

Diesel Emission Technology

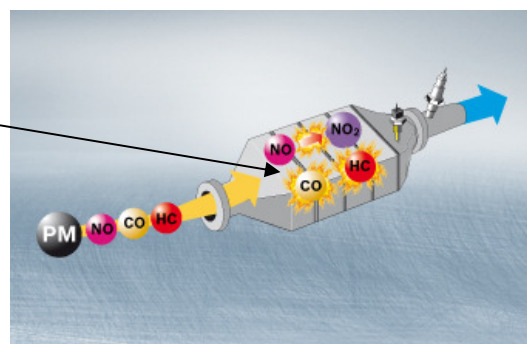
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Diesel-powered trucks are the workhorses of today's society, delivering the vast majority of goods used in North America. Now, after two decades of dramatic emissions reductions, the North American heavy truck industry has been challenged to develop even cleaner diesel engine solutions to meet the Environmental Protection Agency's new standards for 2010.

In the case of diesel engine exhaust, the catalyst oxidizes CO, HC, and the liquid hydrocarbons adsorbed on carbon particles. In the field of mobile source emission control, liquid hydrocarbons adsorbed on the carbon particles in engine exhaust are referred to as the **soluble organic fraction** (SOF) -- the soluble part of the particulate matter in the exhaust.

Diesel oxidation catalysts are efficient at converting the soluble organic fraction of diesel particulate matter into carbon dioxide and water, typically can achieve 25% to 40% over all particulate reduction by simply burning the SOF component of particulate matter. Before 2007 emissions, DOC and DPF after-treatment method with advanced engine EGR system would be sufficient to reduce the emission that EPA required.

Diesel Oxidation Catalyst



Under certain operating conditions, DOCs have achieved SOF removal efficiencies of 80 to 90 percent. Actual emission reductions vary however, as a result of engine type, size, age, duty cycle, condition, maintenance procedures, baseline emissions, test procedure, product manufacturer and the fuel sulfur level. However, as all chemical reactions always occur in the simplest possible way - the existing O₂ in the exhaust gas stream would react first, and the NO_x will be somehow remained in the exhaust gas stream.

Regulations

There are different emission standards around the world, and in US, generally speaking, Congress has given EPA the authority to regulate emissions from newly manufactured heavy-duty diesel engines, and has left regulation of emissions from existing, or in-use, engines to the states and local government authorities. The four main pollutants covered by vehicle emission legislation are Nitrogen Oxide (NO_x), Particulate Matter (PM), Carbon monoxide (CO), and Hydrocarbons (HC).

Diesel engines are more durable and are more fuel efficient than gasoline engines, but they can pollute significantly more. Heavy-duty trucks and buses account for about one-third of nitrogen oxides emissions and one-quarter of particle pollution emissions from transportation sources. In some large cities, the contribution is even greater. Similarly, off-road diesel engines such as construction and agricultural equipment emit large quantities of harmful particle pollution and nitrogen oxides, which contribute to ground-level ozone and other pervasive air quality problems.

Federal Regulation

In the USA, emissions from vehicles are regulated by the Environmental Protection Agency (EPA) regulation called "Clean Air Act" – which is incorporated into the United States Code as Title 42, Chapter 85. The Clean Air Act is the law that defines the protection and improvement of the nation's air quality and the stratospheric ozone layer (<http://www.epa.gov/air/caa/>). The last major change in the law, the Clean Air Act Amendments of 1990, was enacted by Congress in 1990. Legislation passed since then has made several minor changes. The House of Representatives maintains a current version of the U.S. Code.

In recent years, EPA has adopted a "systems approach" to the regulation of new diesel engines, thus, regulating the emissions and the fuel together. This makes sense because the removal of sulfur from diesel fuel is necessary to allow the efficient use of highly effective after-treatment emission control devices. With this system approach, EPA regulations will:

- Reduce nitrogen oxides (NO_x) and fine particulate matter PM_{2.5} from new heavy-duty highway diesels (e.g., trucks and buses) by about 90%, effective in 2007 for PM, and 2007-2010 for NO_x. Effective as of January 1st 2010, the emission level of particulate matter should be reduced from 2002 level of 0.1 g/bhp-hr to 0.01g/bhp-hr (brake horsepower hour). Nitrogen oxide (NO_x) exhaust emissions — which contribute to acid rain, smog and greenhouse gas levels — must be reduced from 1.2 g/bhp-hr in 2007 emission levels to 0.20 g/bhp-hr in 2010 emission level.
- Reduce nitrogen oxides (NO_x) and fine particulate matter PM_{2.5} from new heavy-duty non-road diesels (e.g., construction, farming and logging equipment) by about 90%, effective in the 2011-2014 time frame depending on the pollutant and the size of engine.
- Reduce the sulfur content in highway diesel fuel to 15 ppm ("ultra-low sulfur diesel" fuel, or "ULSD" fuel) beginning in late 2006.
- Reduce the sulfur content in land-based non-road diesel fuel in two steps, to 500 ppm in 2007 and 15 ppm beginning in 2010.
- Reduce the sulfur content in diesel fuel used in new locomotive and many marine engines in two steps, to 500 ppm in 2007 and 15 ppm beginning in 2012.

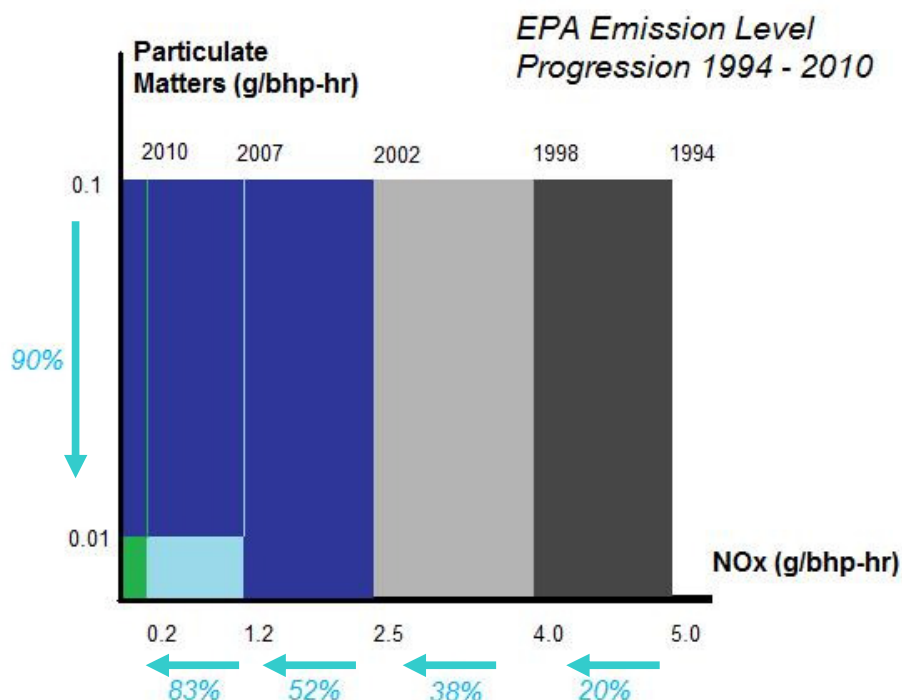
EPA has also announced its intention to commence a rulemaking designed to substantially reduce emissions from new locomotives and many marine engines, taking advantage of the highly effective after-treatment control devices made possible by the availability of ULSD fuel. The challenging task is urging EPA to adopt the most stringent limits achievable with reasonable, cost-effective approaches.

