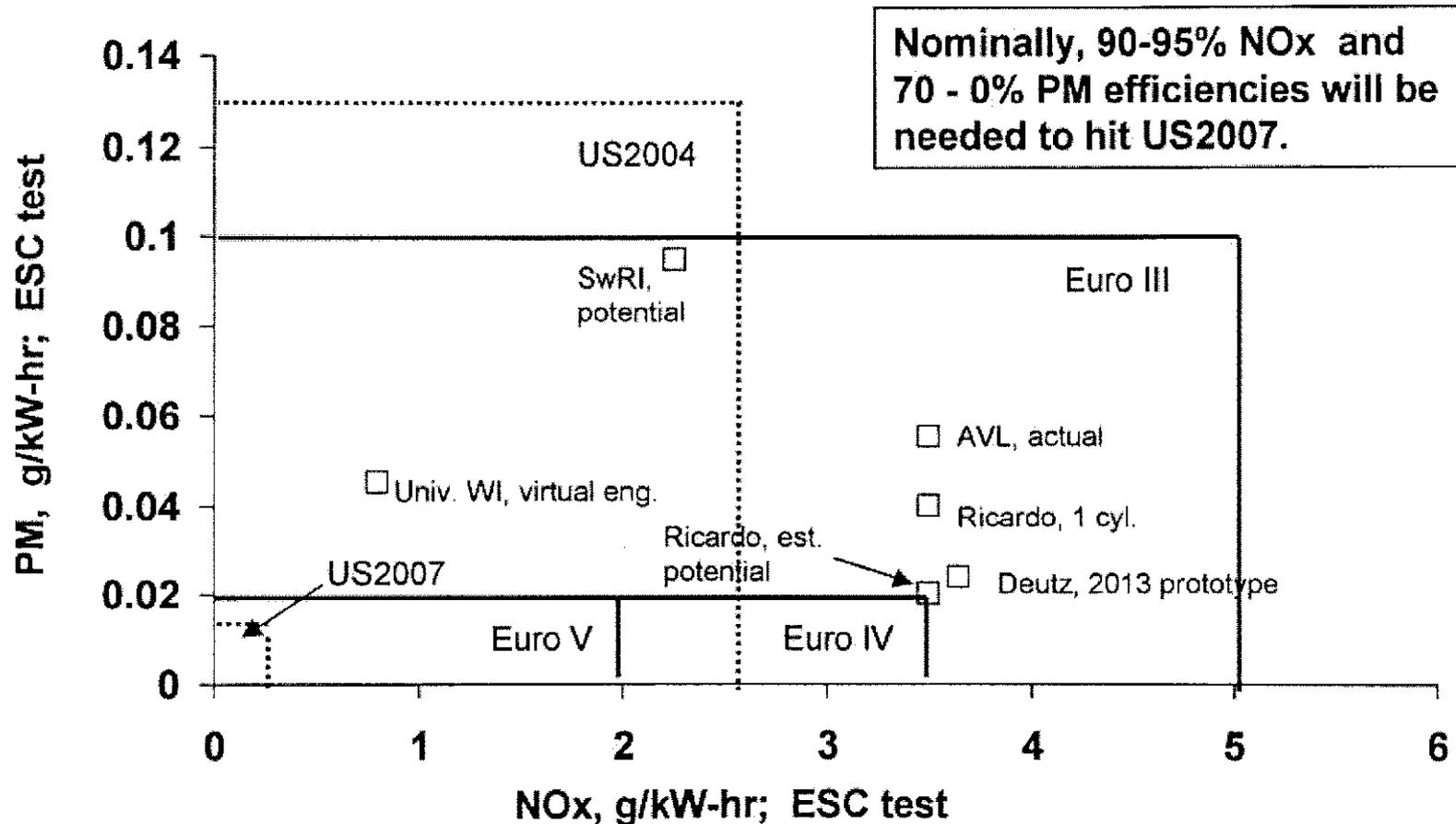

Review - HDD Regulations and Emission Control Systems

DEER Conference
San Diego
August 20-24, 2000

Timothy V. Johnson
Corning Incorporated

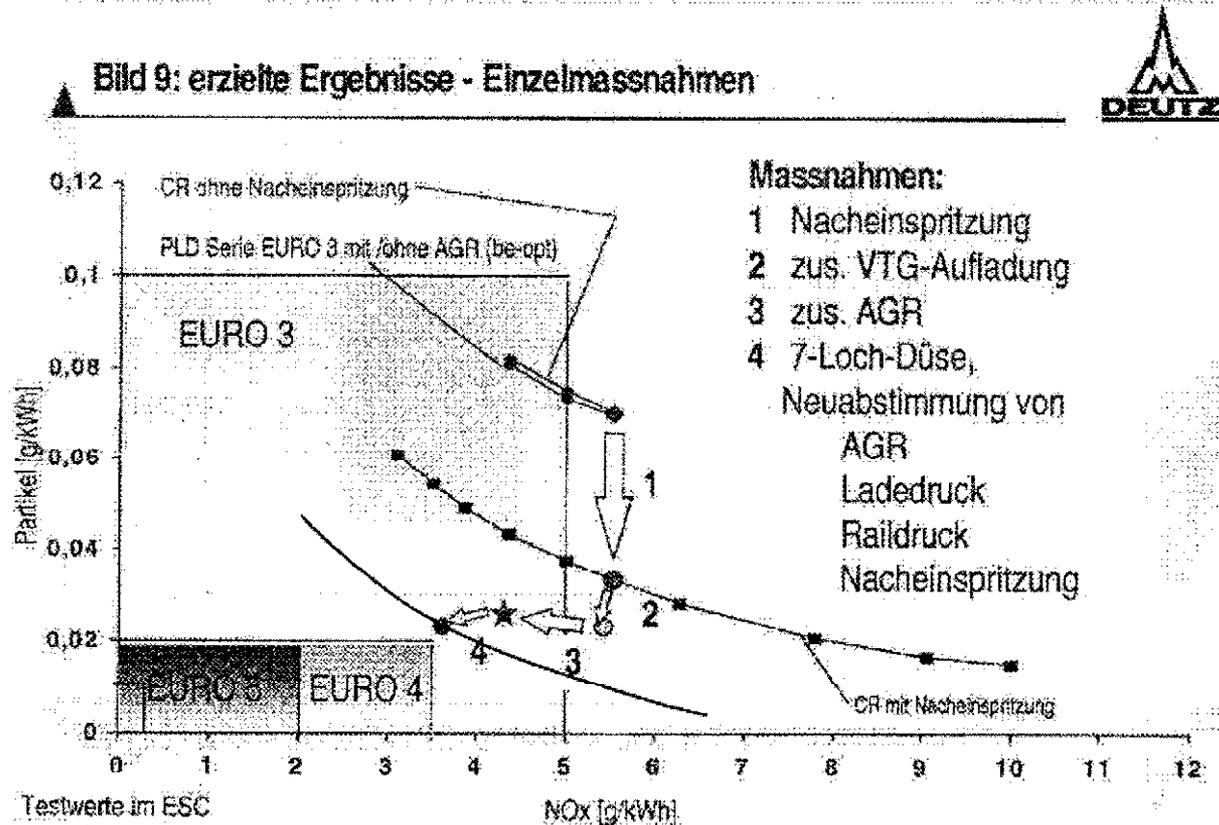
Regulatory and Engine Perspectives

Where will HDD engines be in 5 to 7 years?



- Prototype Engines with cooled EGR, combustion optimization, fully flexible fuel injection, staged turbocharging, multi-hole injectors, high pressure injection.

Improvements to the prototype Deutz 2013 engine bring it close to Euro IV without traditional emission control equipment



With the Deutz prototype engine, 88 - 96% NOx and 73 - 0% PM efficiency will be needed to hit US2007, depending on where on the PM/NOx tradeoff curve the engine is operating (curve added for point 4).

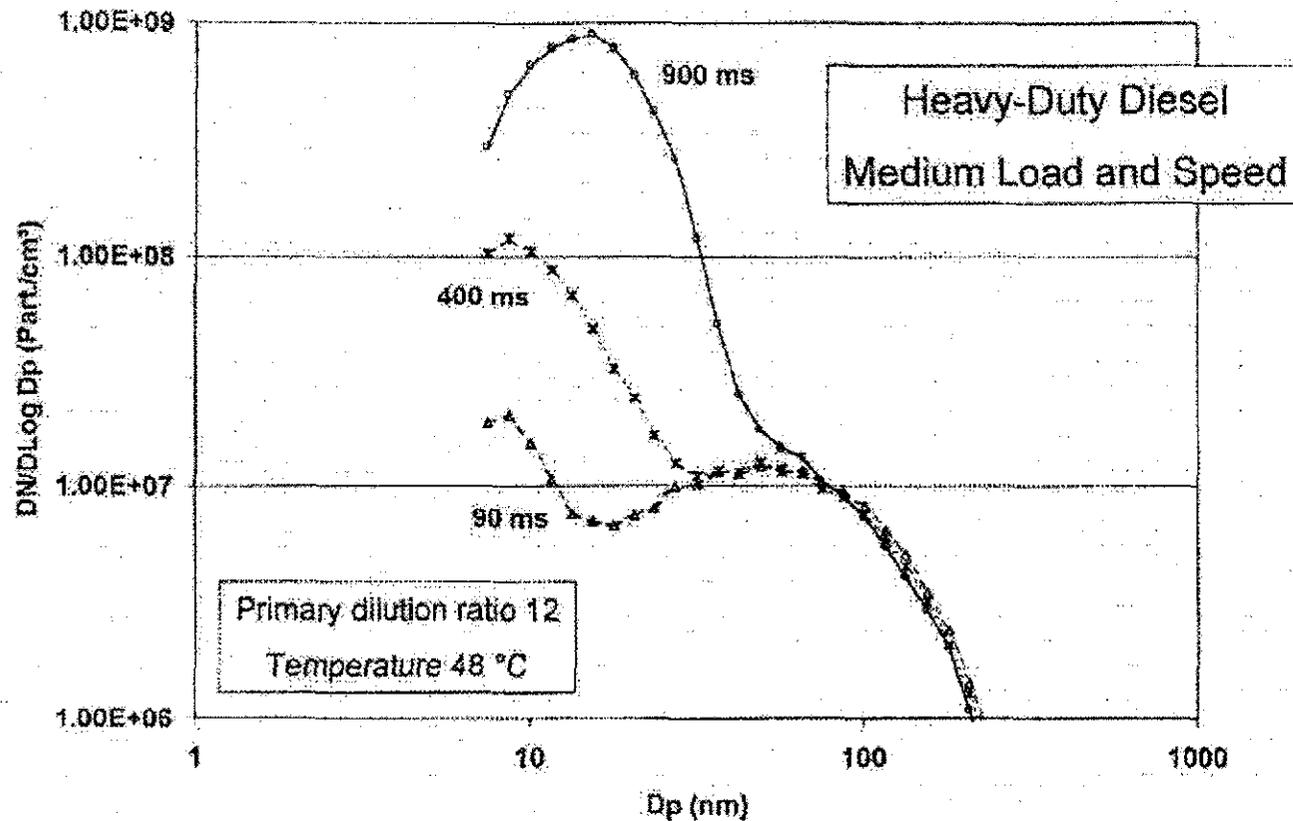
Deutz, Vienna Motor Symposium, May 2000

What is the prognosis for obtaining 70% PM efficiency and 90% NOx efficiency?

