Development of the 2011MY Ford Super Duty Diesel Catalyst System

2011 DEER Conference

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Outline

- Background of Ultra-Clean Fuels Program
- Tech Selection for 2010 Emissions
- Development Challenges with SCR
- Diesel MDV Impact on Sustainability
- Next Steps
- Conclusions & Acknowledgements

DOE Ultra-Clean Fuels Program

Outline of Ford's program to achieve Tier 2 FTP emission standards for 2007 using ultra low sulfur diesel (ULSD) as a key enabler for a high efficiency aftertreatment system.

Primary Contractor

Research and Advanced Engineering

Subcontractors

ExxonMobil Research and Engineering

FEV

Catalyst Suppliers

ENGELHARD

JM Johnson Matthey

umicore

Phase I - Initial build/test phase (July 01-July 02)
- Establish baseline emission control system
- Deliver engine dynamometer NOx and PM test results
- Deliver prototype vehicle NOx and PM test results
- Deliver urea delivery (infrastructure) prototype

Phase II - System/component optimization phase (July 02-July 04)
- Define final system hardware components
- Deliver NOx and PM performance data from fresh system

Phase III - Durability phase (July 04-Dec 05)
- Definition of durability test procedure
- Final NOx and PM emission levels
- Final report for the completed program

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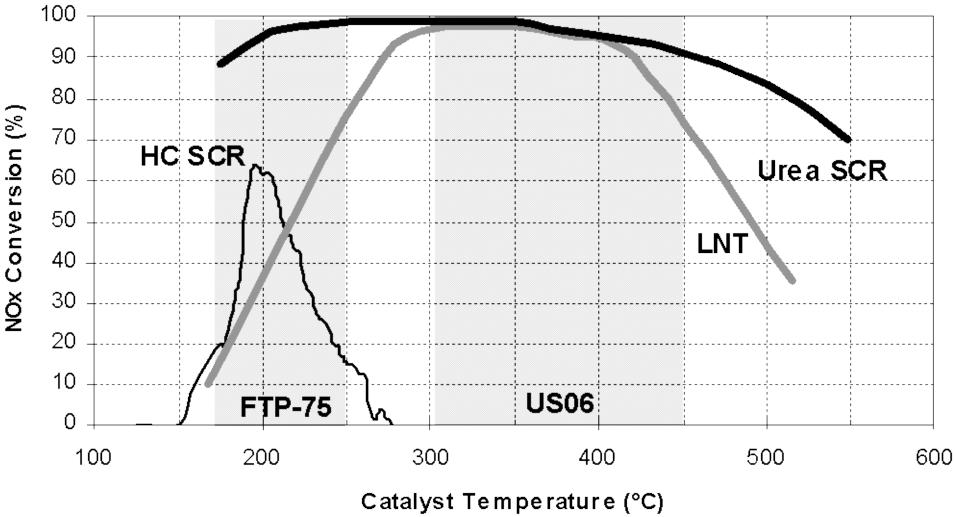
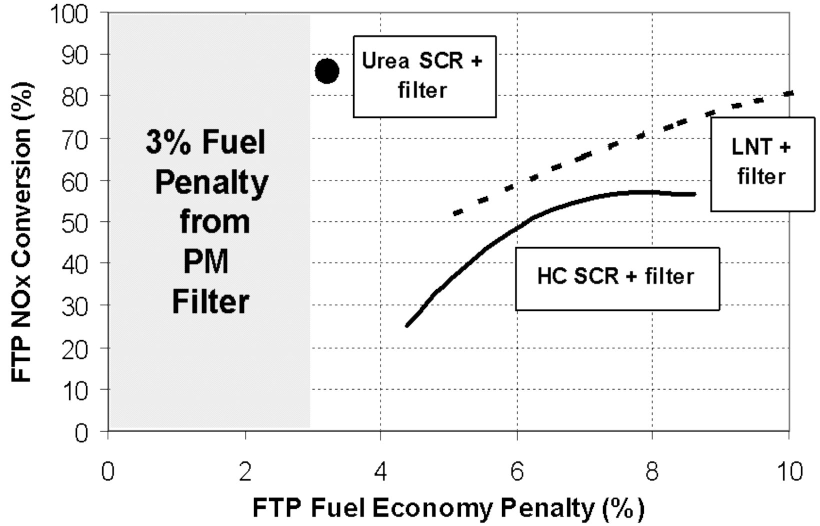
Diesel NOx Control Options

Typical performance curves for slightly aged catalysts



Estimated fuel penalties of for the LD FTP-75



Based on the above data, urea SCR was chosen as the prime option for Ford's UCF Program.