State and Local Regulation

Although recent EPA rulemaking will eventually reduce diesel emissions substantially, that will take some time. The federal rules affect only on new engines, and due to the long lives of heavy-duty diesels – 30 years or more in many cases – substantial turnover of the existing diesel fleet will not likely occur until for 2 or 3 decades after the rules become effective in the 2007-2014 time period. Most of these existing diesels are quite dirty, and it is a public health imperative to clean them up before another generation or two is exposed to this pollution.

The task of regulating diesel emissions from the existing fleet of heavy-duty highway, non-road, marine and locomotive diesels will largely fall on state and local authorities. California has clear authority to regulate emissions from all types of heavy-duty diesel engines, subject to EPA approval, the limits of California's jurisdictional reach and so long as it does not unduly interfere with or discriminate against interstate commerce. Other states also have clear authority to regulate emissions from in-use highway diesels. However, their authority to regulate existing non-road, marine and locomotive emissions is presently limited – in general, they are free to copy California emission standards for non-road engines, but it is not clear that they may adopt separate and different standards.

Therefore, California action on reducing diesel emissions is important, not only for California but also for other states and localities. Fortunately, California is leading the way in regulating in-use diesel emissions, based on its finding that diesel exhaust is a potent air toxic, and on its resulting Diesel Risk Reduction Plan. The Plan recommends that the state adopt **retrofit** requirements for most types of existing highway and non-road mobile diesels and stationary diesel engines, in conjunction with ultra-low sulfur diesel fuel. Thus far, the California Air Resources Board (CARB) has enacted regulations requiring many in-use urban buses and waste collection trucks, as well as stationary and portable diesel engines (used as generators, etc.) and transport refrigeration units, to substantially reduce NOx and PM emissions. Regulations reducing emissions from other California in-use highway, non-road, marine and locomotive diesels are planned. Below chart will show the progression of the PM and NOx emission level in the recent years.

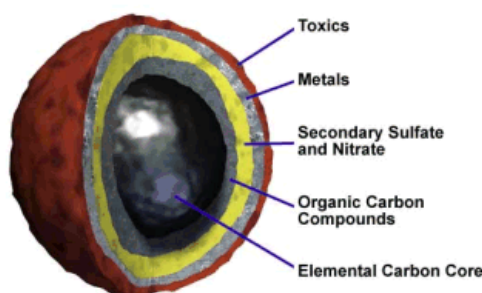


Two Important Pollutants

Diesel Soot – Particulate Matters

Complex directly emitted carbon-core particles – commonly referred to as "soot" (illustrated below) form as a fresh byproduct of diesel combustion. Other secondary particles such as organics, sulfates and nitrates form from exhaust gases, such as hydrocarbons, sulfur dioxide and nitrogen oxides, respectively. For those directly emitted particles, typically have a carbon core coated with a variety of hazardous substances such as metals, toxics and organic compounds. Fresh diesel exhaust contains 'ultrafine' particles that are so small they can directly enter the bloodstream from the lung. Ultrafine particles begin right away to combine to form larger fine particles (PM2.5) quite near the emissions source.

Fine particles (PM2.5) - Particles less than 2.5 micrometers in diameter are called "fine" particles. These particles are so small they can be detected only with an electron microscope. Sources of fine particles include all types of combustion, including motor vehicles, power plants, residential wood burning, forest fires, agricultural burning, and some industrial processes.



Combustion-related particulate matter is associated with a host of severe impacts such as heart attacks, stroke, cardiovascular death (*Dockery et al., 2002*) and lung cancer (*Pope et al., 2002*) in adults. In children, fine particles are associated with upper and lower respiratory impacts as well as retardation of lung growth (*Gauderman et al., 2004*) and crib death. Carbon soot particles from diesel engines adsorb onto their surfaces other metals and toxic substances produced by diesel engines such as cancer-causing aldehydes (like formaldehyde) and PAH (polycyclic aromatic hydrocarbons.)

According to EPA, single pollutants that are likely to cause cancer are generally of concern if they exceed a "one in a million" risk of cancer over a lifetime of exposure. **One-in-a-million** is thus considered an acceptable risk of cancer for a single pollutant. The average person living in the US today is exposed to hundreds of toxic chemicals everyday by eating, drinking water, or just by breathing. Using a "one-in a-million" risk level as a guidepost to protect public health can help address the uncertainty about a toxic chemical's potential.

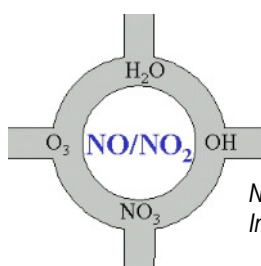
Diesel exhaust exposure is unusually problematic because the majority of the nation's population is exposed to a greater than one in a million level of cancer risk. In fact the modeled averaged risk in all U.S. counties exceed this level. According to the state of California, a lifetime exposure to an average of one microgram of diesel PM in a cubic meter of air carries a cancer risk of 300 in a million.

Based on the single CARB unit risk multiplied by the average diesel soot concentration in the U.S., the nationwide average lifetime cancer risk posed by diesel exhaust is 363 cancers per million. In the analysis counties are designated as 'rural' or 'urban.' In the rural counties we estimate a risk of 142 cancers per million based on the average concentration in rural counties. In the urban counties, the risk is 415 cancer per million. The ratio of urban to rural risk $415/142 = 2.92$, rounding up to a relative factor of 3.

Nitrogen oxides (NO_x)

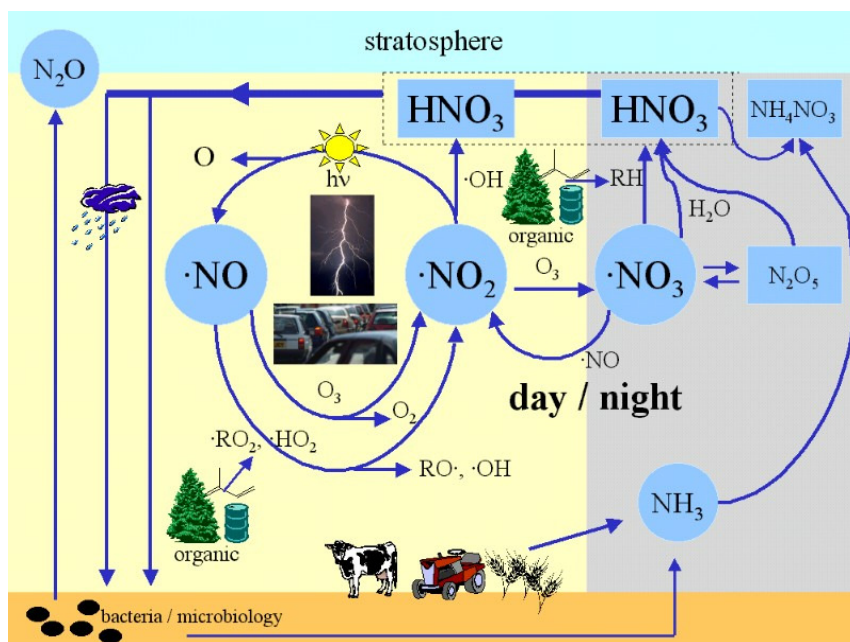
Nitrogen oxides are released to the air from the exhaust of motor vehicles, the burning of coal, oil, or natural gas, and during manufacturing processes such as arc welding, electroplating, engraving, and dynamite blasting. Nitrogen oxides are very important in the formation and loss of troposphere ozone. They are involved in catalytic cycles and continuously react and reform. **Ammonia** (NH₃) is also the most important basic gas in the atmosphere. It reacts in the atmosphere with acid species like nitric acid to form aerosol particles.