- **Leading PM technologies**
 - continuous regenerating filter systems: 80 -95%
 - catalyzed soot filters (including fuel-borne catalysts): 80 - 95%
 - efficiency depends on how “dry” the particulates are
- **Leading NOx technologies**
 - SCR: 70 to 90%
 - NOx adsorbers: 50 to 95%
 - non-thermal plasma methods: 60%

Diesel Particulate Filters

**Nano-particles are aerosols of sulfuric acid and hydrocarbons.
Concentrations depend on time, temperature, and dilution ratio.**



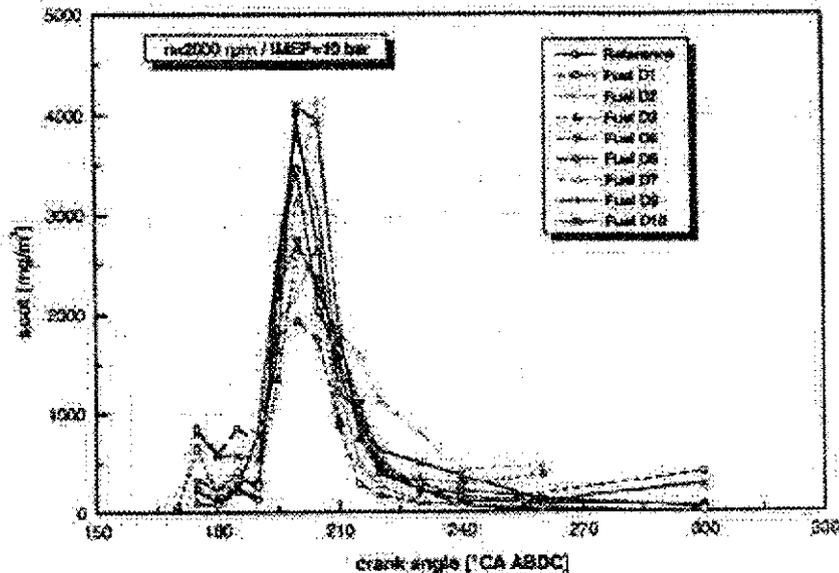
Kittelson, University of
MN, EPA MSTRS,
July 1999

Current theory is that nano-particles precipitate as sulfuric acid, and grow with HC adsorption. Ultra-low sulfur fuel and oxidation catalysts will minimize or even eliminate them. Filters will take out carbon soot.

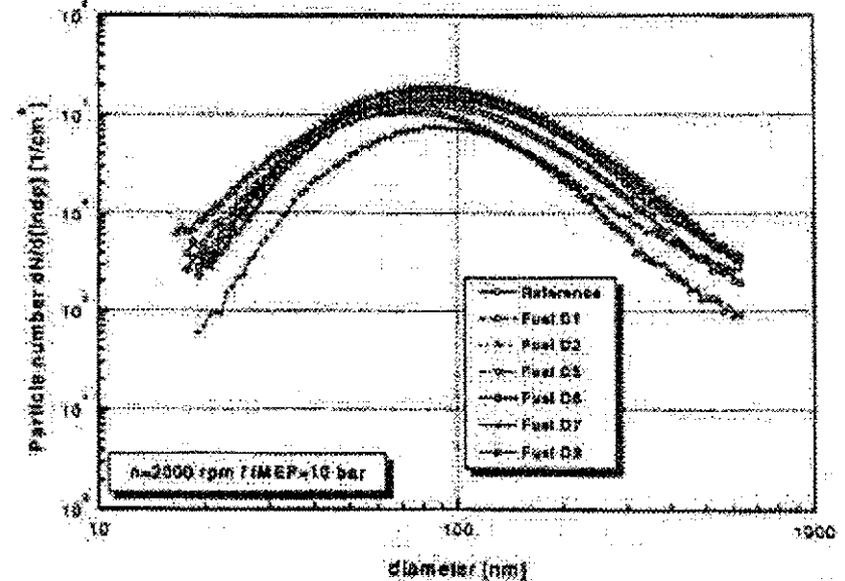
CORNING
Discovering Beyond Imagination

Carbon soot is formed in combustion and changes little with fuel, some burning of soot in exhaust pipe.

Heated lines, high dilution ratio; analyses are for carbon soot only.



Soot mass increases with PAH content in fuel; D1 = 1% PAH, D10 = 14% PAH. Soot generated at same crank angle.



Particle size distribution of soot in cylinder is independent of fuel.

FEV SAE 2000-01-1999

Filters can clean exhaust to ambient air quality levels, but fuel sulfur levels can have a big impact

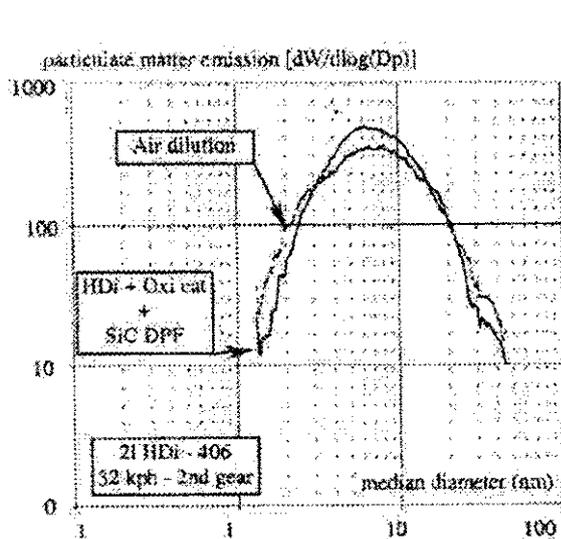
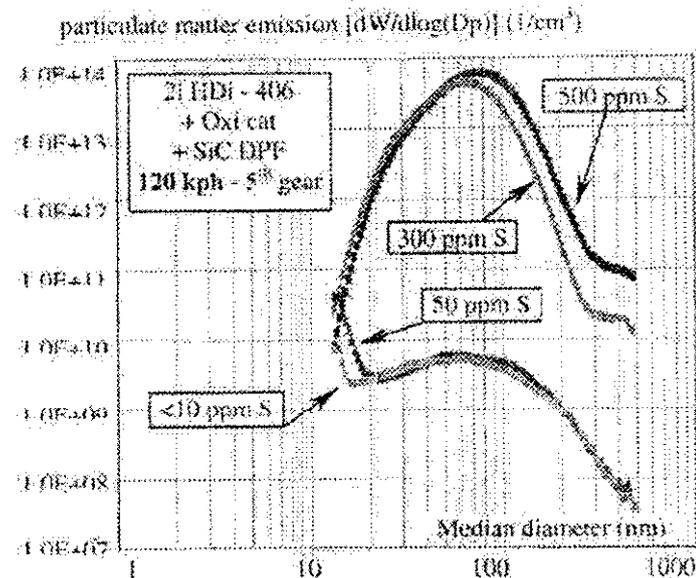


Figure 17. Comparison of SIC filter particulate matter emission with air dilution on a 406 - 21 HDi (32kph)

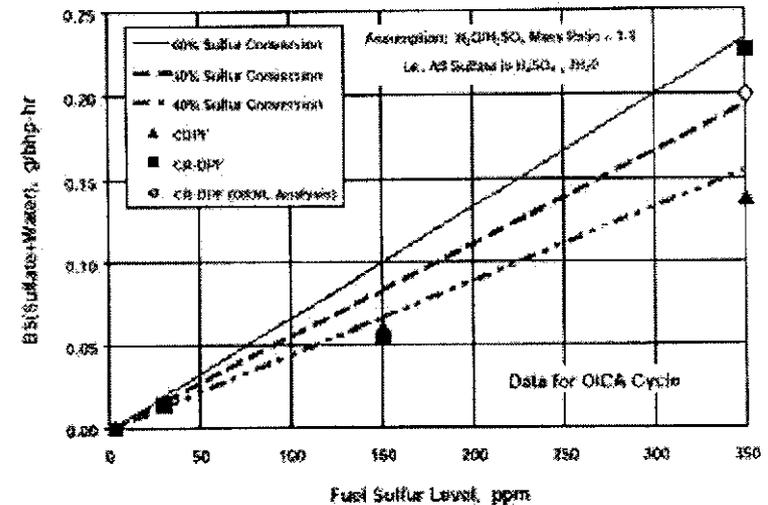
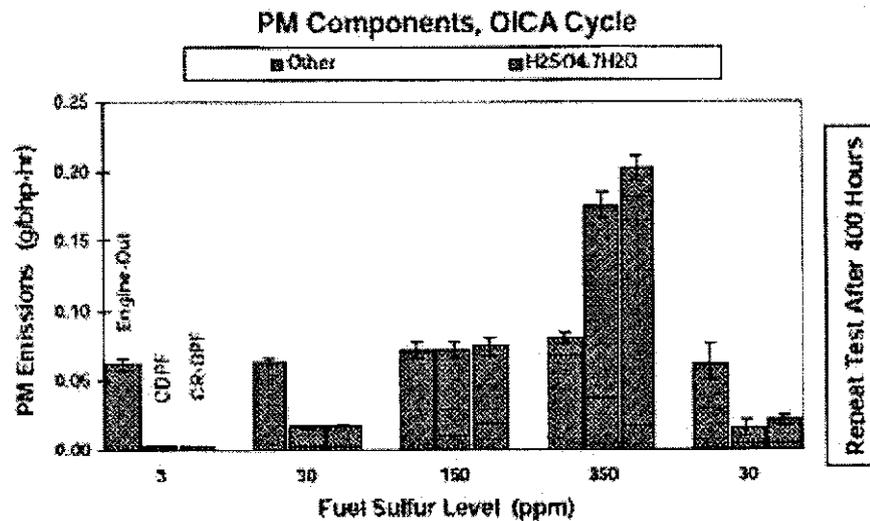
The filters clean the exhaust to ambient air levels.



