Status Report on Diesel NOx Adsorbers

Tim Johnson

October 2001

Regulatory requirements are force NOx emission control technology

- Unlike for filters, in which green marketing is key, US diesel regulations are driving NOx technology
- US Tier 2 caps larger vehicle LDD NOx at 0.6 g/mile (60% tightening), and phase-in to 0.2 gpm begins (MY04-07)
  - to offset each truck at 0.6 gpm, three trucks at 0.07 gpm will be needed
- In MY08, 0.2 gpm cap and phase-in to 0.07 gpm avg.
  - nominally 90% NOx removal for LDD needed to hit average
- In 2007 HDD needs to hit 1.1 g/bhp-hr NOx
  - nominally 45% tightening from 2004
- In 2010, 0.2 g/bhp-hr will be needed
  - 90% tightening from 2004

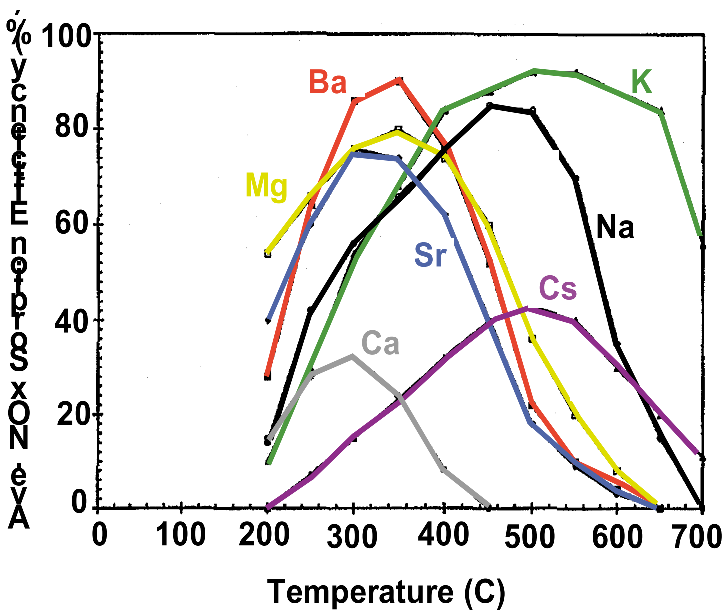
NOx adsorbers might offer the best efficiency/fuel penalty tradeoff

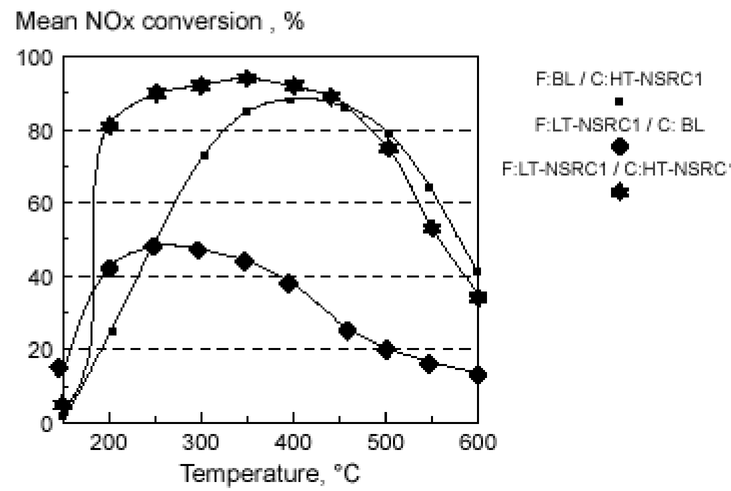
- SCR
  - five years of work in mobile applications; +/-15 years in stationary
  - 70-80% NOx removal efficiency
  - 3-5% effective fuel penalty
  - durability well-documented at 60-70% efficiency
- NOx traps
  - three years of work in diesel; two years on vehicle
  - 70-95+% efficiency
  - 2-5% fuel penalties
  - durability issues need to be addressed
    - aging
    - sulfur

NOx Adsorber Performance

NOx adsorbers can achieve >80% efficiency at temperatures from 200 to 500C

Steady State Testing





A study of differentiation with relevant low and high temperature NSR catalyst amounts. Hydrothermally aged (700°C/20h) samples by laboratory simulation in lean-rich mixture 1 (60s/5s, SV over flat foil 75.000 h^{-1} and over corrugated foil 50.000 h^{-1}).

Depending on formulation, NOx adsorber efficiencies in excess of 90% at temperatures up to 650C are possible. (from Ford)

Corrugated and flat portions of metal substrate are coated with HT and LT NOx adsorber materials and tested in synthetic gas