Nitrogen dioxide (NO₂) is broken down by sunlight to form nitrogen monoxide (NO). NO then re-reacts to form more NO₂. Ozone and unstable oxygen compounds known as proxy-radicals can also be involved in this cycle. Nitrogen oxides are really at the centre of atmospheric chemistry as shown below. Most chemical compounds which are oxidized and removed from the air or are transformed into other chemical species come into touch directly or indirectly with NO or NO₂.



Nitrogen oxides - at the centre of atmospheric chemistry. Image Elmar Uherek.

NO_x (= NO + NO₂) and other nitrogen oxides are important in almost all atmospheric reactions. Another form of nitrogen oxide, the very reactive nitrate radical (NO₃) is formed in the dark and this controls the chemistry of the night time atmosphere. Nitrogen oxides react with water to form nitric acid (HNO₃). Nitric acid is not only a major contributor to acid rain but is also the main way in which nitrogen oxides are removed from the air, either by dry deposition of the acid directly or by removal in rain. Nitric acid is also important in polar stratospheric cloud chemistry. Here it occurs as nitric acid tri-hydrate and this species plays a part in the formation of the ozone hole.



This figure gives an overview of the role of nitrogen oxides in atmospheric chemistry. By Elmar Uherek.

Nitrogen oxides are a mixture of gases that are composed of nitrogen and oxygen. Two of the most toxicologically significant nitrogen oxides are nitric oxide and nitrogen dioxide; both are nonflammable and colorless to brown at room temperature. Nitric oxide is a sharp sweet-smelling gas at room temperature, whereas nitrogen dioxide has a strong, harsh odor and is a liquid at room temperature, becoming a reddish-brown gas above 70 °F.

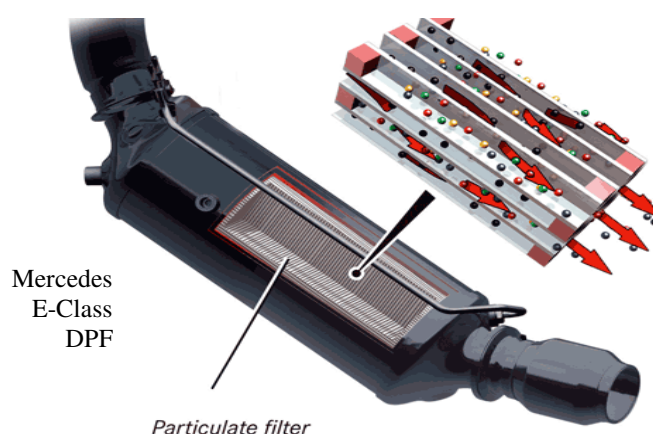
Nitrogen oxides are broken down rapidly in the atmosphere by reacting with other substances commonly found in the air. The reaction of nitrogen dioxide with chemicals produced by sunlight leads to the formation of nitric acid, which is a major constituent of acid rain. Nitrogen dioxide also reacts with sunlight, which leads to the formation of ozone and smog conditions in the air we breathe. The general population is primarily exposed to nitrogen oxides by breathing in air. People who live near combustion sources such as coal burning power plants or areas with heavy motor vehicle use may be exposed to higher levels of nitrogen oxides.

The EPA has established that the average concentration of nitrogen dioxide in ambient air in a calendar year should not exceed 0.053 parts of nitrogen dioxide per million parts of air (0.053 ppm). The Occupational Safety and Health Administration (OSHA) has set a limit of 25 ppm of nitric oxide in workplace air during an 8-hour workday, 40-hour work week. OSHA has also set a 15-minute exposure limit of 5 ppm for nitrogen dioxide in workplace air.

As described in article “Catalytic Converter”, the HC and CO in exhaust gas were oxidized in light-off DOC before they flow further down into exhaust stream. Therefore, this article will be focusing on particulate matters and nitrogen oxidizes as diesel after-treatment.

Diesel Particulate Filters (DPF)

Diesel particulate filters remove particulate matter found in diesel exhaust by filtering exhaust from the engine. In order to meet the stringent particulate emissions that are required for diesel light duty vehicles starting with the 2007 model year, the highest efficiency particulate filter is required. The filters are commonly made from ceramic materials such as cordierite, aluminum titanate, mullite or silicon carbide.



The basis for the design of wall flow filters is a honeycomb structure with alternate channels plugged at opposite ends. As the gasses passes into the open end of a channel, the plug at the opposite end forces the gasses through the porous wall of the honeycomb channel and out through the neighboring channel. The ultrafine porous structure of the channel walls results in greater than 90% percent collection efficiencies of these filters. Wall flow filters capture particulate matter by interception and impaction of the solid particles across the porous wall. The exhaust gas is allowed to pass through in order to maintain low pressure drop.

Particulate Filter Regeneration

Since a filter can fill up over time by developing a layer of retained particles on the inside surface of the porous wall, engineers that design engines and filter systems must provide a means of burning off or removing accumulated particulate matter and thus regenerating the filter. A convenient means of disposing of accumulated particulate matter is to burn or oxidize it on the filter when exhaust temperatures are adequate. By burning off trapped material, the filter is cleaned or "regenerated" to its original state, this is called "**regeneration**". The frequency of regeneration is determined by the amount of soot build-up resulting in an increase in **back pressure**. Two simple pressure sensors will provide feed back to ECU as a part of regeneration control. To facilitate decomposition of the soot, a catalyst is used either in the form of a coating on the filter or a catalyst added to the fuel.

Filters that regenerate in this so-called "passive" fashion cannot be used in all situations. The experience with catalyzed filters indicates that there is a virtually complete reduction in odor and in the soluble organic fraction of the particulate. Despite the high efficiency of the catalyst, a layer of ash may build up on the filter requiring replacement or servicing. The ash is made up of inorganic oxides from the fuel or lubricants used in the engine and will not decompose during the regular soot regeneration process.

In some applications or operating cycles, the exhaust never achieves a high enough temperature to completely oxidize the soot even in the presence of a catalyst. In these instances, an "**active**" **regeneration** system must be employed. Active regeneration utilizes a fuel burner or a resistively heated electric element to heat the filter and oxidize the soot. Active regeneration can be employed either in-place on the vehicle or externally.

- **Active regeneration** - In place vehicle regeneration, the DPF will periodically undergo active regeneration. In this process, a small mist of diesel fuel is injected into the exhaust stream at the turbocharger outlet; the mist travels through the exhaust pipe to wet the DPF's pre-catalyst. This causes a chemical reaction which raises DPF temperatures to the level required to convert the soot into CO₂. Active regeneration normally takes about 15 minutes and the operation is not noticeable to the driver. This event is triggered when sensors – in most cases pressure sensors located at the inlet and outlet end of the DPF that alert the vehicle computer (ECU) that the restriction across the particulate trap is increasing (a back pressure change) and the particulate trap is becoming full.
- **External Regeneration** - During external regeneration, the filter is removed from the vehicle and heated in a controlled chamber to remove the PM.

There is another fact, when a diesel engine combusts fuel, it produces NO_x, and also puts out some soot. If there is an extremely efficient engine that produces little soot, that same engine - unfortunately will produce even more NO_x. With more recent technologies, some of the unusually efficient engine, which provides the obvious benefits of fuel efficiency and very low particulate emissions. To combat the resultant NO_x emissions, the exhaust gas and an injected of DEF enter an additional catalytic converter, which turns the NO_x into harmless nitrogen gas and water vapor. This new system is the one that not only meets the EPA's near-zero NO_x emissions requirement, but meanwhile also can eliminates DPF "regeneration" process. The key of this combination is the advanced engine technology with sophisticated vehicle ECU system. This will relieve the driver from ever having to worry about active regeneration in normal highway operations.