High fuel sulfur results in 3.5 orders of magnitude more fine particulates.

Recent studies (CEC/CRC June 2000, Paris) have shown that particles <70 nm are quite variable and are mainly comprised of sulfuric acid.

Filters are very efficient if the fuel sulfur level is low



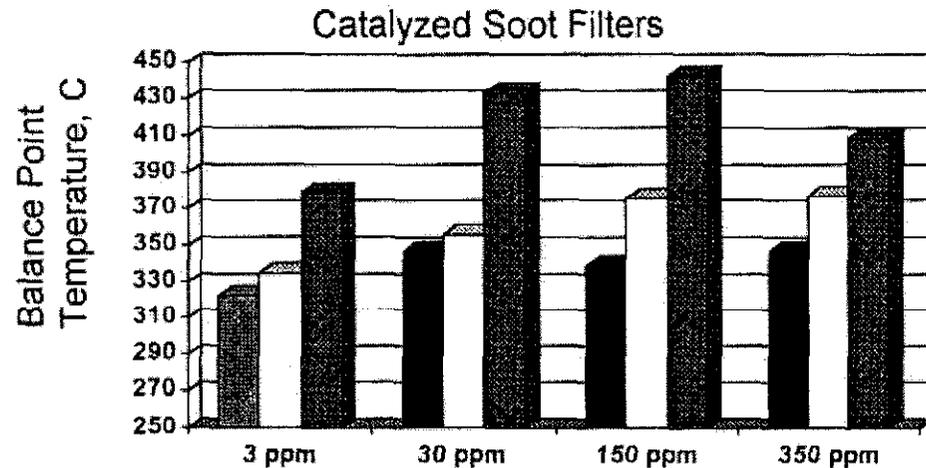
Effect of fuel sulfur on calculated and observed sulfate emissions

At >3 ppm sulfur, filtered exhaust PM is made up of mainly sulfuric acid species.

With reasonable assumptions on sulfate formation, <15 ppm sulfur is needed to hit the 0.010g/bhp-hr proposed PM regulation

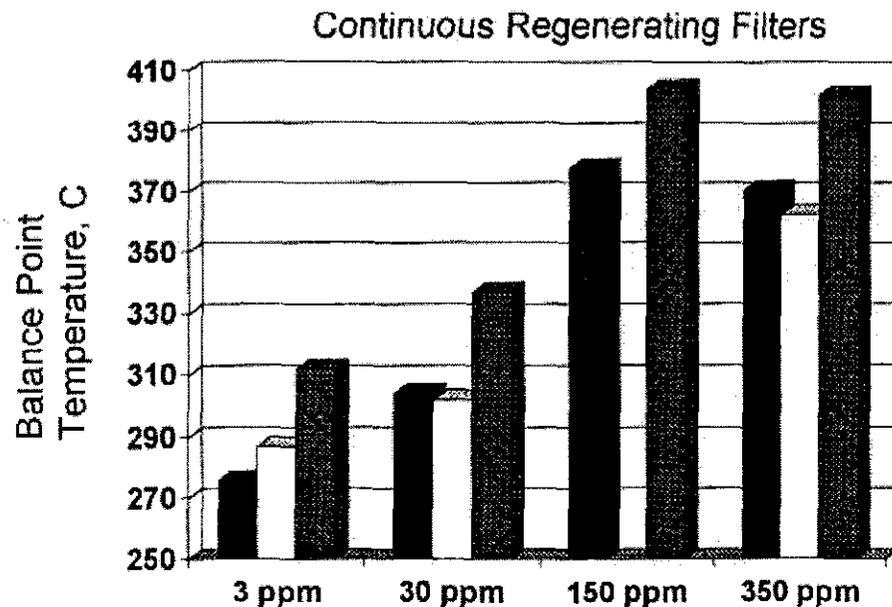
Some reports (AVL at SAE TopTec 9/99) show high nano-particulates after filter with low-sulfur fuel. Issue is one of catalyst formulation/loading, and time/temperature balance in the exhaust pipe.

The regenerating temperature of filters increases significantly when going from 3 to 30 ppm sulfur in the fuel



The filter regeneration temperature increases 24 to 55C going from 3 to 30 ppm sulfur, for catalyzed soot filters.

(Note: Filter formulations not optimized to decrease regeneration temperature)

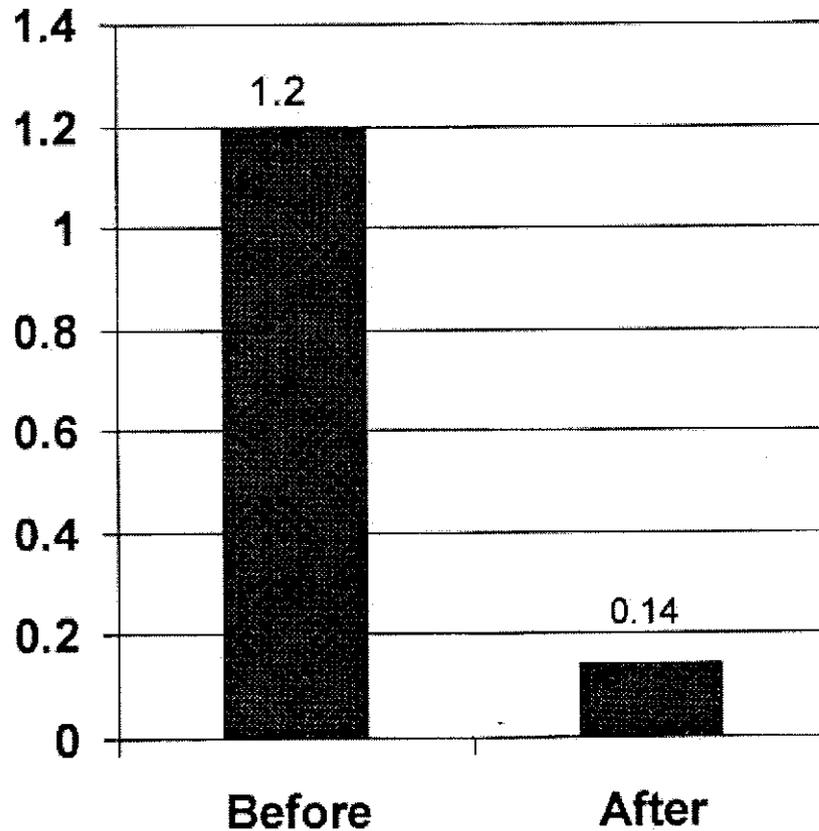


The filter regeneration temperature increases 15 to 28C going from 3 to 30 ppm sulfur, for continuous regenerating filters

DOE DECSE, Interim Report Phase 1, #4

Filters Destroy Large Fractions of Toxic Emissions

PAH, mg/bhp-hr



- PAH Emissions Reduced by 89%

Source: MECA 1999

The CRT[®] filter system durability has been verified on a range of different vehicle types.

CRT TM No.	Vehicle Application	Emission Certification Level	Accumulated Distance, km. (mi)	Accumulated In-use time, months	Engine Displacement, litres, and Power, kW	
#1	intercity train	Euro 2	600,000 (372,902)	36	14	310
#2	airport bus	Euro 0	575,267 (357,531)	37	10	210
#3	express bus	Euro 2	490,098 (304,588)	35	10	265
#4	mail truck	Euro 0	473,800 (294,469)	63	7	170
#5	city bus	Euro 0	238,809 (142,265)	46	11	187
#6	garbage truck	Euro 0	206,603 (128,342)	57	7	169
#7	garbage truck	Euro 0	105,780 (65,743)	37	7	169

Seven vehicles from which CRT was removed for evaluation on a 12 liter US 1994 certified engine (steady state) and a 11 liter Euro 0 engine (transient).

>70% HC efficiency and >95% PM efficiency on transient cycles.

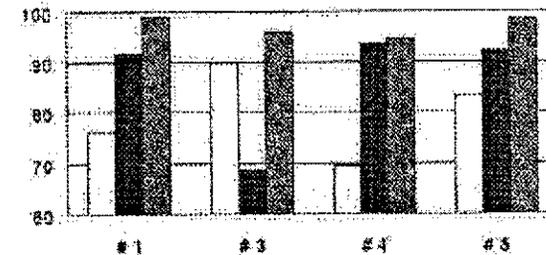
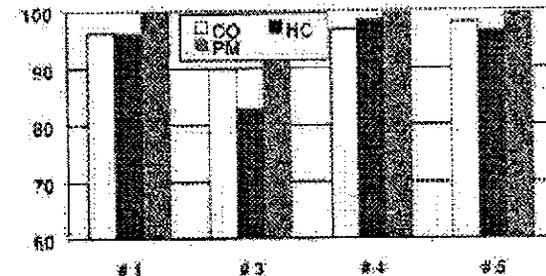
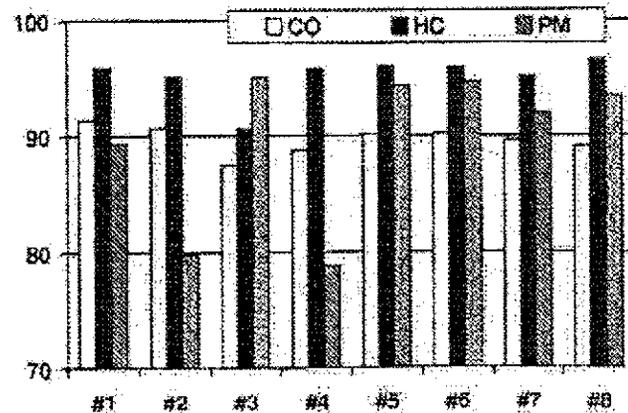


Figure 4. Pollutant conversions over the ETC cycle (upper plot) and the US-FDT (lower plot) for four aged trap systems.