SAE 2004-01-1292

Background of UCF Program

Diesel Fuel Properties

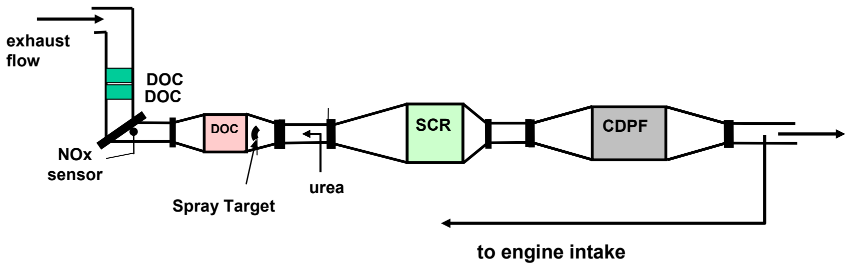
- ExxonMobil blended 14,000 gallon batch to represent typical 2007 ULSD

Fuel Property	Est. Avg. '06 Diesel Properties	Proposed DOE Program Min/Max	Program Fuel Delivered	Proposed 2007 Cert. Fuel
Sulfur, ppm	15*	10 / 15	**12.5**	7 / 15
Density, kg/m³	850	820 / 850	**841.1**	839 / 865
Aromatics, vol. %	32	25 / 32	**29.5**	27 min
Polyaromatics, wt. %	10	6 / 11	**11.0**	no spec
Cetane number	46	44 / 48	**44.9**	40 / 50
T50, C	267	250 / 280	**249**	243 / 282
T90, C	306	300 / 320	**307**	293 / 332

* As delivered to the vehicle

LDT Exhaust System

>90% FTP NOx conversion, 0.05 g/mi TP NOx



- Engine-out NOx lowered by 40% with increased EGR
- Low tailpipe NOx achieved with rapid warm-up strategy
  - lower thermal mass upstream of catalyst system
  - engine calibration changes during cold start (post injection & inc. idle speed)

- Diesel fuel specially blended at <15 ppm-wt Sulfur
- 6000 lbs LDDT used as a demonstrator of aged aftertreatment
- Catalysts aged on engine dynamometer for 120K mi equivalent
- Objective was Tier 2 Bin 5 (120k mi): 0.07 g/mi NOx, 0.01 g/mi PM

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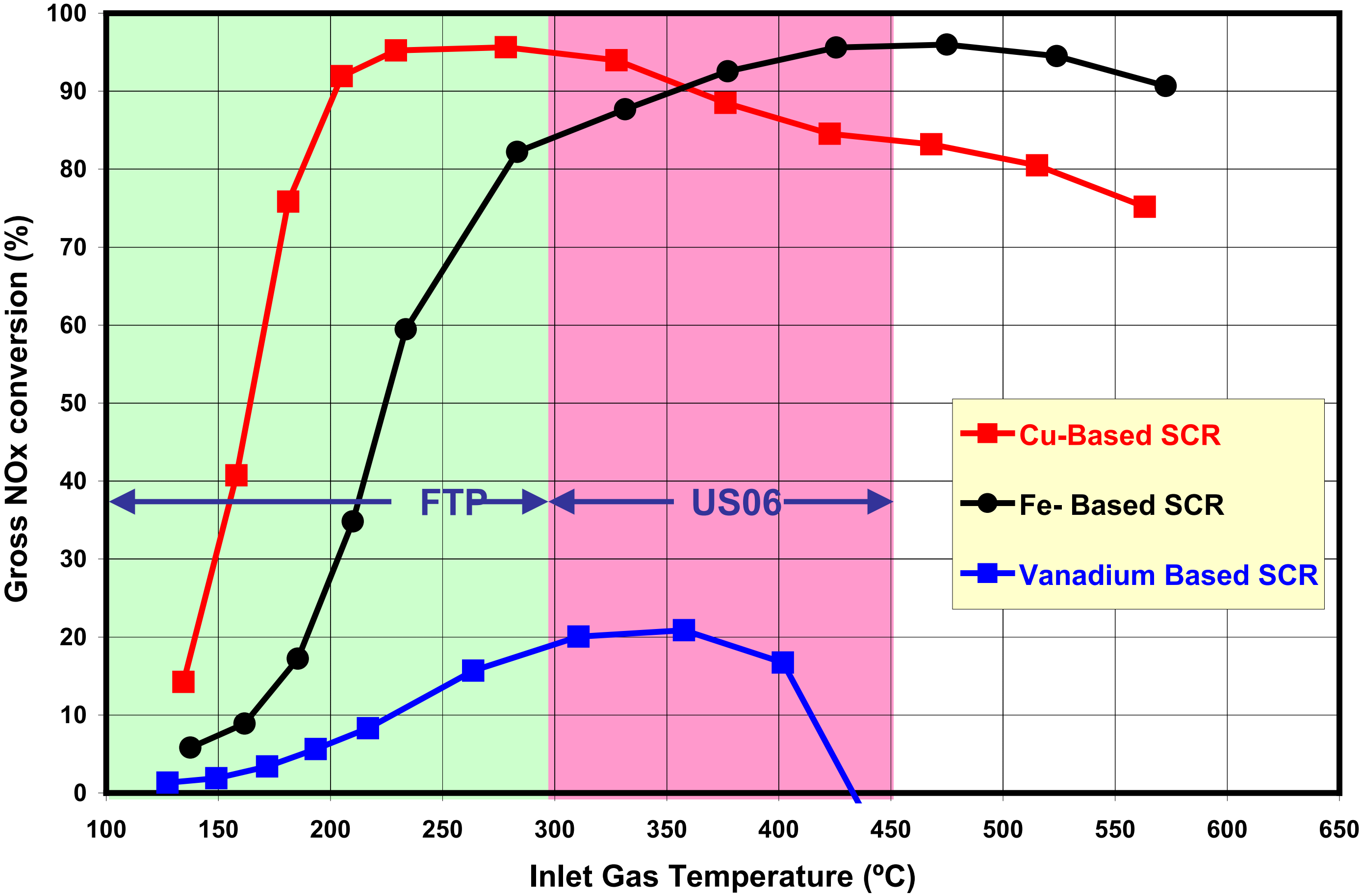
SCR Catalyst Options