However, at 2004, Navistar/Maxxforce diesel started strategic approach in advanced cooled EGR system to eliminate NO_x in cylinder. With increased fuel injection pressure and EGR rate, along with advanced turbocharger, combustion bowl refinement, and new ECU calibration strategies, Maxxforce diesel was able to achieve 2010 EPA emission requirement without SCR application, under the condition where the OEM could use part of the emission credit accumulated over the years.

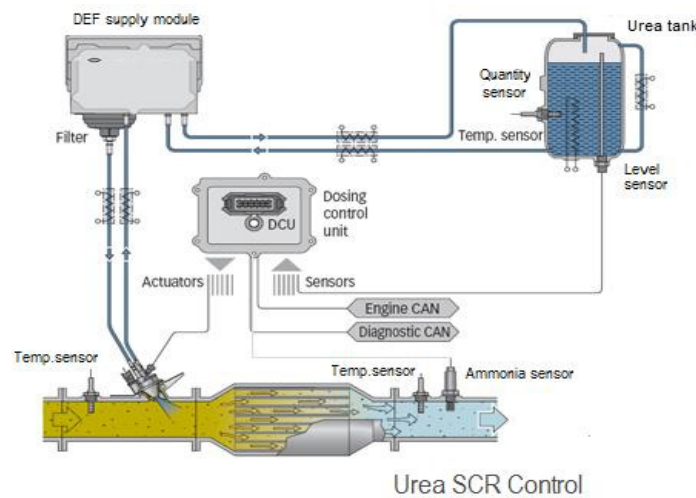
Selective Catalytic Reduction (SCR) Technology

Because of the simple chemical reaction reason, to reduce NO_x on a compression ignition engine, the chemical composition of the exhaust gas must first be changed. There are two ways to accomplish NO_x reduction goal - **selective catalytic reduction (SCR)** and **NO_x traps (or NO_x Absorbers)**.

The leading solution for 2010 is Selective Catalytic Reduction (SCR) - an emissions-reduction technology with the ability to deliver near-zero emissions of Nitrogen Oxides (NO_x), a smog-causing pollutant and greenhouse gas. This technology requires treating the exhaust stream with a spray of diesel exhaust fluid (DEF) - an ammonia based solution. DEF, along with the exhaust heat and a catalyst, converts NO_x into nitrogen and water vapor, which are clean, harmless and present in the air we breathe every day. Three forms of DEF can be used in SCR systems: ***pure anhydrous ammonia, aqueous ammonia and urea.***

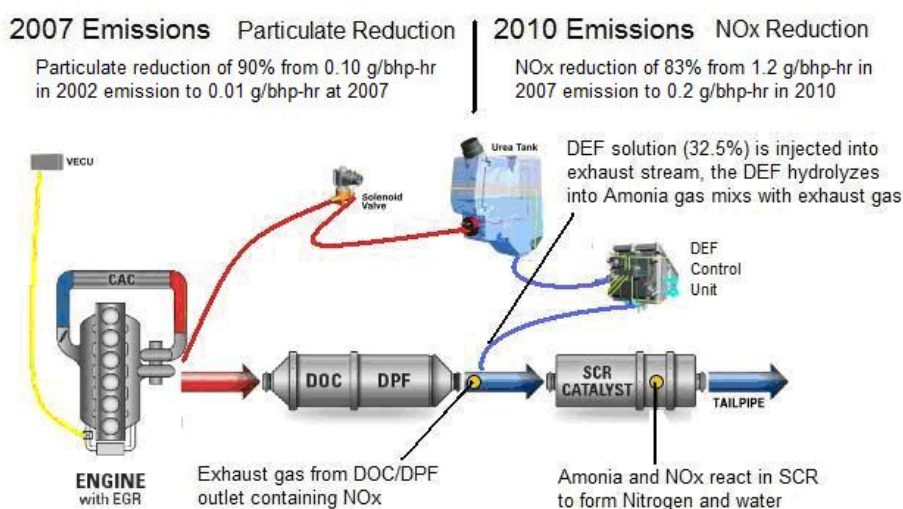
Urea SCR System

The system will still use the existing engine architecture, diesel oxidation catalyst (DOC) and diesel particulate filter (DPF), with additional SCR hardware. This technology allows the engine to function at optimal combustion temperatures, which increases fuel efficiency and reliability. The main components of the SCR system are the SCR catalyst, the DEF injection unit, the DEF storing tank and the DEF dosing control unit - a commonly ***closed-loop control***. The system is benefited from closed-loop control when appropriate exhaust gas sensors are used.



An ammonia sensor, which is based on a non-equilibrium electrochemical principle and outputs emf signals, has been developed by Delphi for use as a feedback element in closed-loop control of urea injection in a diesel SCR after-treatment system. Closed-loop control of SCR dosing enables the SCR system to be robust against disturbances and to meet conformity of production (COP) and in-use compliance norms.

DEF is a solution of purified water and urea, an organic nitrogen compound that turns to ammonia when heated. When DEF is injected into the exhaust pipe downstream of the engine, the heat of the engine exhaust gases decomposes DEF into ammonia and CO₂. Vaporized DEF and hot exhaust gases enter a catalytic converter located in the exhaust system after the DPF (diesel particulate filter). The catalytic converter contains a catalyst, which is a substance that causes or accelerates a chemical reaction, without being affected itself. When the NO_x reacts inside the catalyst with the ammonia, the harmful NO_x molecules in the exhaust are converted to harmless nitrogen and water.



Selective Catalytic Reduction System

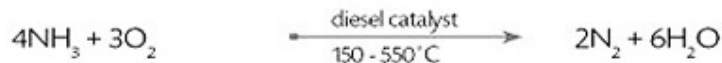
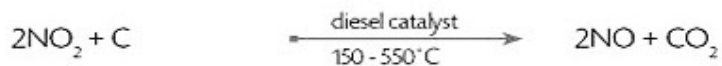
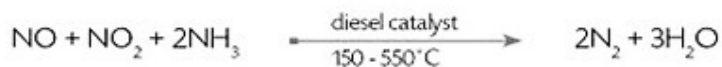
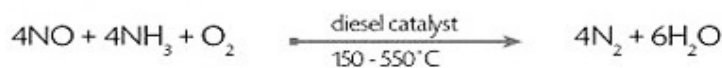
Selective Catalytic Reduction with urea injection is already a proven technology that uses basic chemistry to reduce NOx emissions through a process that is simple, extremely efficient, very reliable and safe. Above figure show the 2007 emissions and 2010 emissions system configuration with focus of particulate matter and NOx emission reduction.

Following are the automotive urea SCR reaction equations:

Urea decomposition:



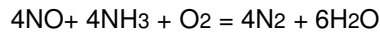
SCR reactions:



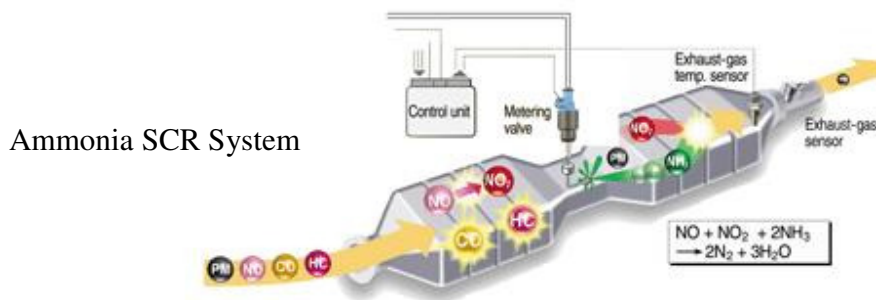
Ammonia SCR System

Selective Catalytic Reduction (SCR) of NOx using an ammonia compound as reductant has been used for many years in stationary diesel engine applications, as well as for mobile applications. In the SCR process, NOx reacts with the ammonia, which is injected into the exhaust gas stream before a special SCR Catalyst.