Kemira SAE 2001-01-3665

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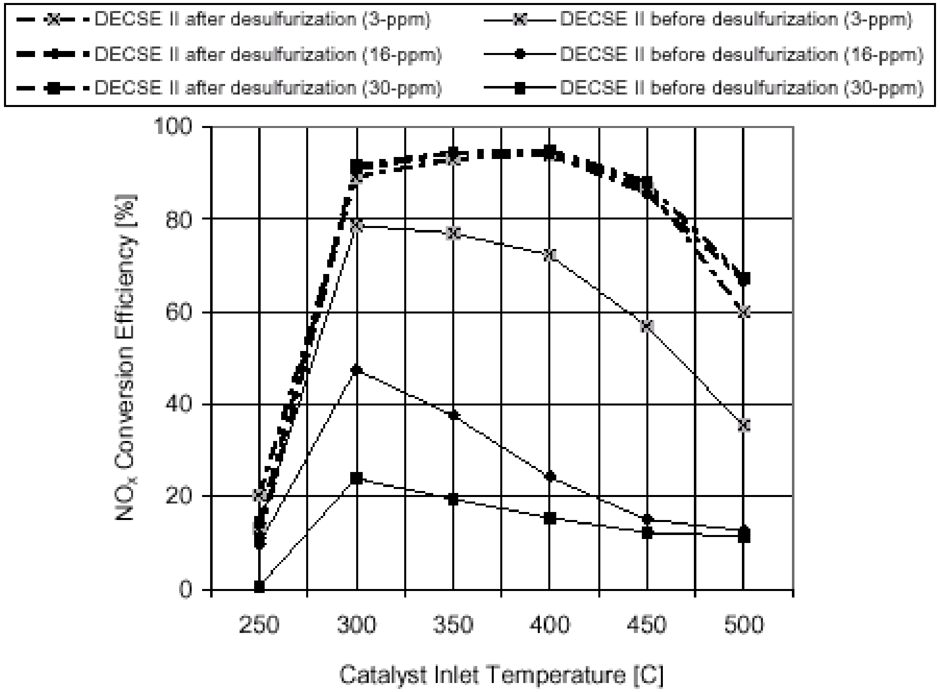
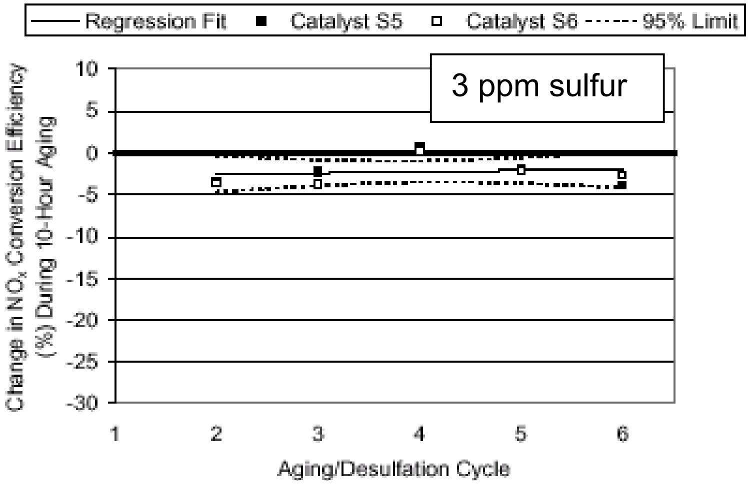
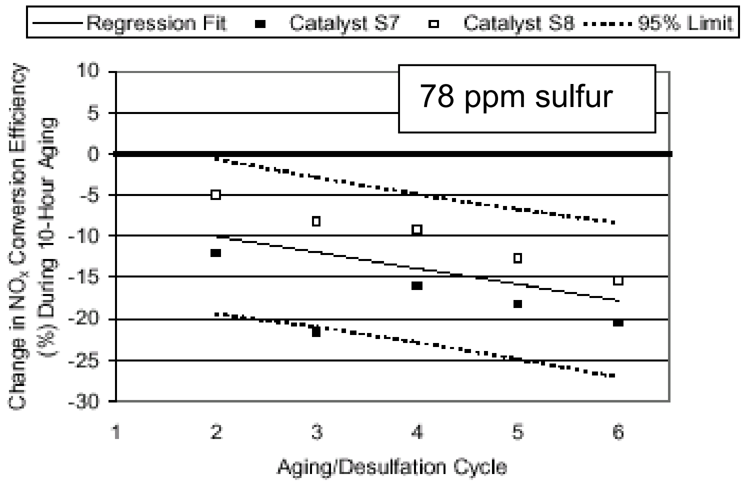
NOx traps can achieve 95% efficiency in steady state HDE tests, but have sulfur sensitivity







NOx trap efficiency is high, but decreases with sulfur exposure; recovery is demonstrated

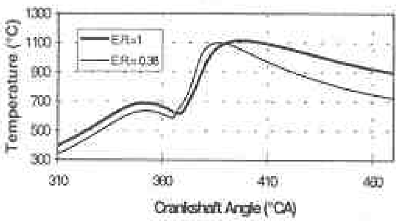
DOE DECSE report, Phase 2 NOx Adsorbers, 10/00

Exposure to 3 ppm sulfur does not degrade NOx trap after desulfation; 78 ppm sulfur does

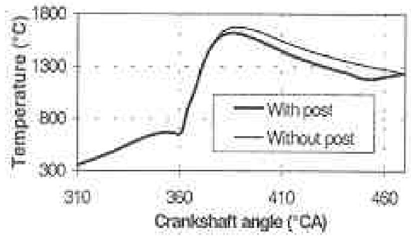
Using NOx traps to hit Euro 5 certification level, 3.8% fuel penalty is measured; 2.6% to hit Euro 4;

1.6 l single cylinder test engine

EGR effect

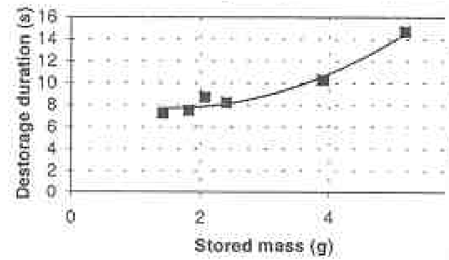


Post-injection effect

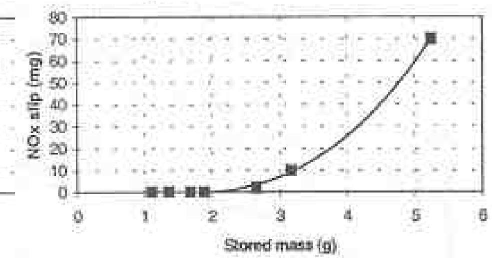


With EGR, rich post injection has minimal effects on peak cylinder temperatures. Engine durability expected to be uneffected.

Regen time vs. NOx capacity

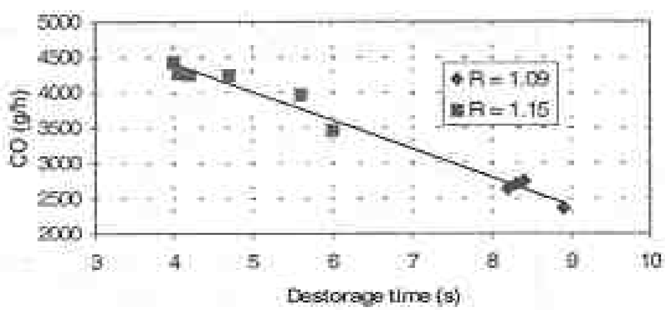


NOx emission vs. NOx capacity

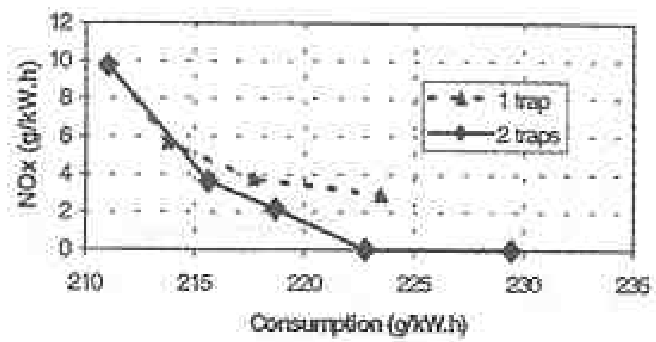


Because regeneration time and regeneration NOx emissions increase disproportionate to stored NOx , maximum of 3 g of NOx capacity was chosen. Equiv Ratio = 1.09

Influence of CO on regeneration



Regeneration time is most dependent on CO content. Derived under a variety of fuel injection timings and quantity.



Two parallel traps (SVR = 3.1) results in lower fuel consumption. Increased regeneration time is offset by higher NOx efficiency.

RVI and IFP Vienna Motor Symposium 4/01

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Increased cell density and substrate length aid in efficiency of NOx adsorbers.