All CRT systems had 80% or better PM efficiency and 90% or better HC efficiency on the ESC cycle.

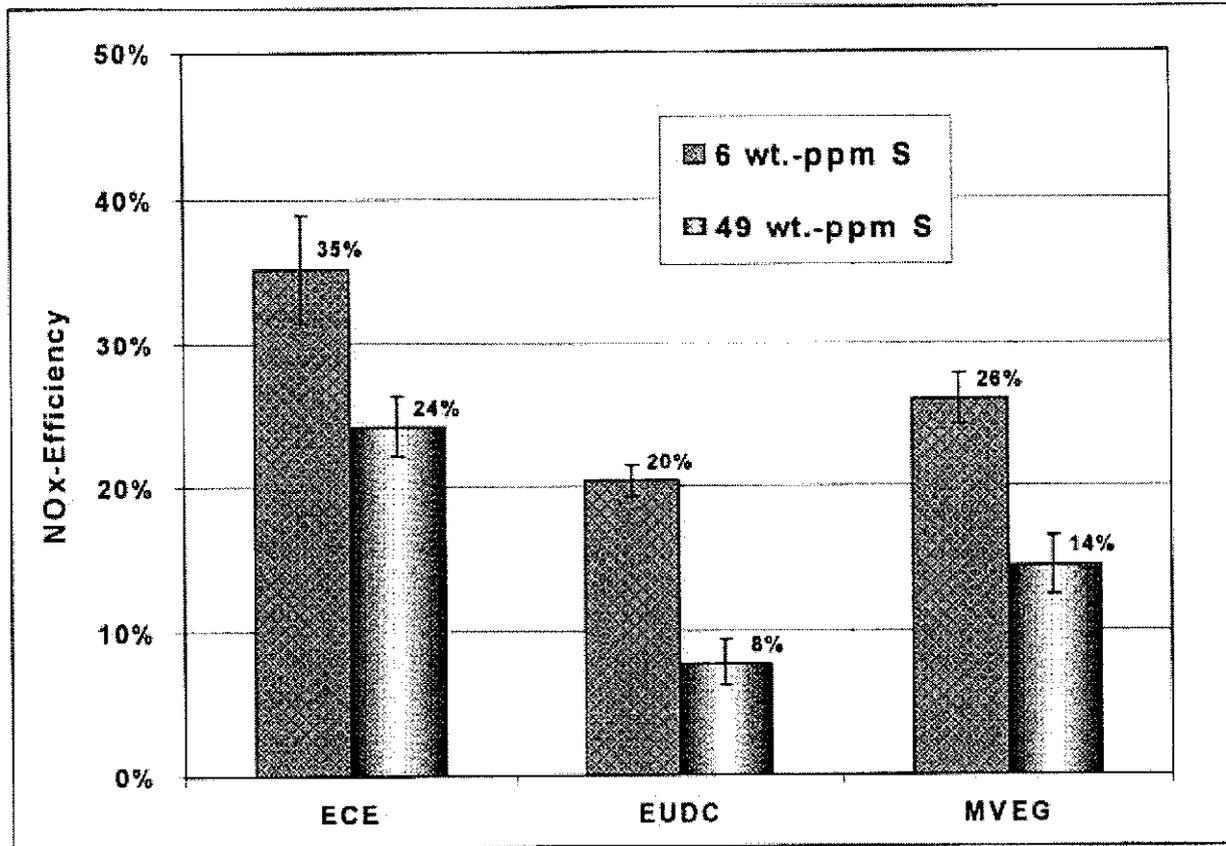
JMI SAE 2000-01-0480

Filter summary

- Nanoparticle chemistry is complex and dependent on many variables.
- Filters are retrofitted onto 10,000 vehicles in Europe,
 - early issues, but now with minimal operating problems
 - OEMs will be offering filters very shortly
- Very high efficiencies are obtained
 - almost immeasurable particulates
 - <15 ppm sulfur is needed to hit 0.01 g/bhp-hr
 - Toxins are significantly reduced with filters

NOx Solutions

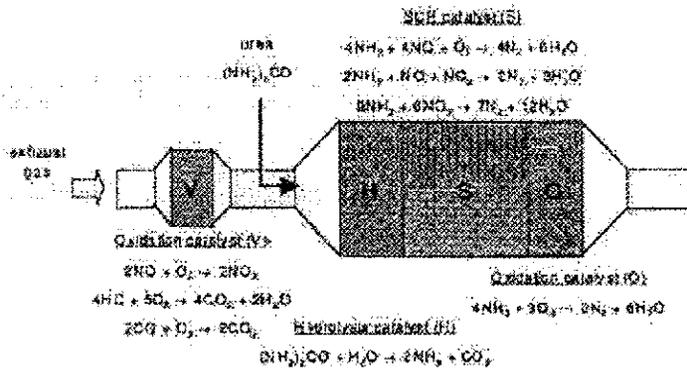
Passive deNOx catalyst efficiency drops from 28 to 14% when the fuel sulfur is increased from 6 to 49 ppm



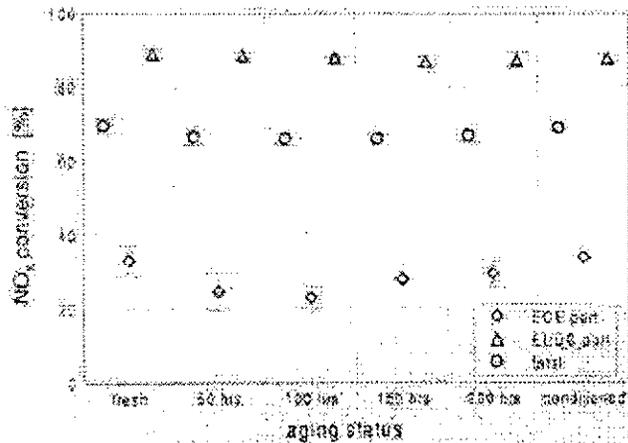
1.9 liter, TDI,
Euro 2
calibration; 5.8
liters of catalysts;
baseline MVEG
NOx of about
0.68 g/km; no
added HCs

AECC, FEV SAE 2000-01-1877

SCR systems are being optimized for T, SV, and urea injection rates. 90% efficiency obtained

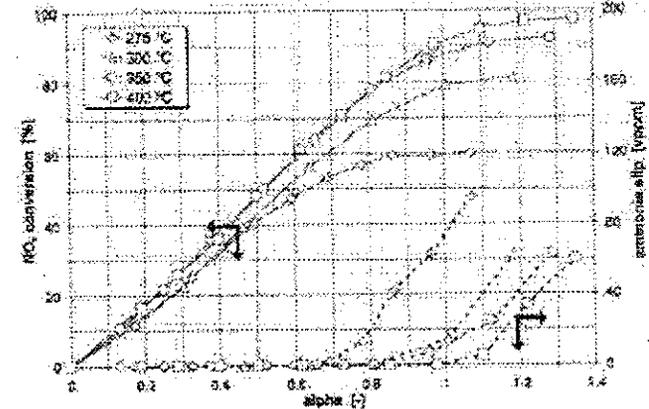


Four part SCR system.

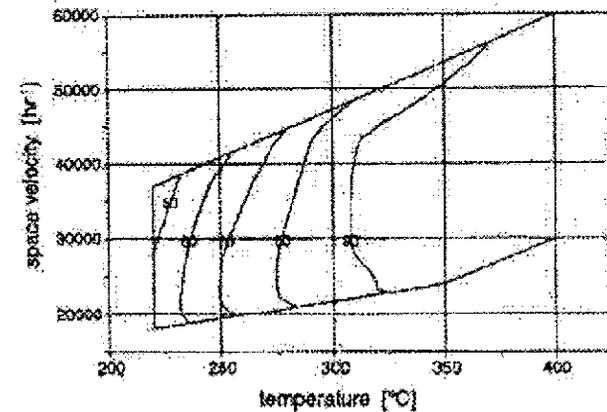


SCR system applied to LDD obtained 70% efficiency on the MVEG cycle. 2.5 liter TDI, aged; Results from engine dyno.

Alpha = NH₃/NOx system efficiency requires balancing urea injection with NOx and NH₃ emissions.



NOx efficiency of up to 90% obtained at optimum NH₃/NOx ratios, 300°C, and 40,000/hr space velocity; no NH₃ emission.



On-Vehicle SCR tests gave 70% NOx efficiency

Exhaust emission	Baseline (engine-out)	Urea-SCR (catalyst-out)
NO _x (g/bhp-hr)	5.25	1.55 (-70.5%)
HC (g/bhp-hr)	0.06	0.00 (-100.0%)
PM (g/bhp-hr)	0.08	0.06 (-25.0%)
NH ₃ (ppm avg)	0.00	0.40
CO (g/bhp-hr)	1.12	1.54 (+37.5%)
CO ₂ (g/bhp-hr)	552	554 (+0.4%)

Hot US transient results show 70% NOx reduction, and elimination of HC. Very low NH3 slip.