The main chemical reaction which occurs in ammonia SCR system is shown by this Equation:



The ammonia SCR process requires precise control of the ammonia injection rate. An insufficient injection may result in unacceptably low NO_x conversions. An injection rate that is too high results in release of undesirable ammonia to the atmosphere. These ammonia emissions are known as **ammonia slip**. The ammonia slip increases at higher NH₃/NO_x ratios. The stoichiometric NH₃/NO_x ratio is about 1.0.



An ammonia SCR system for the automotive diesel engines works in the same way of urea SCR system with the exception of the injection control system. The ammonia SCR control system is an **open loop configuration**, where a pre-programmed map of engine NO_x emissions is used to control the ammonia injection rate. This open loop configuration is capable of some 95% NO_x reductions. The automotive industry recognizes that it offers the most effective SCR solution for mobile applications.

The System is comprised of sensors for exhaust gas temperature, intake air temperature, engine load information, throttle position, engine rpm, exhaust back-pressure, the electronic control unit (ECU) and a SCR converter. The ECU is responsible for controlling the amount of ammonia being injected for maximum NO_x reduction and includes circuitry for the redundant fail-save and OBD (On Board Diagnostic) system.

The ECU calculates the correct amount of Ammonia needed, by "reading" the information supplied by the various sensors and compares these values with the appropriate point of the factory-programmed ECU Map. The fail-save system assures that possible ammonia leaks do not go undetected and the OBD system alarms the vehicle operator of any problems. High quality electromagnetic valves assure auto-shutoff of the ammonia supply in case of accidents or system malfunctions.

The prevention of ammonia slippage and a high NO_x conversion rates is guaranteed by the advanced Electronic Control Unit (ECU) and high-sensitivity engine and ambient parameter sensors. Without an advanced ECU, low to no ammonia slippage and high NO_x reduction cannot be guaranteed.

Ammonia SCR systems have several benefits over urea SCR systems.

- Low temperature climate compatibility, ammonia is injected directly into the exhaust stream, unlike the urea that needs heat to decompose into ammonia at first.
- An advantage concerning infrastructure issues,
- A higher conversion rate and a smaller less complex system.

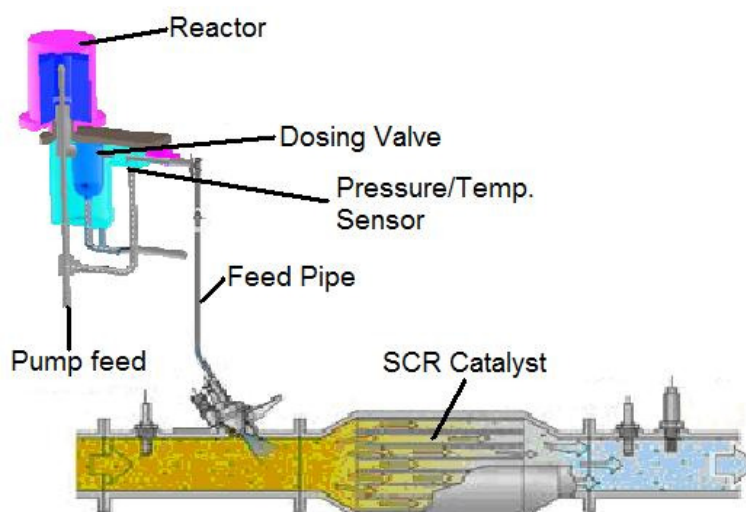
Solid SCR System

Any liquid ammonia based SCR system will have additional weight (up to 400lbs) of the hardware adding to the vehicle causing the sacrificing of fuel economy, packaging and cost. The Solid SCR System is a viable alternative to a liquid urea injection system. With a volume reduction of approximately 70 percent, the solid SCR system still offers equivalent or better performance than liquid urea systems.

| | Pure Ammonia (liquid Phase) | Solid Urea | Urea Solution (34.4% / 65.6%) | Ammonia Carbamate |
|-------------------------|--|--|---|---|
| Mass / 1g of NO | 0.57 g | 1 g | 2.9 g | 1.3 g |
| Volume @ Density | 0.93cm ³ @0.61 g/cm ³ | 0.75cm ³ @1.34g/cm ³ | 3.0cm ³ @0.97g/cm ³ | 0.81cm ³ @1.6g/cm ³ |

FEV have invested significant resources in the development of solid SCR after-treatment technologies, and in 2009 SAE conference, FEV unveiled the solid-SCR NOx reducer for diesel engines. This technology offers high potential due to its packaging advantages and the fact that it does not present the same low temperature issues that exist with liquid urea systems.

Now, FEV is working with supplier Tenneco to market the system and the retrofit market is seen as a prime target for the system. The solid SCR could be adapted to older buses and trucks to bring them up to modern emissions standards. They have been through two generations of SSCR system by retrofitting the system into 2004.5 Dodge Ram truck for testing, and measuring of the emission reduction in steady state and the transient conditions both in the lab and on the road.



Solid SCR System

The basic principle of the Solid SCR is the same as the urea injection systems found on most of the new 50-state legal diesel vehicles coming to market. Ammonia is reacted with the NOx in the exhaust gases to convert it to nitrogen and water. Where it differs is the source of the ammonia. Instead of an aqueous urea solution that is injected into the exhaust stream, this one uses a solid known as an ammonium carbamate that is a byproduct of fertilizer production.

The ammonium carbamate is stored within a canister similar to an oil filter. A small amount of diesel fuel is passed through the canister after being heated to just 60° C which causes the ammonium carbamate to sublime directly into gaseous ammonia. The ammonia and diesel are

passed through an oil separator to recover the fuel. The ammonia is injected into the exhaust stream to react with the NO_x. No diesel is consumed in the process and the solid system is one third the volume of a urea system. The solid system provides easier handling and packaging and doesn't require the heated storage tanks that urea needs to keep from freezing in cold weather.

The amount of reductant to be injected into the exhaust gas depends on several factors:

- NO_x concentration in the exhaust.
- Exhaust gas temperature.
- Overall exhaust gas composition and flow rate.
- Selectivity and ammonia adsorption capability of the catalyst.

Ammonium carbamate was chosen as the prime reductant among the possible options. One major reason for this decision was that it sublimates at 140°F (60°C), resulting in relatively high sublimation rates at lower temperatures. This process is also reversible; in a closed system, cooling of the gas phase will lead to the formation of ammonia carbamate. This process ensures that the amount of ammonia that is temporarily stored inside the closed system is very low. Ammonium carbamate is a precursor during the urea production process and can be readily manufactured. However, current production capabilities would have to be increased in order to eventually support a future infrastructure.

Meanwhile, the Danish technology company **Amminex**, a developer of another “solid-SCR” technology using solid ammonia precursors for selective catalytic reduction of NO_x, has signed agreement with Navistar to offer similar tool for Navistar to explore cost-effective, customer-friendly technologies that fit the MaxxForce® Advanced EGR platform, meeting emissions requirements while removing the burden liquid urea places on the HD truck industry.