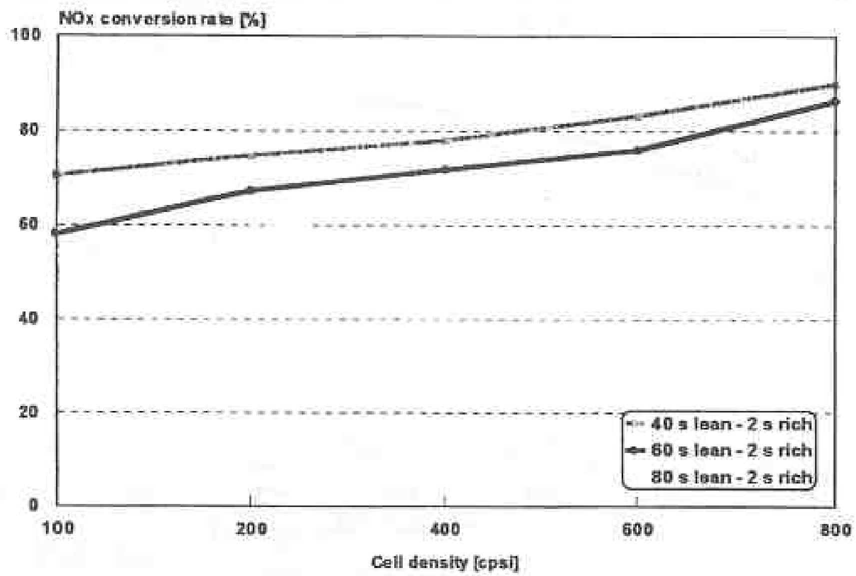

Fig. 7: NO_x conversion dependent on cell density

Catalyst dimensions: Ø 17 × 24 mm
Test conditions:
Gas inlet temperature = 300 °C
Space velocity (lean and rich) = 45000 h^{-1}
NO concentration in front of catalyst = 750 vppm

The greater GSA of high cell density substrates helps NOx efficiency. 800 csi requires half as much rich period to regenerate as the 400 csi.

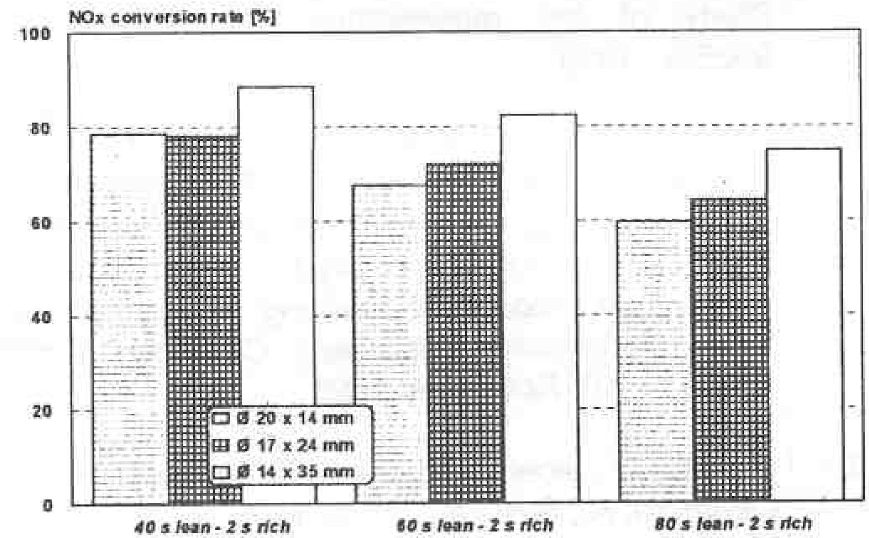

Fig. 9: NO_x conversion dependent on catalyst design

Catalyst dimensions: 400 cpsi
Test conditions:
Gas inlet temperature = 300 °C
Space velocity (lean and rich) = 45000 h^{-1}
NO concentration in front of catalyst = 750 vppm

For fixed volume and space velocity, longer substrates regenerate easier and have higher efficiency.

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Emitec SAE 2000-01-0504

The Sulfur Issue

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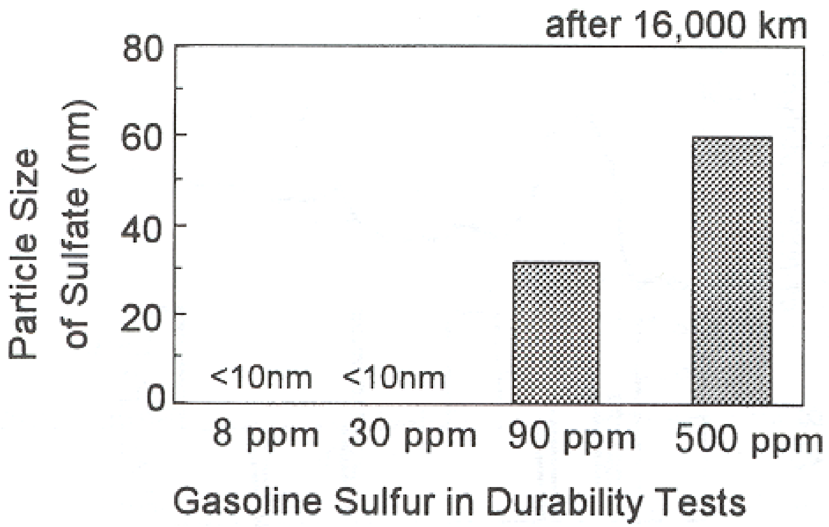
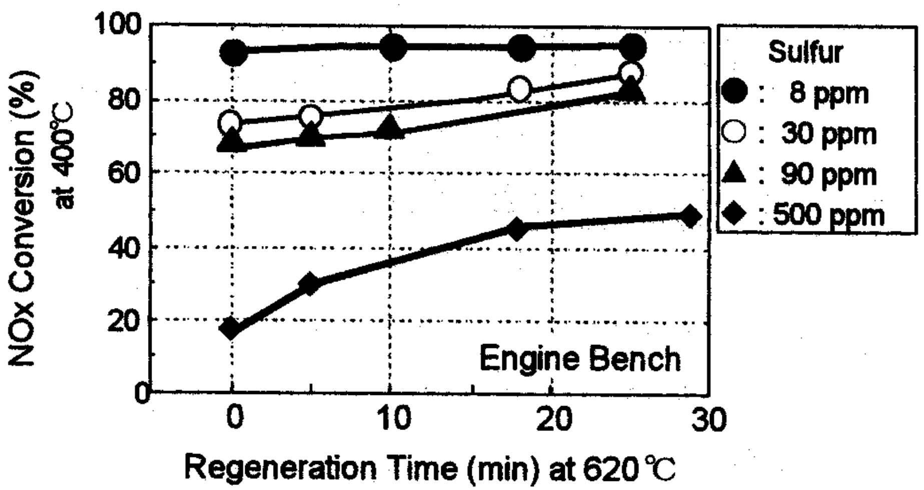
Discovering Beyond Imagination

In NOx traps, the size of the $BaSO_4$ grains depends on the sulfur level in the fuel (gasoline here)





Sulfate grain size increases as the fuel sulfur level increases. The above data are for long exposures (16,000 km) and the effect was not seen at 30 ppm sulfur. The XRD methods used here for measuring grain size are crude. Experimental results may be more discerning.

