCR catalyst feels like. This porosity is what gives the catalyst the high surface area essential for reduction of NO_x . However, the pores are easily plugged by a variety of compounds present in combustion/flue gas. Some examples of plugging contaminants are: fine particulate, ammonia sulfur compounds, ammonium bisulfate (ABS) and silicon compounds. Many of these contaminants can be removed while the unit is on line, for example by sootblowers. The unit can also be cleaned during a turnaround or by raising the exhaust temperature. Of more concern to SCR performance is poisons, which will destroy the chemistry of the catalyst and render the SCR ineffective at NO_x reduction or cause unwanted oxidation of ammonia (forming more NO_x). Some of these poisons include: halogens, alkaline metals, arsenic, phosphorus, antimony, chrome, copper.

Most SCR require tuning to properly perform. Part of tuning involves ensuring a proper distribution of ammonia in the gas stream and uniform gas velocity through the catalyst. Without tuning, SCR can exhibit inefficient NO_x reduction along with excessive ammonia slip due to not utilizing the catalyst surface area effectively. Another facet of tuning involves determining the proper ammonia flow for all process conditions. Ammonia flow is in

general controlled based on NO_x measurements taken from the gas stream or preexisting performance curves from an engine manufacturer (in the case of gas turbines and reciprocating engines). Typically, all future operating conditions must be known beforehand to properly design and tune an SCR system.

Ammonia slip is an industry term for ammonia passing through the SCR un-reacted. This occurs when ammonia is: over-injected into gas stream; temperatures are too low for ammonia to react; or catalyst has degraded (see above).

Temperature is one of the largest limitations of SCR. Gas turbines, cars, and diesel engines all have a period during a start-up where exhaust temperatures are too cool for NO_x reduction to occur.

Table 1. Euro VI emission limits [11]

6. Procedure for the measurement of

Euro VI emission limits

	Limit values							
	CO (mg/kWh)	THC (mg/kWh)	NMHC (mg/kWh)	CH ₄ (mg/kWh)	NO _x ^(†) (mg/kWh)	NH ₃ (ppm)	PM mass (mg/kWh)	PM ^(‡) number (#/kWh)
ESC (CI)	1 500	130			400	10	10	
ETC (CI)	4 000	160			400	10	10	
ETC (PI)	4 000		160	500	400	10	10	
WHSC ^(§)								
WHTC ^(¶)								

Note:

PI = positive ignition.

CI = compression ignition.

(†) The admissible level of NO_x component in the NO_x limit value may be defined at a later stage.

(‡) A number standard is to be defined at a later stage and no later than 1 April 2010.

(§) The limit values relating to WHSC and WHTC, replacing the limit values relating to ESC and ETC, will be introduced, at a later stage, once correlation factors with respect to the current cycles (ESC and ETC) have been established, no later than 1 April 2010.

ammonia from engine exhaust systems

Two measurement principles are specified for NH₃ measurement and each principle may be used provided that it meets the criteria specified in section 1 or 2, respectively. Gas dryers shall not be permitted for NH₃ measurement. [11]

1. Laser Diode Spectrometer (LDS)

The LDS employs the single line spectroscopy principle. The NH₃ absorption line is chosen in the near infrared spectral range and scanned by a single-mode diode laser.

The analyzer shall be installed either directly in the exhaust pipe (in-situ) or within an analyzer cabinet using extractive sampling in accordance with the instrument manufacturers instructions. If installed in an analyzer cabinet, the sample path (sampling line, pre-filter(s) and valves) shall be made of stainless steel or PTFE and shall be heated to 463 ± 10 K (190 ± 10 °C) in order to minimize NH₃ losses and sampling artefacts. In addition, the sampling line shall be as short as practically possible.

Influence from exhaust temperature and pressure, installation environment and vibrations on the

measurement shall be minimized, or compensation techniques be used.

If applicable, sheath air used in conjunction with in-situ measurement for protection of the instrument, shall not affect the concentration of any exhaust component measured downstream of the device, or sampling of other exhaust components shall be made upstream of the device.