The Amminex technology - based on a metal ammine NO_x reductant delivery system—is a tool which Navistar will use to explore exhaust gas NO_x reduction for specific applications. Navistar 2010 - compliant engines have achieved 0.4-0.5 g/bhp-hr of NO_x using in-cylinder NO_x reduction technology with “MaxxForce Advanced EGR”. The difference from the 0.2 g/bhp-hr NO_x emission standard will be initially covered by emission credits accumulated by the company. Navistar considers the Amminex ammonia delivery system a potential cost-effective added component to eventually reach the 0.2 g/bhp-hr NO_x standard. In addition, several automotive OEMs are evaluating the technology's use in light-duty vehicles such as autos and pick-ups.

The metal ammine-based delivery system by Amminex involves storage of non-pressurized ammonia in the form of metal chloride amines, such as strontium chloride ammine, Sr(NH₃)Cl₂. On-vehicle, gaseous ammonia is released through thermal decomposition of the ammine at temperatures on the order of 150°C.

Amminex was formed in 2005 by a group of scientists from the Technical University of Denmark (DTU) led by Tue Johannessen. Amminex has raised DKK 150 million in connection with a capital increase by existing investors: SEED Capital, Nordea Foundation, Conduit Ventures and Yasuda Enterprise Development Company, as well as by Navistar.

Overall, the solid SCR technology provides several benefits:

- High NO_x reduction efficiencies (even at low exhaust temperatures).
- Supported by economically feasible infrastructure.
- Stores only small amounts of ammonia on vehicle or at the retails.
- Exhibits benefits in dosage dynamics
- Lower energy consumption.
- Compact (packaging) and low cost.

Diesel Exhaust Fluid (DEF)

Diesel Exhaust Fluid (DEF) is the key elements of the SCR process. Three forms of reductants can be used in SCR systems: (1) urea, (2) pure anhydrous ammonia and (3) aqueous ammonia. The most commonly used is urea. It is a solution of 67.5% purified water and 32.5% urea. When DEF is injected into hot exhaust as a fine mist and passed over a SCR catalyst, it helps convert NO_x into nitrogen gas and water vapor. The amount of injected urea used will be approximately 2-3% of diesel used - 2 to 3 gallons of urea will have to be used every 100 gallons of fuel.

Per ISO 22241, urea has the below properties:

- Maximum pH 9.75
- Viscosity at 25°C 1.4 mPA
- Density at 20°C 1.085 kg/L
- Freezing point -11°C

It must allow a minimum of 12% freeze expansion, and it is a nontoxic or hazardous material, but very corrosive - not compatible with low carbon steels, it is compatible with most plastics, rubbers, and stainless steel.

Urea solution DEF is stable, colorless and odorless compound of nitrogen that turns to ammonia when heated. Various actions can affect the quality of DEF. To prevent contamination, it is imperative that foreign materials do not come in contact with the solution. Using contaminated DEF can lead to expensive catalyst replacement costs.

DEF is classified as non-hazardous by EPA. Urea is naturally occurring, but is also commonly made from natural gas. International standards ensure quality is maintained during the DEF production and distribution. At 86°F DEF has a shelf life of 1 year, and it begins freezing at 12 degree Fahrenheit (-11° Celsius). If DEF freezes, the engine will start but run properly (no de-rate or malfunction lights). An immersion heater in the DEF tank thaws the fluid for use, and when it thaws, the product will retain its initial quality and vehicles will remain operational throughout the DEF tank thawing process.

Advantage

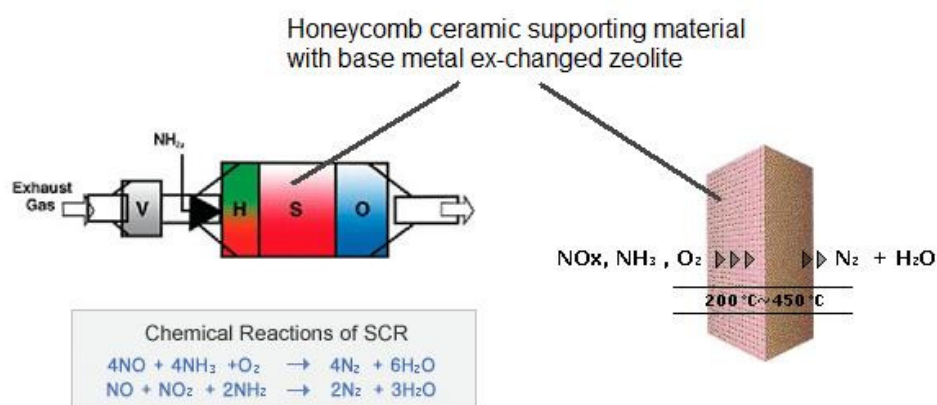
The advantage of using SCR is a lower rate of engine exhaust gas recirculation (EGR) can be used to meet the near-zero NO_x emissions requirement, while at the same time achieving greater fuel efficiency than a diesel using massive EGR. Results show that there will likely be an overall fuel savings of approximately 5% to 9% when comparing a SCR engine to a massive EGR (non-SCR) engine, making SCR as good for business as it is good for the environment.

Since DEF is made from common substances - water and urea - a supply base is already in place. A coalition of industries, including truck manufacturers, truckstops, retail fuel facility owners, fuel distributors and urea providers is developing a network of bulk DEF filling stations at truckstops and diesel service stations across North America. In other words, it will be available at the same places as diesel fuel, and will be available by 2010 at dealerships, parts stores truckstops, and other retail locations.

DEF combined with SCR offers a fuel efficient solution, with lower CO₂ emissions than competitive solutions. Most North American truck manufacturers currently offer SCR equipped models. SCR is a proven technology that brings diesel vehicles and fleet owners a payback with low maintenance and fuel economy.

SCR Catalysts

Diesel SCR catalyst support are manufactured from various ceramic materials, such as titanium oxide in a honeycomb shape just like the DOC support, and active catalytic components are usually either oxides of base metals (such as vanadium and tungsten), zeolites, and various precious metals, and each of catalyst component has advantages and disadvantages.



Base metal catalysts, such as the vanadium and tungsten, lack high thermal durability, which is particularly important for automotive SCR applications that also incorporate the use of a diesel particulate filter with forced regeneration.

Zeolite catalysts have the potential to operate at substantially higher temperature than base metal catalysts; they can withstand prolonged operation at temperatures of 1160 degree F and transient conditions of up to 1556 degree F.

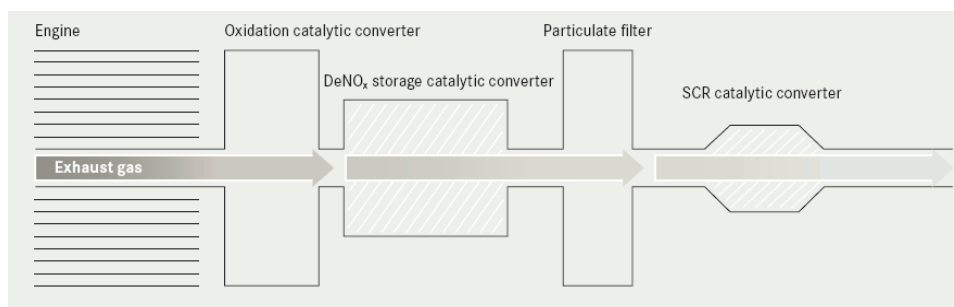
Iron- and Copper-exchanged Zeolite urea SCRs have been developed with approximately equal performance to that of vanadium-urea SCRs if the fraction of the NO₂ is 20% to 50% of the total NO_x. Studies were done by automotive industry OEMs before the SCR approach had been selected. Ford completed one of the studies to compare three after-treatment methods, HC SCR using diesel fuel, Lean NO_x Trap (LNT) and SCR with ammonia-based reductant.