Table 4. OICA Emissions Results

Exhaust emission	Baseline (engine-out)	Urea-SCR (catalyst-out)
NO _x (g/bhp-hr)	4.86	0.70 (-85.6%)
HC (g/bhp-hr)	0.01	0.00 (-100.0%)
PM (g/bhp-hr)	0.04	0.04 (equal)
NH ₃ (ppm avg)	0.00	0.24
CO (g/bhp-hr)	0.29	0.29 (equal)
CO ₂ (g/bhp-hr)	506	515 (+1.8%)

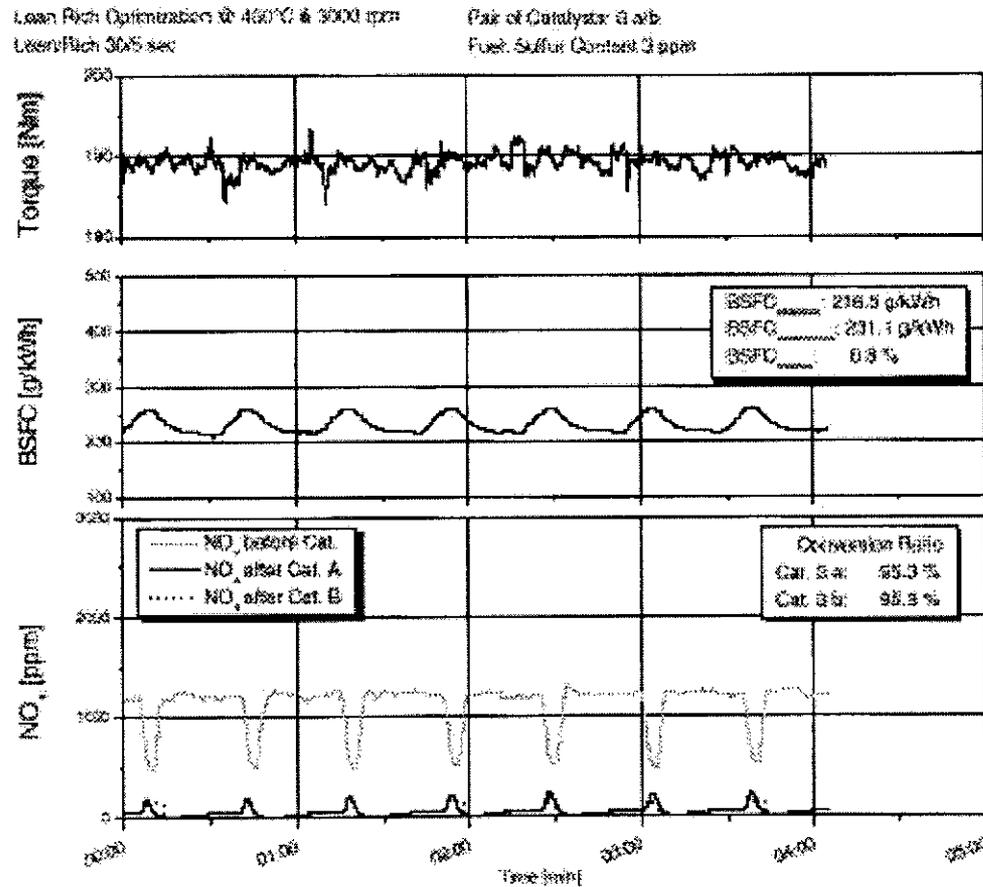
Steady state results results show 86% NOx reduction, and elimination of HC. Very low NH3 slip.

Siemens SAE 2000-01-0190

SCR is relatively insensitive to sulfur, but is not without issue

- Efficiencies in the 70+% range are reported, but some reports of 90% efficiency are surfacing
- Issues:
 - truckers resist SCR and there are several unknown risks (ammonium nitrate PM, other by-products)
 - urea might have costs of \$0.50 to \$1.00 per gallon, and is consumed at up to 7% of the fuel rate
 - 2 to 5% effective fuel penalty
 - ammonia slip of a couple ppm's; can be addressed with catalysts
 - tampering - NOx sensors may address
 - distribution, adding a component to the network - perhaps solid urea might help
 - volumes are 1/4; LDD: 8.4 liters for 30,000 km (LDD, FEV 9/99)
 - pellets can be loaded on HDD from bags

NOx adsorbers can work well under controlled conditions.

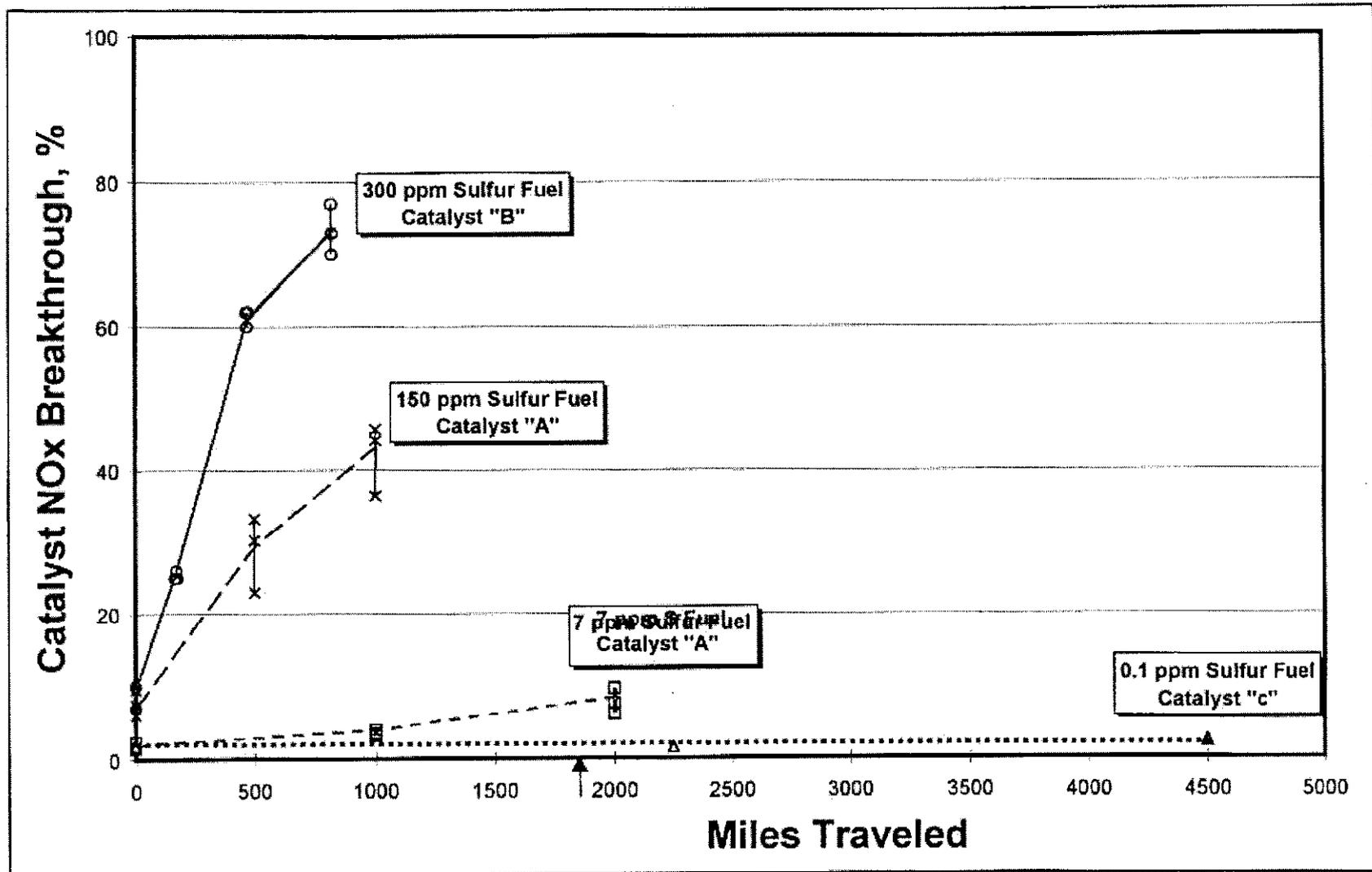


Periodic injections of excess fuel causes the NO_x to be released and reduced. Fuel consumption and torque are affected.

DECSE, DOE Interim Report #2, 10/99

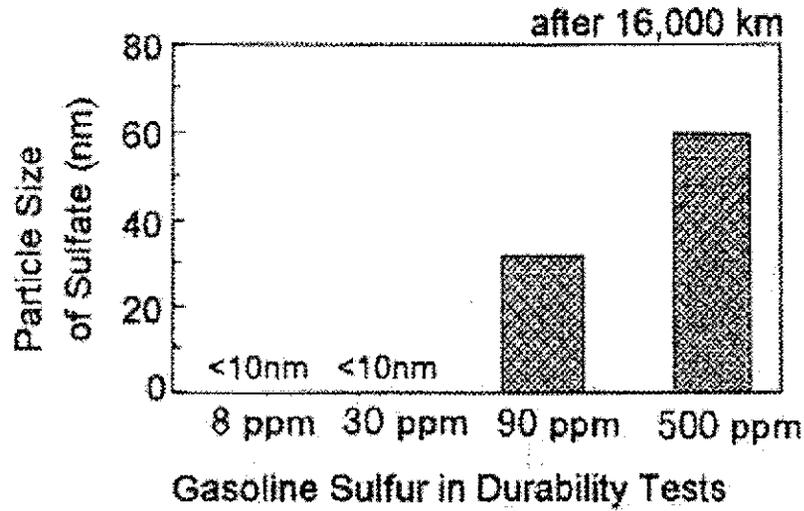
CORNING
Discovering Beyond Imagination

Low Levels of Sulfur Are Needed to Maintain NOx Adsorber Catalyst Efficiency

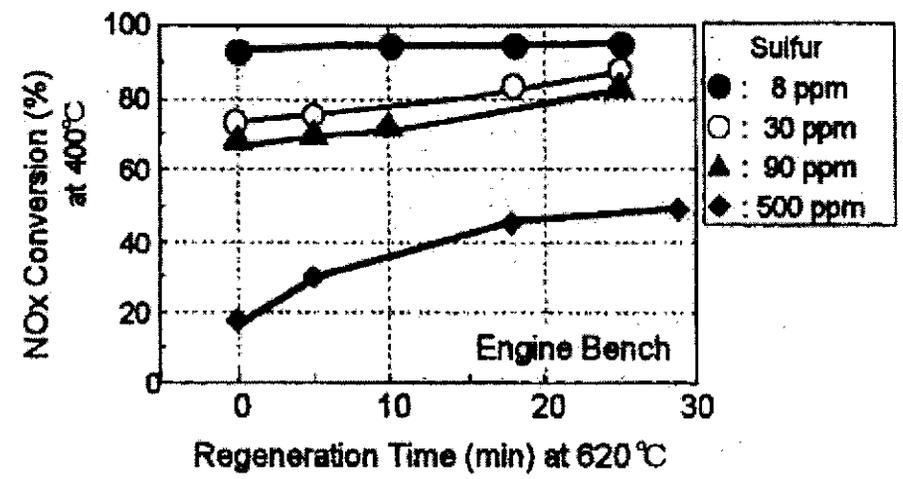


MECA and ASEC, 4/00

In NOx traps, the size of the BaSO₄ 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.