The spectral resolution of the laser shall be within 0,5 cm⁻¹ in order to minimize cross interference from other gases present in the exhaust gas.

2. Fourier Transform Infrared (hereinafter "FTIR") analyzer

The FTIR employs the broad waveband infrared spectroscopy principle. It allows simultaneous measurement of exhaust components whose standardized spectra are available in the instrument. The absorption spectrum (intensity/ wavelength) is calculated from the measured interferogram (intensity/ time) by means of the Fourier transform method.

The FTIR shall be installed in accordance with the instrument manufacturer's instructions. The NH₃ wavelength shall be selected for evaluation. The sample path (sampling line, pre-filter(s) and valves) shall be made of stainless steel or PTFE and shall be heated to 463 ± 10 K (190 ± 10 °C) in order to minimize NH₃ losses and sampling artefacts. In addition, the sampling line shall be as short as practically possible.

The spectral resolution of the NH₃ wavelength shall be within 0,5 cm⁻¹ in order to minimize cross interference from other gases present in the exhaust gas.

The average NH₃ concentration (ppm/test) shall be determined by integrating the instantaneous values over the cycle. The following equation shall be applied:

$$C_{NH_3} = \frac{1}{n} \sum_{i=1}^{i=n} C_{NH_3,i}$$

where:

C_{NH₃,i} is the instantaneous NH₃ concentration in the exhaust gas, ppm,

n is the number of measurements.

For the WHTC cycle, the final test result shall be determined with the following equation:

$$C_{NH_3} = (0,14 \times C_{NH_3,cold}) + (0,86 \times C_{NH_3,hot})$$

where:

C_{NH₃,cold} is the average NH₃ concentration of the cold start test, ppm,

C_{NH₃,hot} is the average NH₃ concentration of the hot start test, ppm.

The NH₃ limits in euro VI standard are shown in table 1. Maximal concentration in test cycle should not be greater than 10 ppm.

Analyser specifications

The analyser using for engine measurement shall have a measuring range and response time

appropriate for the accuracy required to measure the concentration of NH₃ under transient and steady state conditions.

Minimum detection limit	< 2 ppm under all conditions of testing
Accuracy, defined as the deviation of the analyser reading from the reference value	shall not exceed $\pm 3\%$ of the reading or ± 2 ppm, whichever is larger
Zero drift	The drift of the zero response and the related time interval shall be specified by the instrument manufacturer
Span drift	The drift of the span response and the related time interval shall be specified by the instrument manufacturer
System response time	≤ 20 s
Rise time	≤ 5 s
NH ₃ calibration gas	NH ₃ and purified nitrogen (The true concentration of the calibration gas shall be within $\pm 3\%$ of the nominal value.

	The concentration of NH ₃ shall be given on a volume basis (volume per cent or volume ppm)
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7. Conclusion

The use of SCR-type reactors in internal combustion engines has resulted in the appearing of another pollutant in exhaust gases – ammonia.

Due to the toxic nature of ammonia the Euro VI standard introduced a restriction on the permissible levels of this component concentration in the exhaust gases.

The analyzers for the determination of ammonia concentration in the exhaust gases can be devices operating on the principle of LDD and FTIR.

Motor Transport Institute recently has purchased to its laboratory an equipment of AVL AMA i60 LDD. Currently there are performed an engine testing using this device in the work carried out by the Environmental Protection Center. The first results will be available in the near future.

Nomenclature/Skróty i oznaczenia

SCR Selective Catalytic Reduction/*selektywna redukcja katalityczna*
 LDS Laser Diode Spectrometer/*spektrometr laserowo-diodowy*
 FTIR Fourier Transform Infrared Analyzer/*analizator podczerwieni z transformacją Fouriera*

ESC European Steady-state Cycle/*europaeski cykl stacjonarny*
 ETC European Transient Cycle/*europaeski cykl dynamiczny*
 WHSC World Harmonized Steady-state Cycle/*zharmonizowany światowy cykl stacjonarny*

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