The study showed that Cu/Zeolite performed better at lower temperatures, Fe/Zeolite was better at high temperatures, and they were both able to handle the DPF regeneration temperature, and vanadium-urea SCR is not appropriate for North America. With optimization of EGR, coating modification of DOC for a better HC, CO and NO oxidation, and better dosing of DEF, Ford SCR system should be able to handle the 2010 emission objectives.

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. Honeycomb configurations are smaller than plate types, but have higher pressure drops and plug much more easily.

The 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, and they are not suitable for automotive application, due to the cost and packaging limitation.

Lean NOx Trap and CRT® Process

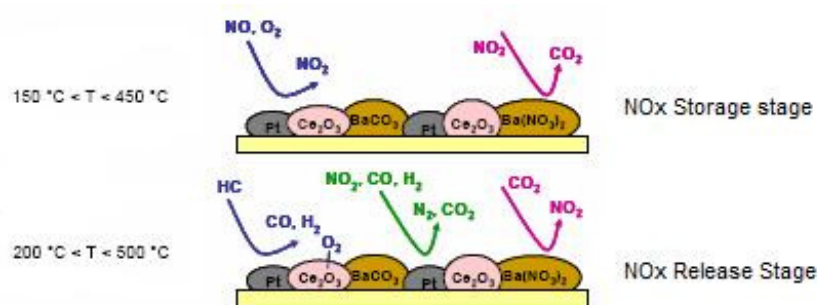


Lean NOx Trap / Storage Catalyst Converter (NSC) System

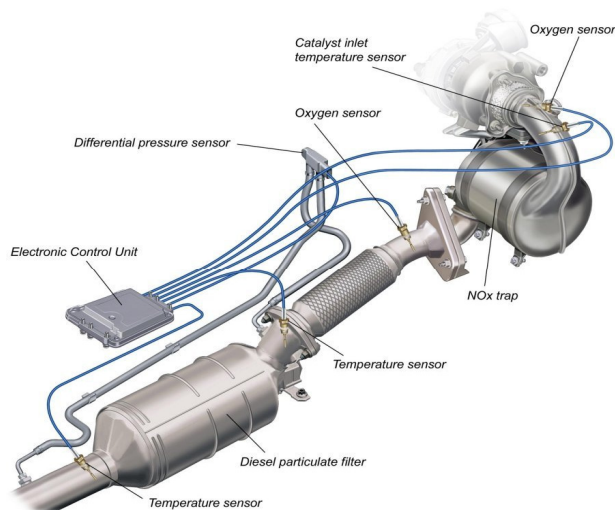
The second method of reducing NOx emission is called Lean NOx trap – a NOx storage converter (NSC) or a NOx absorber. This converter mostly catalyzes the reduction of nitrogen oxides to nitrogen. Today's lean (with high air-fuel ratios) running diesel engines lack sufficient carbon monoxide and hydrocarbons for this reaction. Aside from platinum as catalyst, the NSC converter also contains storage components with high affinity to NOx – the Barium compounds. During the Intermittent short phases when the engine runs on a rich air-fuel mixture, they temporarily provide some of the necessary carbon monoxide and hydrocarbons for the reduction of the nitrogen oxides that were stored and now released.

Renault is one of a few companies that created a lean NOx trap systems operating by the above concept – the NSC is a discontinuously operating after-treatment system. NOx stores during lean engine operation, and NOx reduction during rich operation phases with higher temperatures. It is an on vehicle process that vehicle occupants do not even notice.

During the capture phase, the NOx Trap surface traps the nitrogen oxide contained in the exhaust gas on a porous carrier in the catalytic converter, which is impregnated with precious metals – platinum, barium, and rhodium. The platinum converts nitrogen oxide into nitrogen dioxide (NO₂). The barium, which oxidizes into barium oxide, traps and holds NO₂ as part of an aqueous barium nitrate solution – Ba(NO₃)₂.



In the regeneration phase, a chemical process called reductive elimination purges the NOx Trap of the stored NOx, with the engine operating in rich-burning mode. The nitrogen oxides are converted into neutral gases, mainly nitrogen. In this way the NOx Trap is regenerate and is ready to go on trapping more NOx. This process created another anti-pollution treatment for diesel engines that could be able to capture the nitrogen oxides (NOx) at the tailpipe while still performing the standard oxidization of un-burnt carbons.



Renault NOx Trap System with ECU Control (*reference of Renault technology*)

To ensure the NOx Trap operates smoothly, additional (oxygen and heat) sensors are positioned at the intake manifold and on the tailpipe. The data that the sensors capture is transmitted to the vehicle ECU for managing the NOx Trap purge timing and determining combustion modes.

CRT® Process

Eminox created an unique process called CRT – Continuously Regenerating Trap to regenerate the diesel filter. The Eminox CRT® system uses a patented process that functions on the basis that soot will begin to oxidize in the presence of NO₂ at around 250 °C, compared to 600 °C with oxygen.



This lower temperature is compatible with the typical exhaust temperature of diesel engines. The CRT® system is made up of two chambers, a highly active platinum oxidation catalyst (DOC) followed by an extremely fine ceramic wall-flow filter. The DOC contains a diffuser plate that distributes the exhaust gas evenly through the catalyst, the platinum oxidation catalyst oxidizes the CO and HC into CO₂ and H₂O. It also oxidizes some of the NO to NO₂. This is the key to the removal of soot collected by the CRT® filter down stream.

The wall-flow filter in the second chamber traps the particulate matter in the exhaust gas. This trapped soot is continually oxidized by the NO₂, removing it from the exhaust gas. The Eminox CRT® system eliminates over 90% of all particulate matter, hydrocarbons and carbon monoxide. NOx reduction meanwhile is not guaranteed, is typically in the 5 - 10% range.

In demanding applications a catalytic coating can also be applied to the filter itself. It is called a CCRT® – Catalytic Continuously Regenerating Trap. This enables the CRT® to cover a wider

range of operating conditions, with lower exhaust temperatures or NO_x:PM ratio. In the CCRT®, after the NO₂ has reacted with the soot trapped in the filter, producing NO and CO₂, some of the NO is re-oxidized to NO₂ which then reacts with any soot remaining in the filter. The chemical reactions as follow:

- Soot in the filter reacts with the NO₂: $[C] + 2NO_2 \rightarrow CO_2 + 2NO$
- Some the NO produced in the reaction is re-oxidized into NO₂: $NO + \frac{1}{2}O_2 \rightarrow NO_2$
- The NO₂ reacts with any remaining particulate removing it from the exhaust gas:
 $[C] + 2NO_2 \rightarrow CO_2 + 2NO$

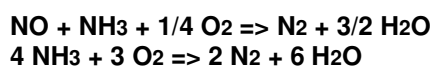
(Reference of www.eminox.com)

Common Problems

Contamination - In order to ensure that the SCR unit remains free from contaminants, correct materials of construction must be used for both storage and dispensing. Ions can pass from the dispensing materials into the porous head on the SCR unit if unsuitable materials are used in the SCR manufacturing process. This reduces SCR efficiency and lifespan by more than 60%.

Tuning - The biggest challenge with SCR is the necessity to tune the SCR system to the engine operating cycle. This requires running the engine through a simulation of the operating cycle to which it will be fitted. The simulation can be run on a dynamometer, or on an actual piece of equipment during its normal work day with data logging. Data logging tends to be inaccurate because of the load, equipment and operator differences.