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

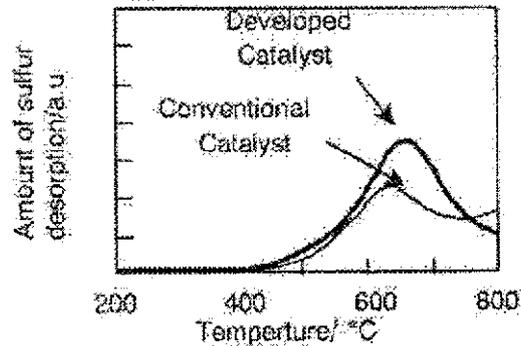


Fig. 14. Profiles of sulfur under rich gas flow after durability test.
 Sample: 35cm³ monolithic catalyst
 Test condition: A/F=12, 200-800°C, in rich gas, analyzed by SO_x analyzer

200 ppm S, 2.0 liter engine, 1.3 liter NSR catalyst. New catalyst desorbs SO₂ faster and at lower T.

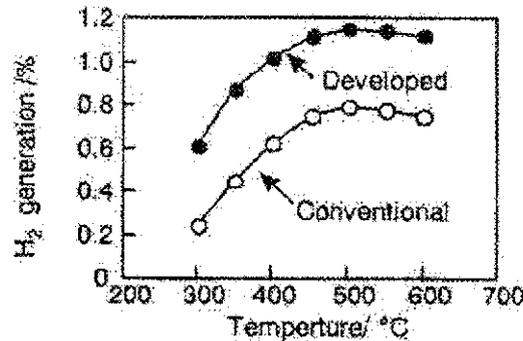


Fig. 13. Amount of H₂ generated by steam-reforming reaction (additive effect).

Sample: Pellet catalyst (Rh/ZrO₂)
 Aging condition: 600°C, 10h in air
 Test condition:
 A/F=12, 300-800°C, H₂ was analyzed by GC
 W/F=3.3×10⁻³ g·cm⁻²·s

Bench work. New Rh/ZrO₂ catalyst generates 50% more H₂ for SO₂ desorption.

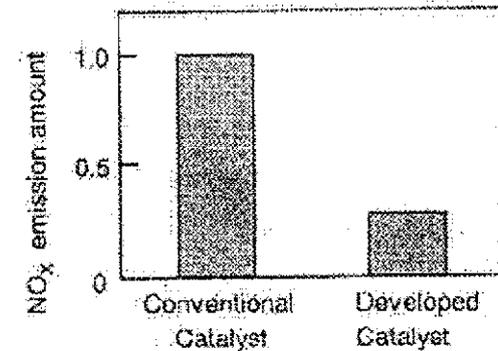


Fig. 16. Relative NO_x emission amount after durability test.

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

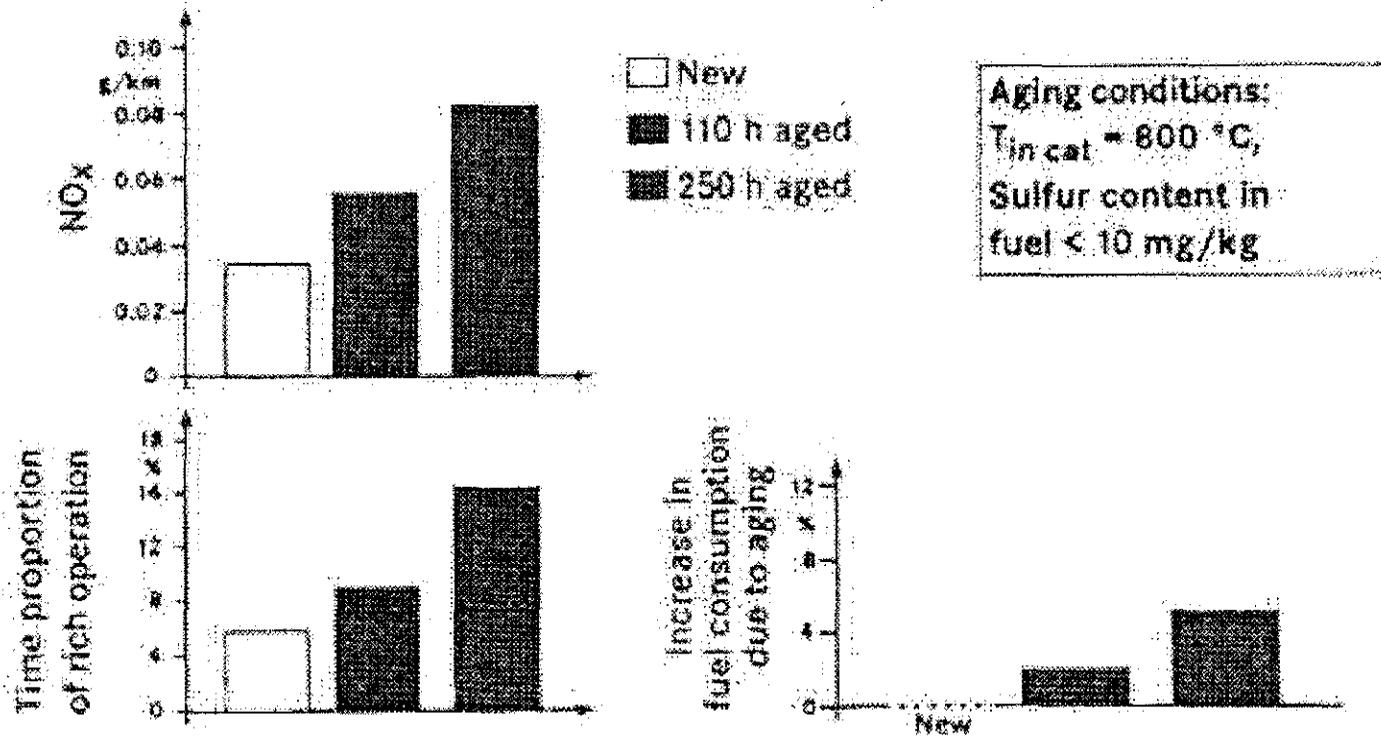
New highly dispersed TiO₂ suppresses SO₂ adsorption and aids in desorption.

Alkali-earth additions to Rh/ZrO₂ catalyst stabilizes ZrO₂ without aging Rh, enhancing H₂ generation.

Aged NOx traps result in reduced fuel efficiency (gasoline here)

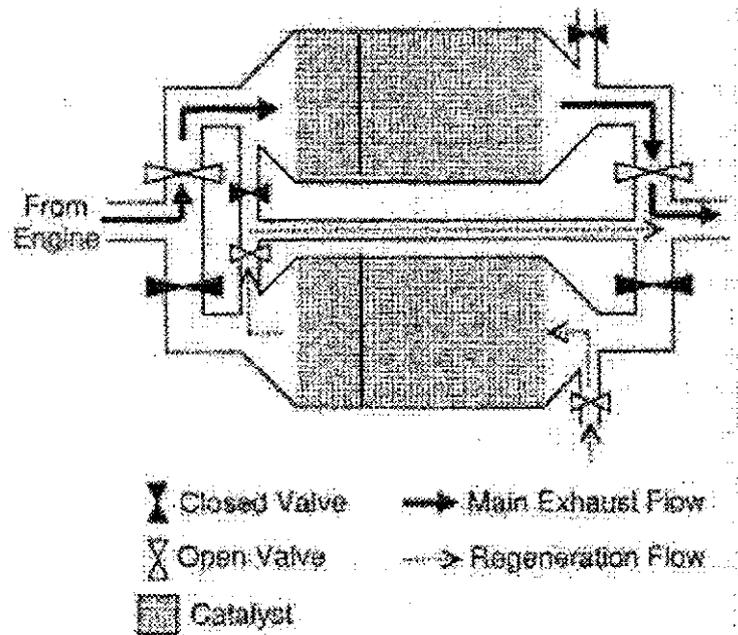
Effect of catalyst aging on NO_x emissions and fuel consumption in the NEFZ test cycle

Note: Regeneration initiated by NO_x-sensor

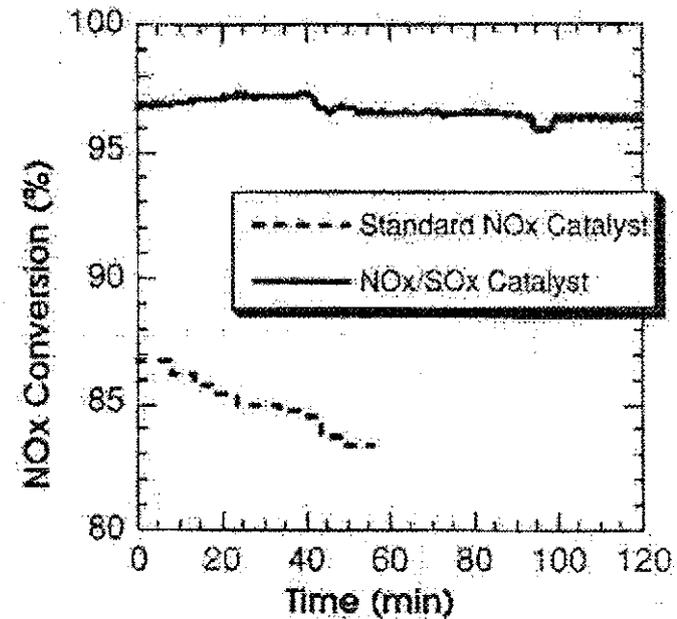


Aged NO_x traps lose capacity and efficiency. Decreasing the portion of lean operation will help, but fuel economy suffers.