It takes longer to desulfate if the fuel sulfur is higher. Note that there isn't much different between 30 and 90 ppm, but there is a big difference between 8 and 30 ppm. These effects might be explained by the sulfate grain size effect.

Toyota SAE 1999-01-3501

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Incremental improvements to current NOx traps enhance sulfur tolerance and reduce NOx emissions by 70% in gasoline applications

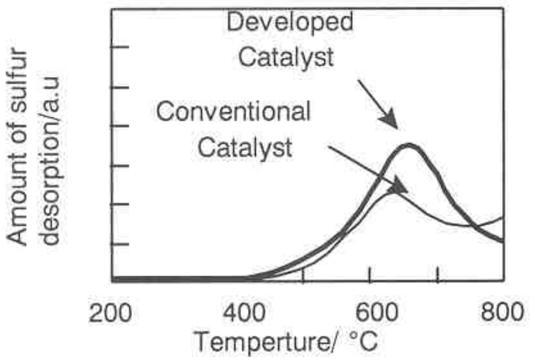

Fig.14. Profiles of sulfur under rich gas flow after durability test.

Sample:35cm[3] monolthic catalyst
Test condition: A/F=12,200-800°C, in rich gas, analyzed by SO_X-analyzer

200 ppm S, 2.0 liter engine, 1.3 liter NSR catalyst. New catalyst desorbs SO_2 faster and at lower T.

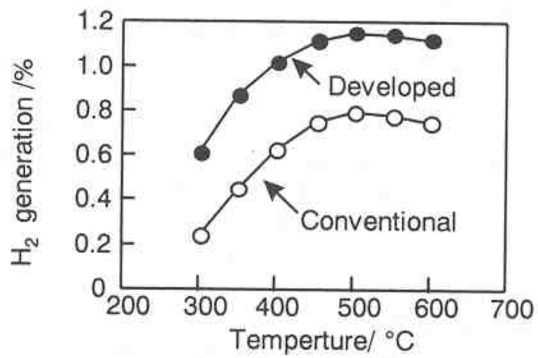

Fig.13. Amount of H_2 generated by steam-reforming reaction (additive effect).

Sample:Pellet catalyst (Rh/ZrO_2)
Aging condition: 600°C, 10h in air
Test condition:
A/F=12, 300-600°C,H_2 was analyzed by GC
W/F=3.3×10^{-3} $g\cdot cm^{-3}\cdot s$

Bench work. New Rh/ZrO_2 catalyst generates 50% more H_2 for SO_2 desorption.

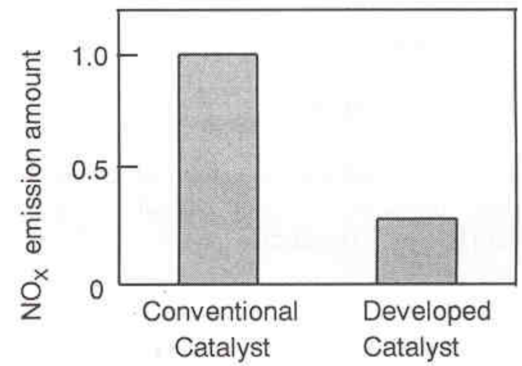

Fig.16. Relative NO_X emission amount after durability test.

Japanese 10-15 mode; 80,000km. New catalyst drops NOx emission to 1/3 of current catalyst; 200 ppm S.

New highly dispersed TiO_2 suppresses SO_2 adsorption and aids in desorption.

Alkali-earth additions to Rh/ZrO_2 catalyst stabilizes ZrO_2 without aging Rh, enhancing H_2 generation.

Toyota SAE 2000-01-1196

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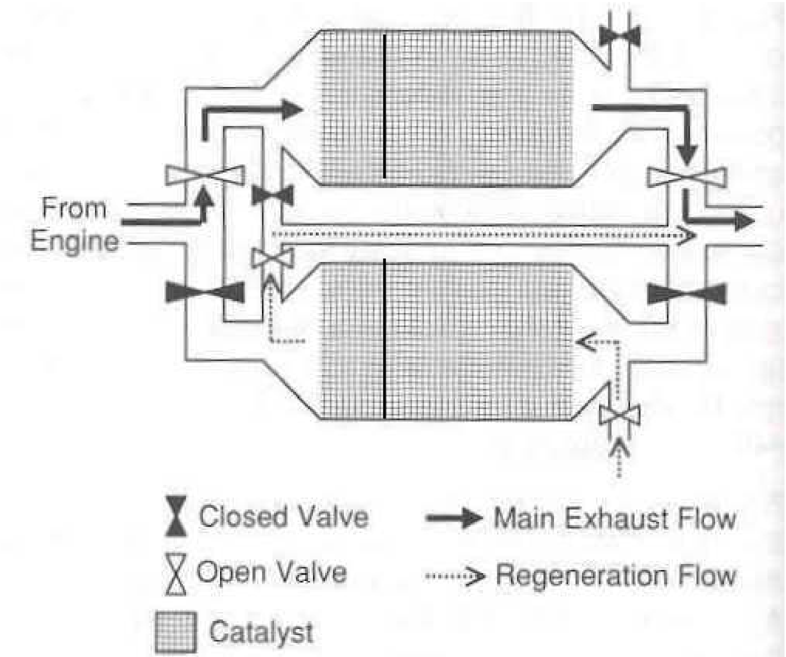
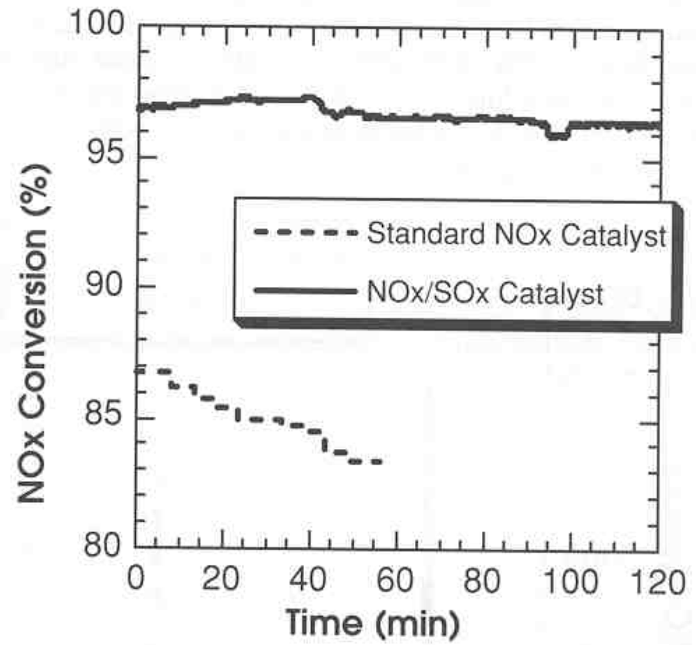
A SOx/NOx trap system is being developed and characterized.