Ammonia Slip - Another common problem with all SCR systems is the release of un-reacted ammonia. This is called ammonia slip. Slip can occur when catalyst temperatures are not in the optimal range for the reaction or when too much ammonia is injected into the process. An additional oxidation catalyst called a slip catalyst is typically fitted downstream of an SCR system to reduce such slip. The chemical reactions in the slip catalytic converter as follows:



Low Temperature – this is especially in the passenger car applications under cold-start conditions, a relatively low temperature of exhaust gas resulting in SCR catalyst temperature below the optimal range.

SCR Offers

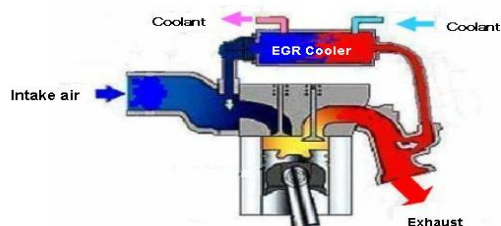
SCR's performance has been proved in millions of miles of real-world truck operations in other countries, as well as in long-term field tests in the U.S. Almost all major diesel engine manufacturers have decided to use this technology to meet the new emission legislation on NO_x emissions. It's also cost-effective, with the reliable and proven engine architecture, SCR is the only clean-air technology that actually pays you back over the life of your vehicle.

- Improves engine life by 20-25% from old in-cylinder EGR system.
- SCR technology achieves a 5-9% fuel economy advantage over In-cylinder EGR by fuel saving of eliminated DPF regeneration.
- CO₂ emissions decrease as fuel economy improves
- Greater component reliability due to less EGR, higher oxygen levels, less heat rejection and fewer changes to moving engine parts, and no complex changes to the engine.
- DEF filter replacement required approximately every 200,000 miles/6,500 hours
- Uses DEF, a safe solution that is less toxic than other shop fluids such as windshield washer and antifreeze

SCR vs. Cooled EGR

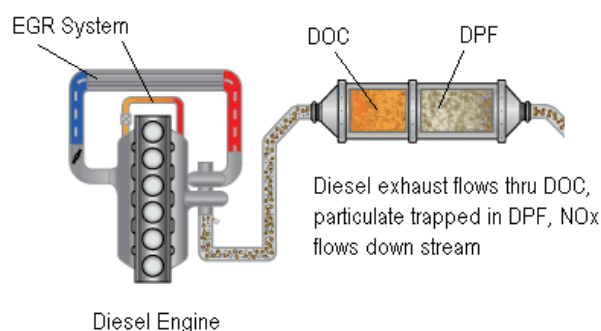
EGR – Exhaust Gas Recirculation

EGR stands for Exhaust Gas Recirculation. The equipment returns part of the exhaust to the engine and decreases the maximum temperature of air-fuel burning mixture to lower the quantity of NO_x. Since diesels always operate with excess air, they benefit from EGR rates as high as 50% in controlling NO_x emissions. When used with particulate matter (PM) reducing products, like highly efficient fuel injection or NO_x reducing intercoolers, it shows more effects.



EGR is placed between the exhaust and the intake of the engine and the purpose of the EGR is to return low-temperature exhaust to the engine. However, adding EGR to a diesel engine reduces the specific heat ratio of the combustion gases in the power stroke. This reduces the amount of power that can be extracted by the piston. EGR also tends to reduce the amount of fuel burned in the power stroke. This is evident by the increase in particulate emissions that corresponds to an increase in EGR. Particulate matter (mainly carbon) that is not burned in the power stroke is wasted energy and an environmental hazardous substance.

Most of the older EGR systems use a vacuum-regulated EGR valve, while newer vehicles tend to have an electronic EGR valve to control exhaust gas recirculation. When the engine is idling, the EGR valve is closed and there is no EGR flow into the manifold. The EGR valve remains closed until the engine is warm and is operating under load. As the load increases and combustion temperatures start to rise, the EGR valve opens and starts to leak exhaust back into the intake manifold. This has a quenching effect that lowers combustion temperatures and reduces the formation of NO_x.



EGR system with DOC & DPF

In addition to EGR, other methods may also be used to minimize NO_x. From engine development, these include increasing camshaft valve overlap, redesigning the intake and combustion chamber, and modifying ignition advance curves. If the EGR system is rendered inoperative because it was disconnected or tampered with, the cooling effect that was formerly provided by the EGR system will be lost. Without EGR, the engine will often knock and ping (detonate) when accelerating or lugging the engine. This can cause engine damage over time.

There are two emission / after-treatment systems that could meet the EPA 2010 emission standards – SCR after-treatment and cooled EGR. The first is SCR, the process reduces the output of nitrogen oxides by adding an Ammonia based solution to the exhaust stream with the high temperature triggering chemical reaction that changes nitrogen oxides to harmless byproducts. The second is Cooled EGR. In this process part of the engine exhaust is re-circulated into the engine air intake and mixes with fresh air, thus lowers the amount of oxygen in the combustion chamber, which means a lower nitrogen oxide output. The exhaust can then be cooled to reduce emissions even further. Both engines can reduce emissions by up to 90%. The differences between them come down to the investment cost.

- **SCR** does not require new engine configuration or a massive engine re-design, it uses a smaller and lighter engine, It requires an added tank for urea, but improves both thermal efficiency and fuel economy. Major considerations will include refilling urea. If it runs out, there will be a 40% reduction in torque output. The cost effectiveness of this application rests on the price stability of the urea solution.
- **Cooled EGR** may require a larger and heavier engine, but has no additive or tank costs and the user wouldn't need to replenish urea to keep the system from powering down. The engine would require a larger radiator and fan to lower heat generated and its fuel cost could be equal or higher than that of SCR.
- **SCR's major advantage** is its ability to deliver excellent fuel efficiency, especially when it's compared to the engines that using higher rates of exhaust gas recirculation (EGR) for NOx control. By controlling NOx emissions in the exhaust through SCR, instead of in the combustion process through EGR, diesel engines can be tuned for optimum fuel efficiency - a critical concern with the high prices for diesel fuel.
- **SCR** is using lower rates of EGR also results in lower heat rejection, and there is no need for massive coolers which is made from exotic metals for an efficient cooling system. Furthermore, SCR enables greater power densities, which means a smaller displacement engine can deliver the horsepower which otherwise would demand a larger, heavier engine.

While Selective Catalytic Reduction (SCR) is a new system for North American trucks, it is not a new technology. SCR is a reliable and proven technology, and is now the dominant emissions reduction technology for heavy-duty trucks in Europe - in fact, there are nearly 500,000 SCR trucks in operation throughout Europe today. In addition, SCR has been used for several decades in marine and large stationary diesel engines.

SCR is an after-treatment technology that requires the addition of DEF approximately every other diesel fill-up. The SCR system itself requires very little maintenance and no driver action while the truck is operating. Also, the alternative solid SCR technology provides the option of minimizing large heated storage tank of urea solution for the packaging and cost concerns.

However, in 2004, Maxxforce diesel started strategic approach in advanced cooled EGR system to eliminate NOx in cylinder through four key improvements.

- Increased fuel injection pressure and EGR rate, taking advantage of high structural strength durable block and head design to achieve in cylinder emission reduction.
- Advanced turbocharger providing the refinement of air management.
- A proprietary combustion bowl refinement.
- Advanced new ECU calibration strategies.

Maxxforce diesel was able to achieve 2010 EPA emission requirement without SCR application, even though the company is using the emission credit to achieve the requirement, and it still could be a big advantage when it comes to 2014 emission.