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



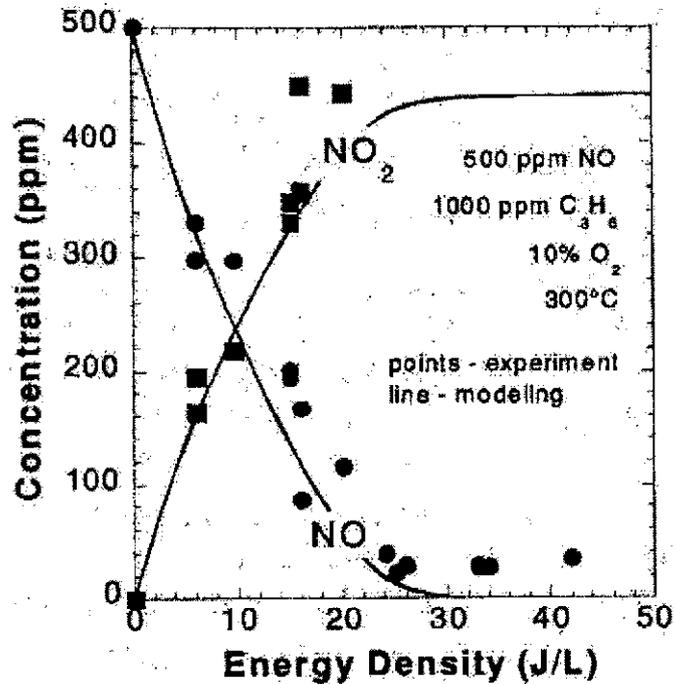
SOx adsorber is in front of NOx adsorber. Flow shows one bank in regeneration mode. 3.9l turbo; 9.8l in each bank.



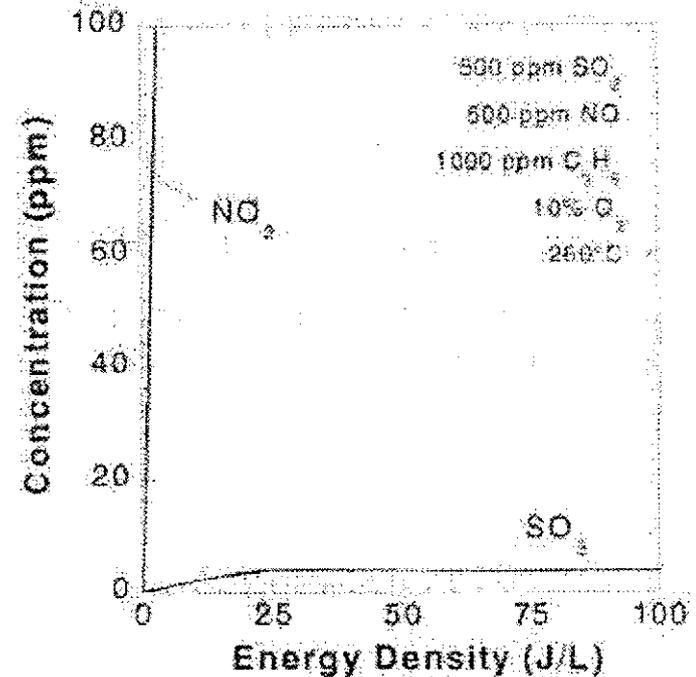
180°C exhaust T, 370 ppm S; no SO₂ out of system.

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

Plasma shows promise for being an excellent, sulfur-tolerant oxidizer of NO_2 without affecting SO_2 .



Plasma is very good for oxidizing NO to NO_2 . Kinetic models are reliable.

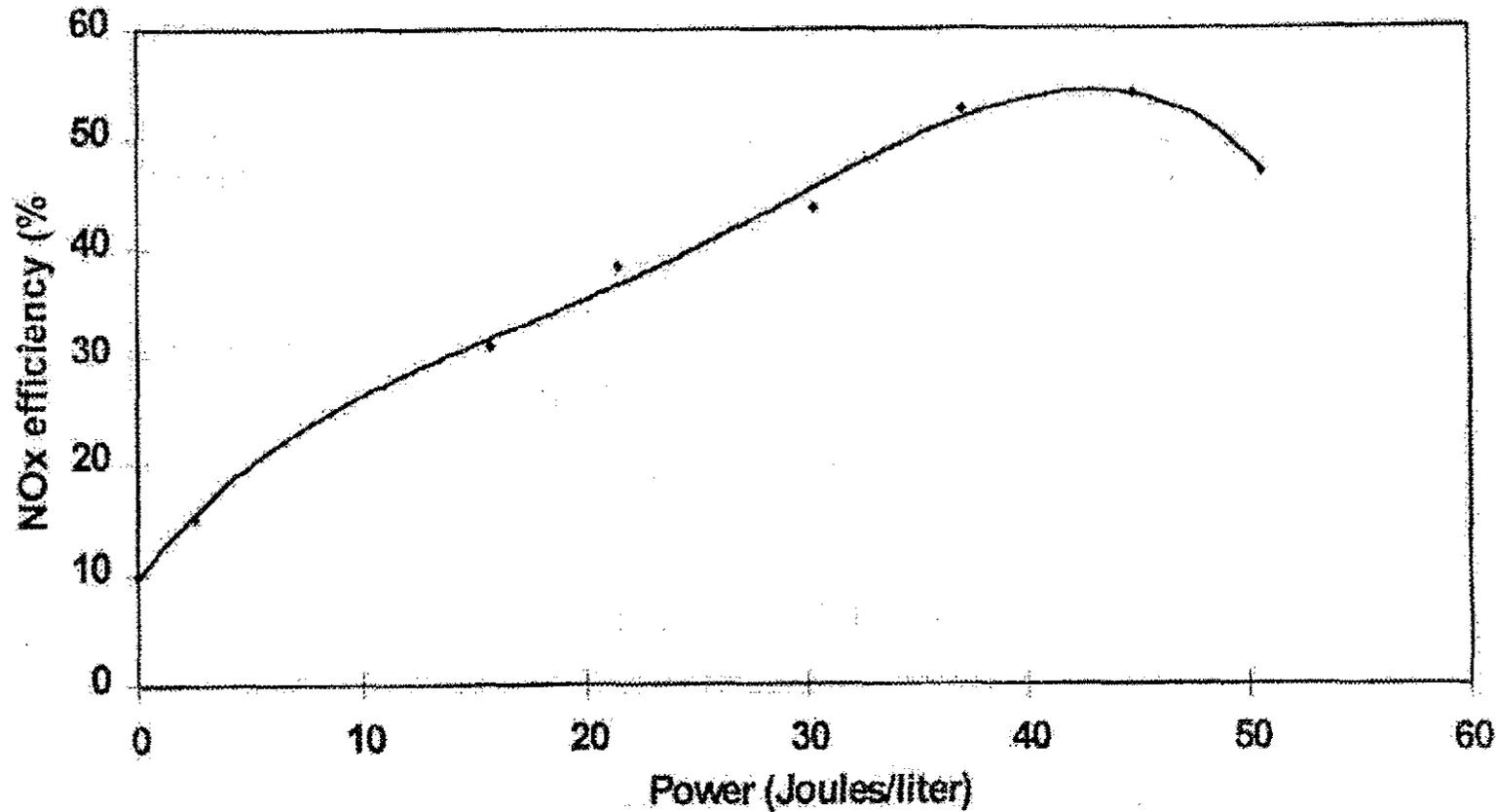


Kinetic model shows that SO_2 is not oxidized.

Such devices, coupled with DPF, deNOx catalysts, SCR catalysts, or NOx traps could result in effective systems.

50 to 60% NOx efficiency is obtained with a non-thermal plasma system

On vehicle at idle; similar efficiencies were obtained at 1/3 the power density using a slip stream



Delphi, DEER Conf., DOE, July 1999

CORNING
Discovering Beyond Imagination

Summary of NOx solutions

- DeNOx catalysts might remove up to 40% of the NOx, with up to a 5% fuel penalty; sensitive to sulfur levels
- SCR is the leading technology in Europe. 70-90% efficiencies reasonable; sulfur tolerance; Much resistance from truckers, and several outstanding issues need to be addressed
- Non-thermal plasma technologies are emerging. Low sulfur sensitivity; efficiencies in the 50% range
- NOx traps are emerging for diesel; the best passive technology opportunity. Signs of 90%+ efficiency. Extremely sensitive to sulfur. Desulfation strategies and/or sulfur traps are being developed that will facilitate NOx adsorbers, but low sulfur fuel (<15 ppm) is needed for long term operation and to minimize associated costs.

Toxins

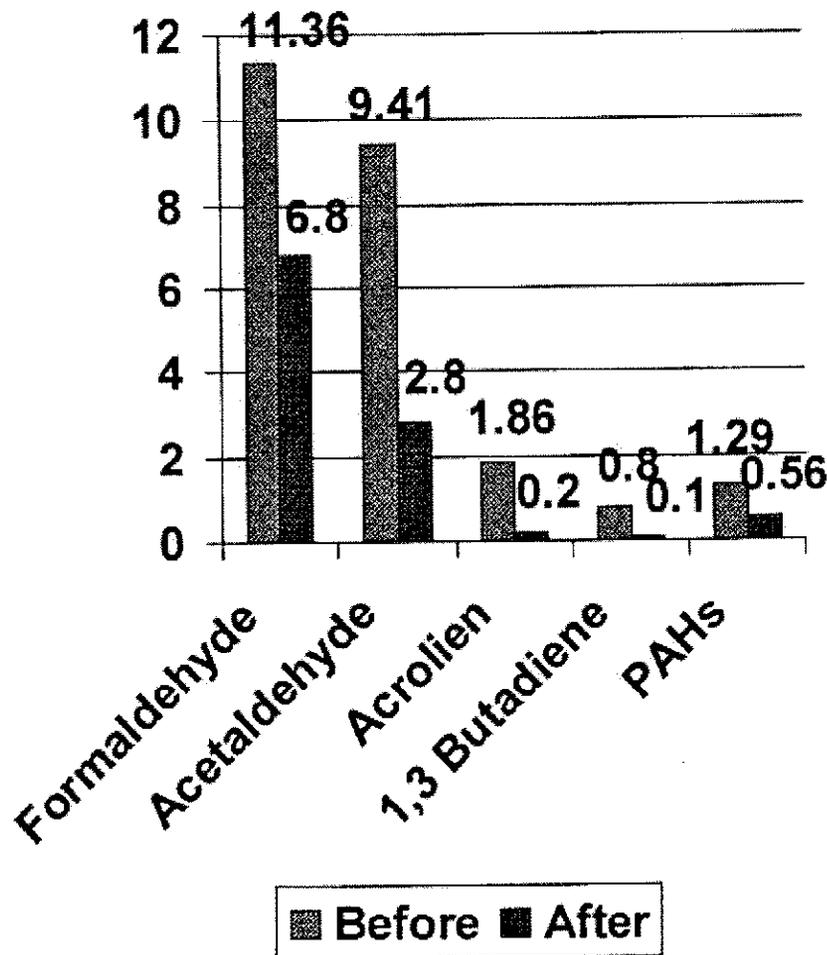
Catalyst in system: HC toxins removed;
Filters, SCR, NOx traps, Oxidation catalysts