SOx adsorber is in front of NOx adsorber. Flow shows one bank in regeneration mode. 3.9l turbo; 9.8l in each bank.

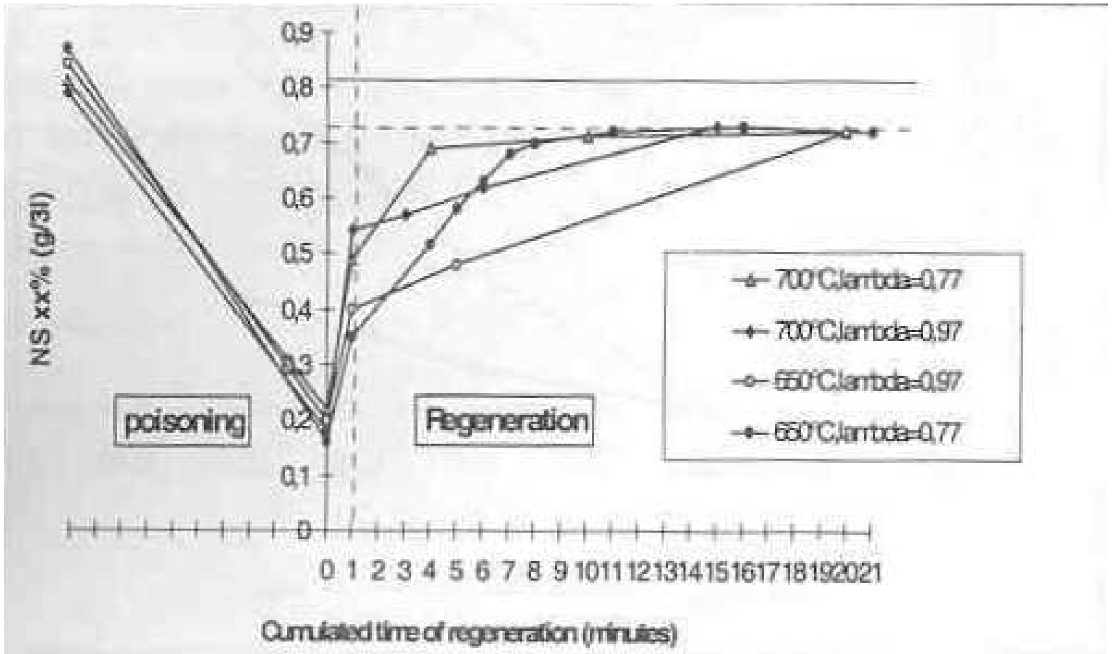


180°C exhaust T, 370 ppm S; no SO_2 out of system.

- **90-95% of SO2 removed at 175 to 500C**
- **sulfur is released as SO_2**
- **system is large and complex; possible COS emission issues (SAE 2000-01-1932)**

Goal Line Environmental
SAE 2000-01-1012

Desulfation is best accomplished using a staged temp:λ profile. At low ppm S, natural desulfation occurs.



Aged adsorber NOx capacity as a function of sulfur regeneration time and conditions.

1.) In early desulfation, high temperature drives recovery

2.) In later stage, λ drives recovery

3.) Full recovery not obtained in any condition.

- In separate work, reasonable desufation conditions are achieved in 125 hrs. of normal driving.
- This corresponds to a sulfur content of 10 ppm (no active desulfation needed for <10ppm sulfur).

Renault SAE 2000-01-1874

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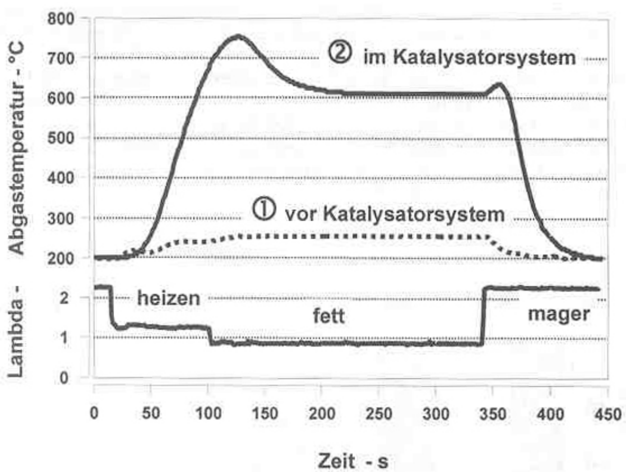
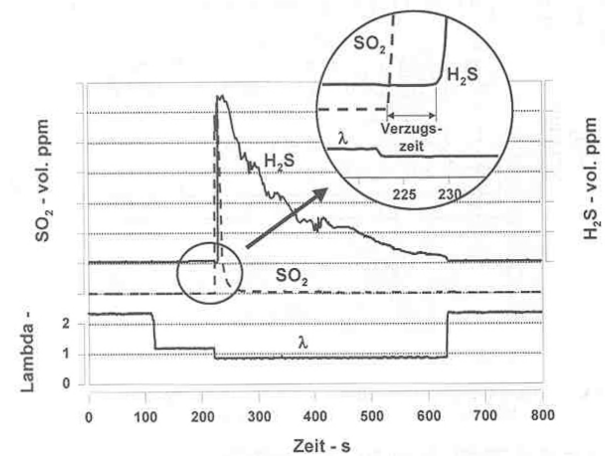
A cycled NOx trap desulfation strategy prevents H_2S formation

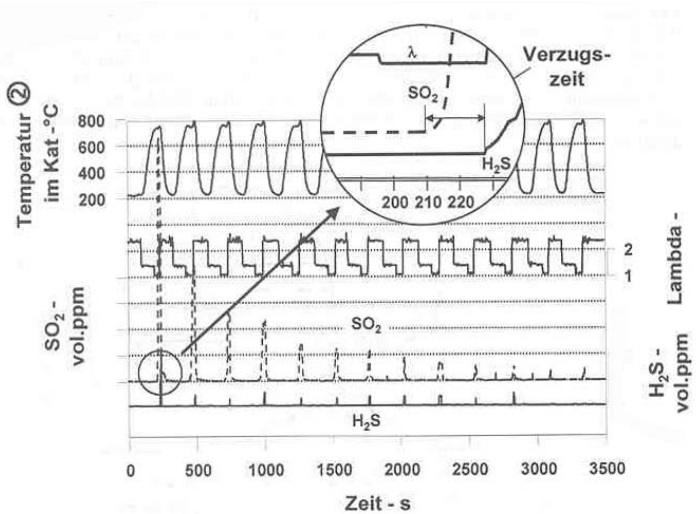


Stepped lean and rich modes are used to generate rich HT modes for NOx trap desulf. 50 km/hr.



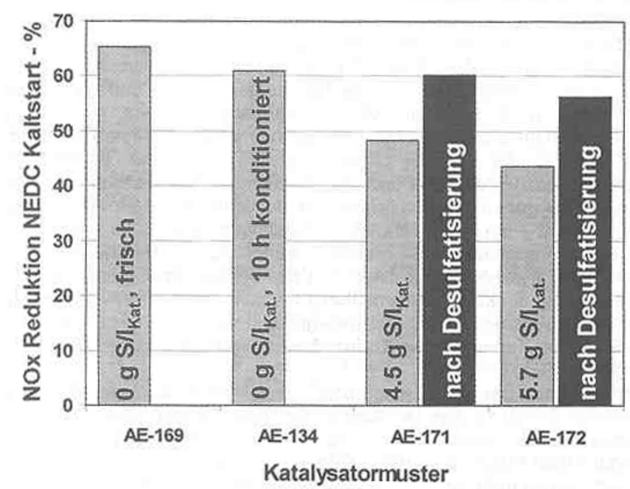
H_2S generation is a problem in rich conditions, but lags SO_2 formation by 8 sec.

- 2 l HSDI Peugeot
- 400 csi NOx trap and DOC
- 2.5 l each 3.2 g/l Pt



Cycled rich-lean modes prevents H_2S generation

One long desulfation mode compared to cycling at 2 different sulfur loads. With cycled desulfation, NOx performance is brought to original sulfur-free performance.



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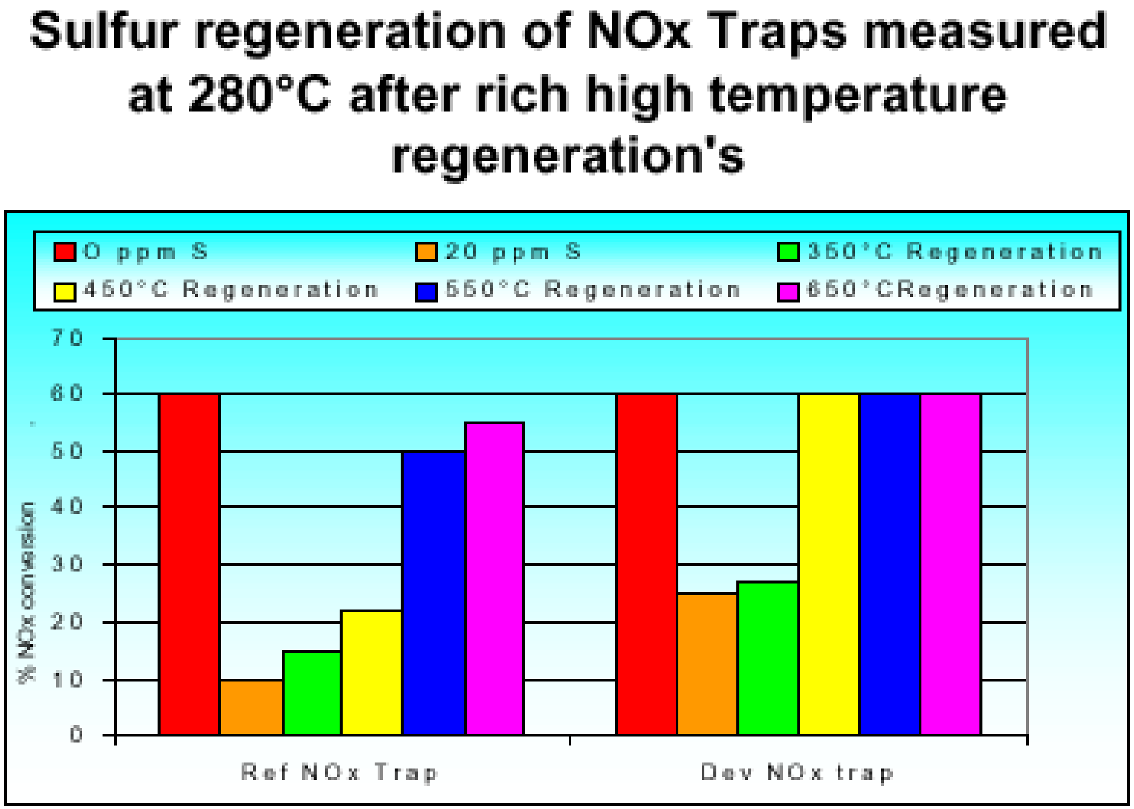
dmc[2], AVL Vienna Vienna Motor Symposium 4/01

NOx traps are in development that will desulfate at as low as 450C



The development NOx trap returns to original performance after desulfating at 450C

JMI AVECC conf. MECA.org

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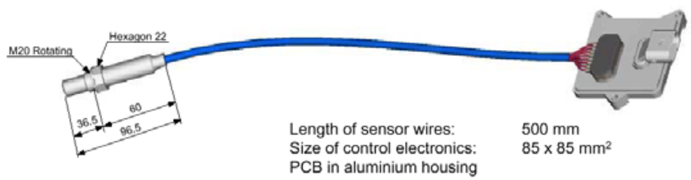
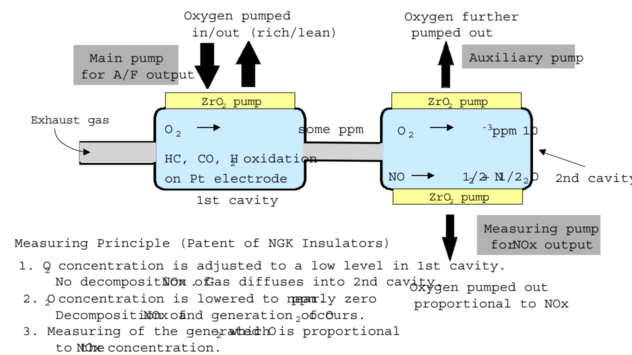
A NOx sensor with ± 5% reproducibility and excellent transient response is being developed for introduction in diesel applications in 2003