Diesel Oxidation Catalysts Are Efficient and Proven

- Oxidation Catalyst Control Capabilities
 - PM -- 20-50% Reduction
 - CO and HC -- >90%
 - Toxic HCs -- >70%

DOCs Destroy Large Fractions of Toxic Emissions

mg/bhp-hr

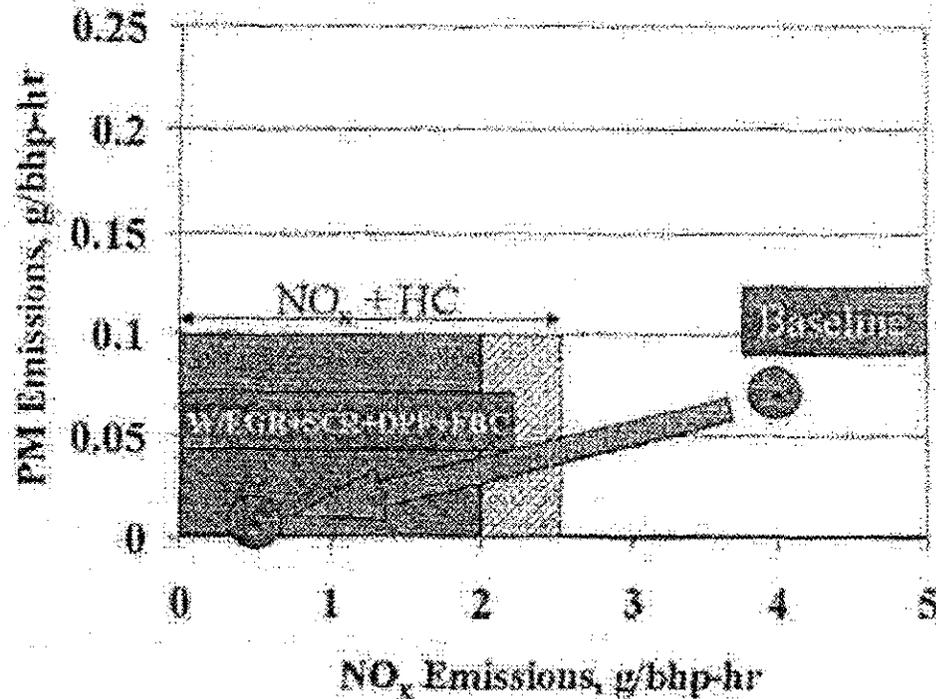


- Toxic Hydrocarbon Compounds Reduced by 68%
- PAH Emissions Reduced by 56%
- Greater Reductions Possible with Low Sulfur Fuel

Source: MECA 1999

Integrated solutions

Prototype integrated systems are already getting close to hitting US2007

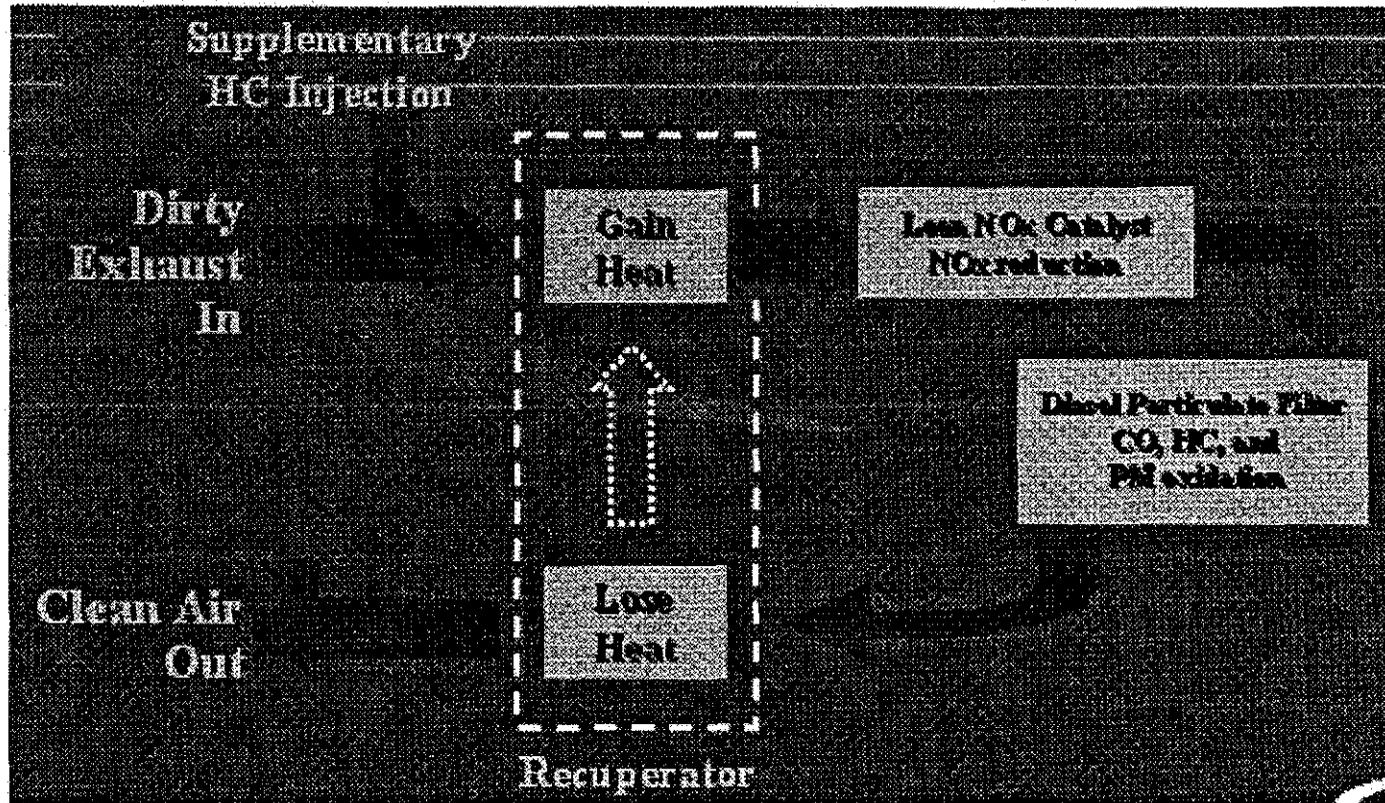


System:

- 1998 Series 60 Engine with retrofit cooled EGR
- SCR system followed by uncatalyzed filter
- Cerium fuel-borne catalyst
- Much room for optimization

Unoptimized system achieved 0.5 g/bhp-hr NO_x and 0.004 g/bhp-hr PM

Systems approaches are emerging, using engine management, heat exchangers, and NOx/PM solutions

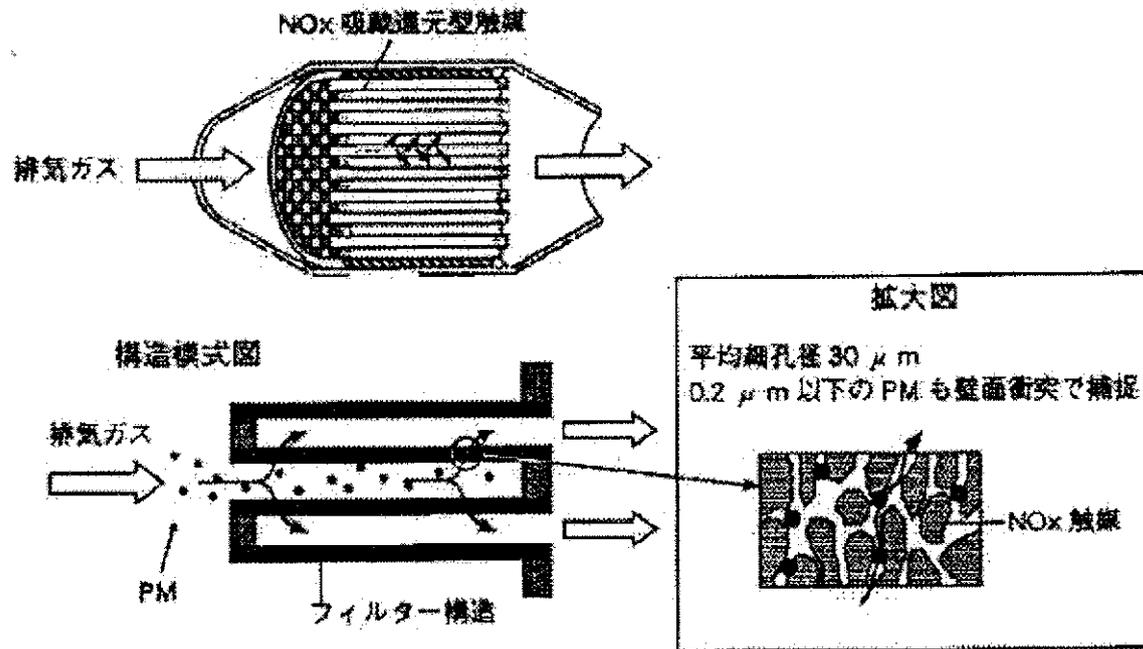


Reportedly gets 35% efficiency with a 3 - 5% fuel penalty

Source: Ceryx

CORNING
Discovering Beyond Imagination

Integrated components are emerging and will likely be key to the solutions



Claim is 80% NOx and PM efficiency. Needs low-sulfur fuel. Testing at 80,000 km on LDD; beginning HDD.

Toyota website

Conclusion

- Engines are in the prototype stage that will require 88 to 96% NO_x efficiency and 73 - 0% PM efficiency to hit US2007 (0.2 and 0.01 g/bhp-hr, respectively)
- Nano-particulates are elusive, but filters are effective in removing them
- Filters are durable, result in clean exhaust, and have a good track record. Sulfur <15 ppm is needed.
- There are many NO_x solutions being evaluated. The most attractive (passive, efficient) are NO_x traps. They are very sensitive to sulfur, and will likely need SO_x traps at 15 ppm for heavy duty applications.