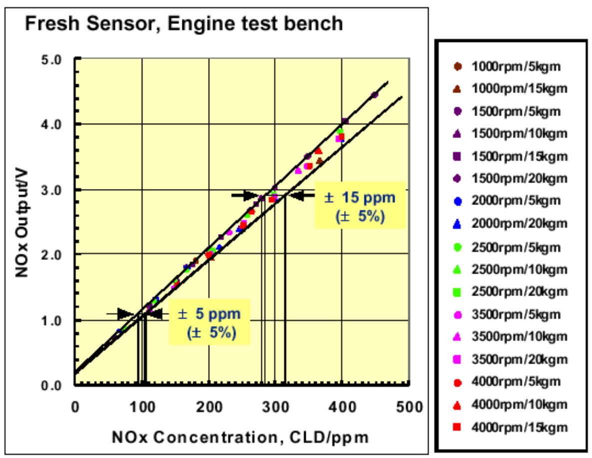
Layout of the sensor



Principle of operation



Accuracy



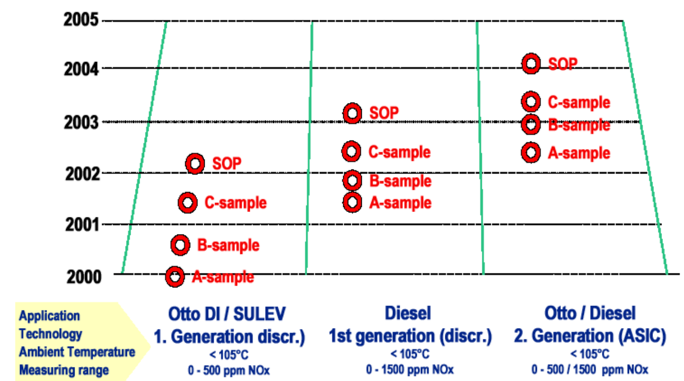
Diesel Engine:
2.5L Turbo-charged

Sensor position:
0.8m downstream of turbo

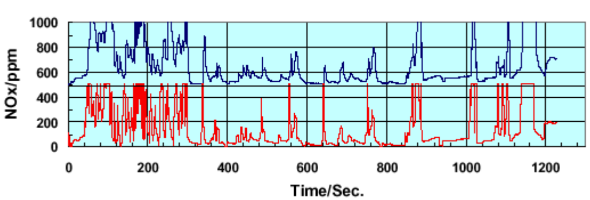
Gas temperature: 190 ~ 760 °C
O_2 concentration: 1.1 ~ 14.7%
NOx concentration: 50 ~ 450ppm

5th generation
NGK electronics

Commercial introduction timeline



Transient Response



CLD gas analyzer
(500ppm offset for clarity)

NGK NOx sensor

NGK and Siemens literature

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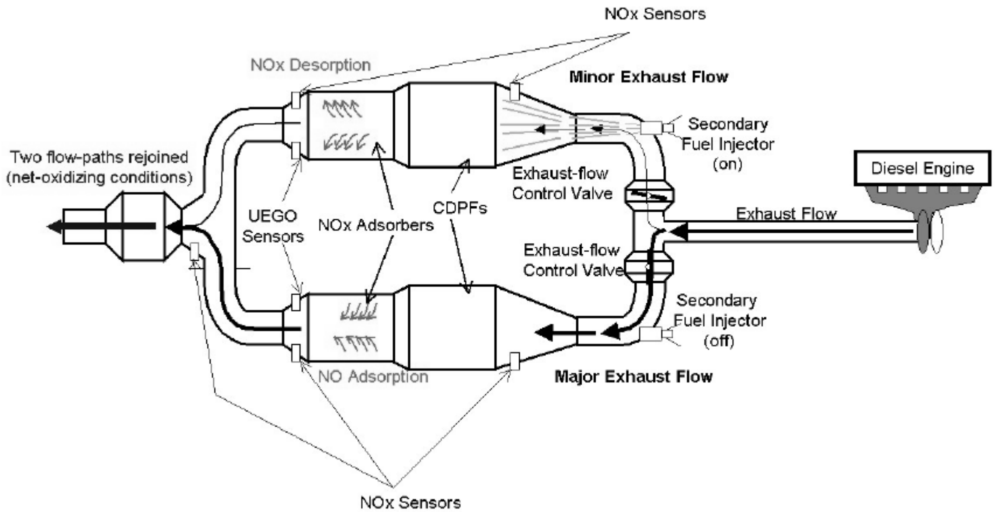
Integration with Filters

A 5.9 liter 1999 engine achieved US2010 requirements in transient testing



One leg is in restricted flow regeneration while other leg is adsorbing.

- 1999 5.9 l Cummins ISB w/ retrofit cooled EGR
- 19 l of DPF and 14 l of NOx adsorber on each leg
- NOx adsorber aged 10 hrs
- 3 ppm sulfur

Next Steps:

Reduce system to one leg
Test and implement desulfation cycle

(US EPA SAE 2001-01-3619)

HDDE Hot Start Transient

	baseline g/bhp-hr	test g/bhp-hr	Change %
NOx	2.67	0.13	-95%
HC	0.33	0.06	-82%
PM	0.29	>0.002	-99%
FC	--	--	+1.5%

In steady state testing, all points were within NTE limits, except for peak torque conditions (1.65X instead of required 1.5X). Engine modifications needed, as baseline was over “2004 NTE” limit at this mode.

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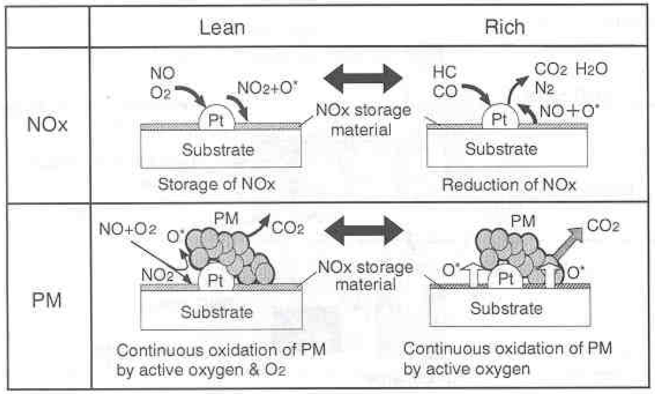
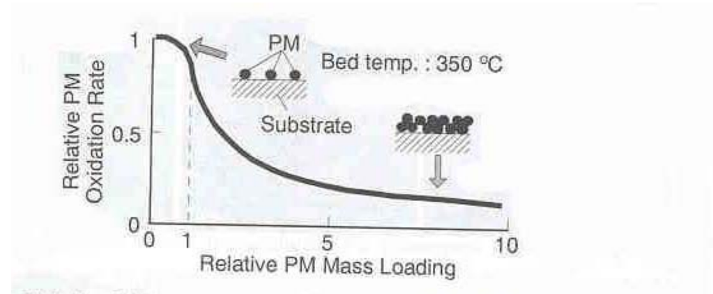
New integrated DPF / NOx trap is described; gets 90% reductions in PM and NOx



The principle of combination diesel particulate/NOx reduction system. PM is oxidized in both lean and rich conditions.

At a bed temperature of 350ºC, a maximum PM load rate of 3 g/l is tolerable before the catalyst blocks. Typical balance point temperature = 250ºC

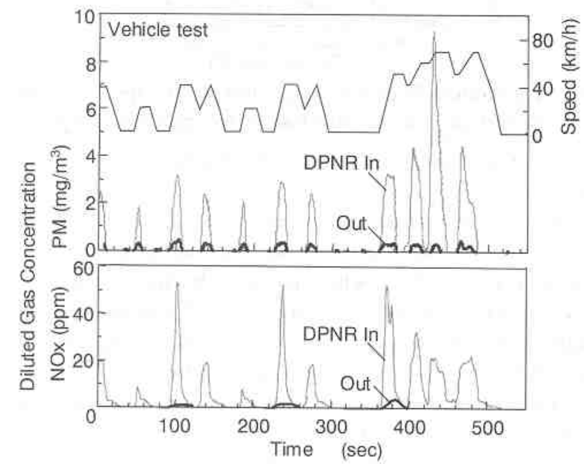


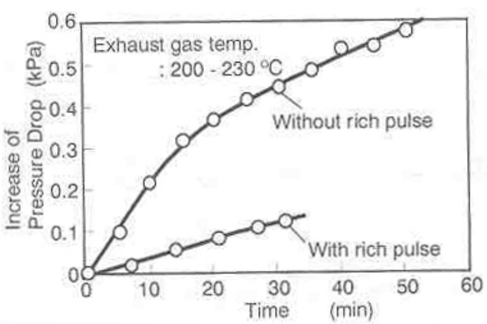
Relationship between the PM mass loading and the PM oxidation rate

$NO + 1/2\ O_2 = NO_2$

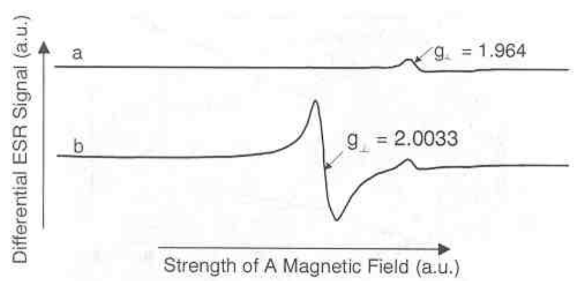
$BaO + 2NO_2 + 1/2\ O_2 = Ba(NO_3)_2$

"$1/2O_2$" is the "free oxygen", and is generated on the forward and reverse reactions





Periodic rich pulse causes PM to oxidize



Influence of air-fuel ratio modulation on ESR spectra in the DPNR catalyst : (a) under lean air-fuel ratio of steady state at 300 °C and (b) under lean air-fuel ratio of 5 sec after rich air-fuel ratio at 300 °C.

DPNR system drops NOx and PM by 90%

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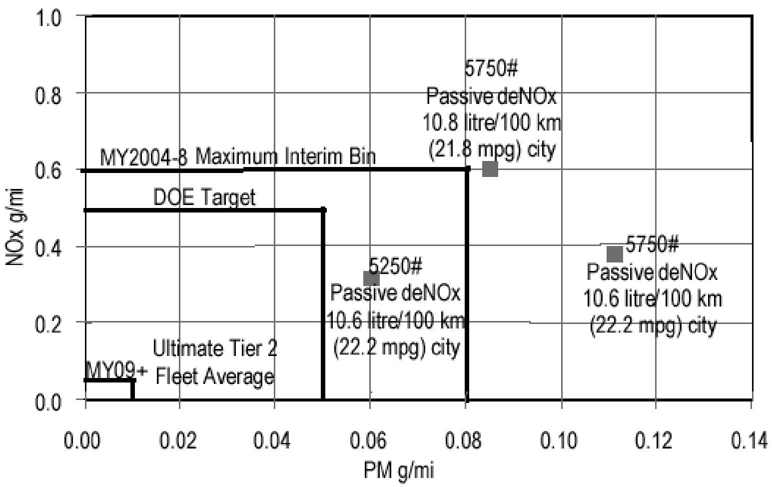
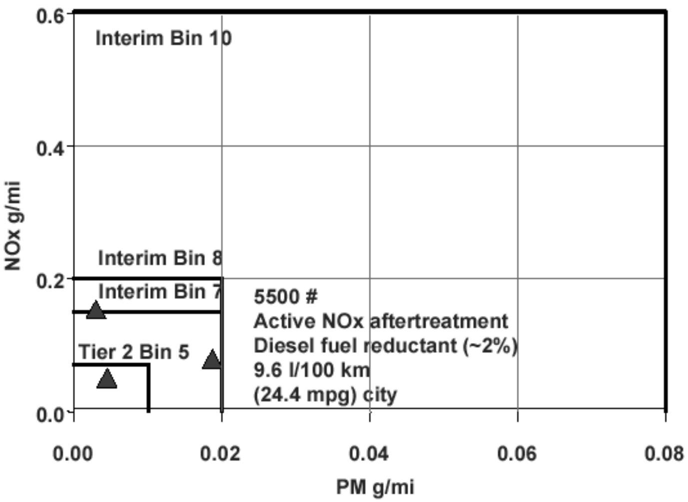
Toyota Vienna Motor Symposium 4/01

A 1997 4.2 liter SUV engine achieved Bin 5-7 emissions levels with retrofit emission control

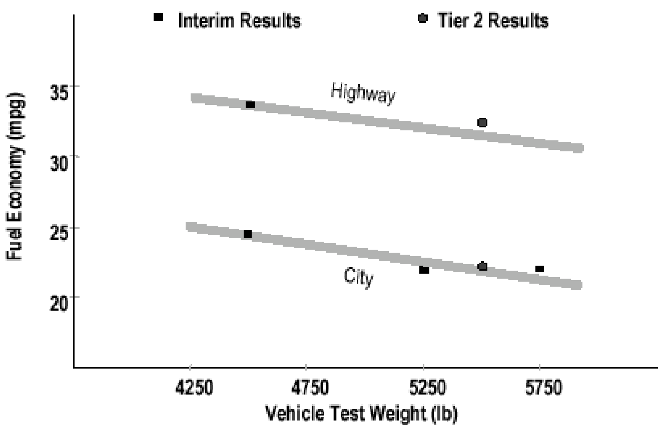




Stock 1997 Euro 4.2 liter engine was dropped from 1.8 gpm NOx and 0.3 gpm PM to hit Bin 10 by adding cooled EGR, VGT, advanced fuel system, and 10% deNOx cat.

Bin 5 was hit (once out of three) by adding a DPF and NOx trap. Diesel fuel reductant. No FTP cold start. Engine dyno simulation using ULSD fuel. System size not disclosed.

Cummins SAE 2001-01-2065



59% better fuel economy observed vs. similar gasoline engine on SUV (within 2%). Bin 10 and Bin 5 configurations had similar results.

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Summary Points

- NOx adsorbers are emerging as a viable LDD NOx solution in Europe, Japan, and the US
- To hit US2007, 50-60% NOx efficiency is needed. NOx adsorbers can hit this, but can they hit the 90%+ needed in 2010. SCR has less uncertainty.
- Some US HDD manufacturers are seriously pursuing NOx adsorbers. All are taking parallel paths.
- NOx adsorber issues:
  - desulfation and durability
  - seems easier to integrate with filters
  - shows much potential

Thank you for listening!

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