- Cu/zeolites are best at low temperatures
- Fe/zeolites perform well at high temperatures
- Vanadium based SCRs are not appropriate for US Diesels with Filters

SAE 2007-01-1575

Key Accomplishments of Ford's UCF Program

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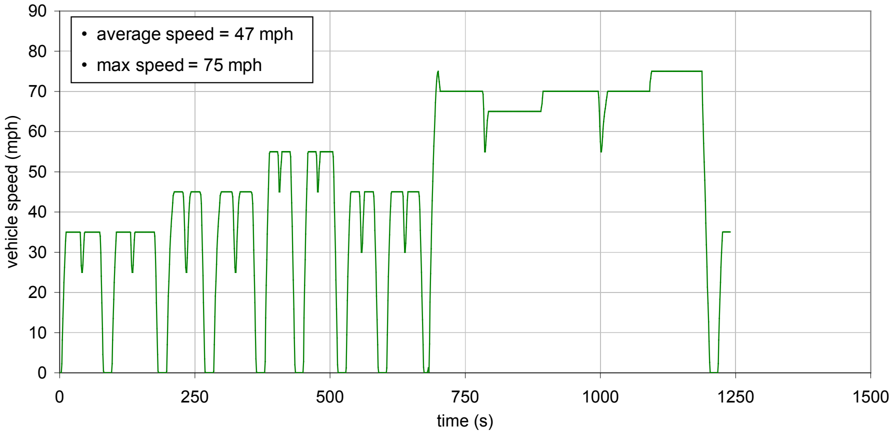
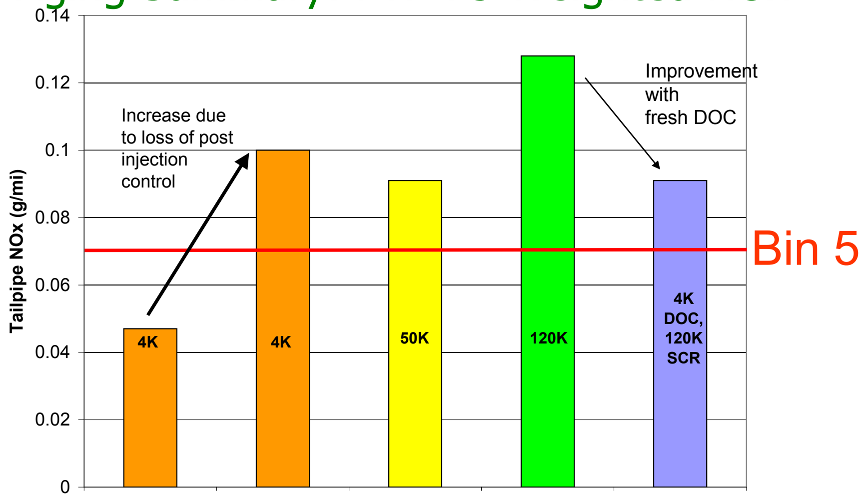
Durability Test Definition

Ford High Speed Cycle (HSC)



Aging Summary: FTP-75 Weighted NOx



- Loss of DOC activity resulted in higher NOx emissions at 120k mi

- >80% NOx reduction was achieved on a 6000 lbs light-duty diesel truck
- Tailpipe NOx was below the T2B8 emission standard (0.2 g/mi NOx)
- Proved Cu/zeolite had sufficient durability to withstand filter regens

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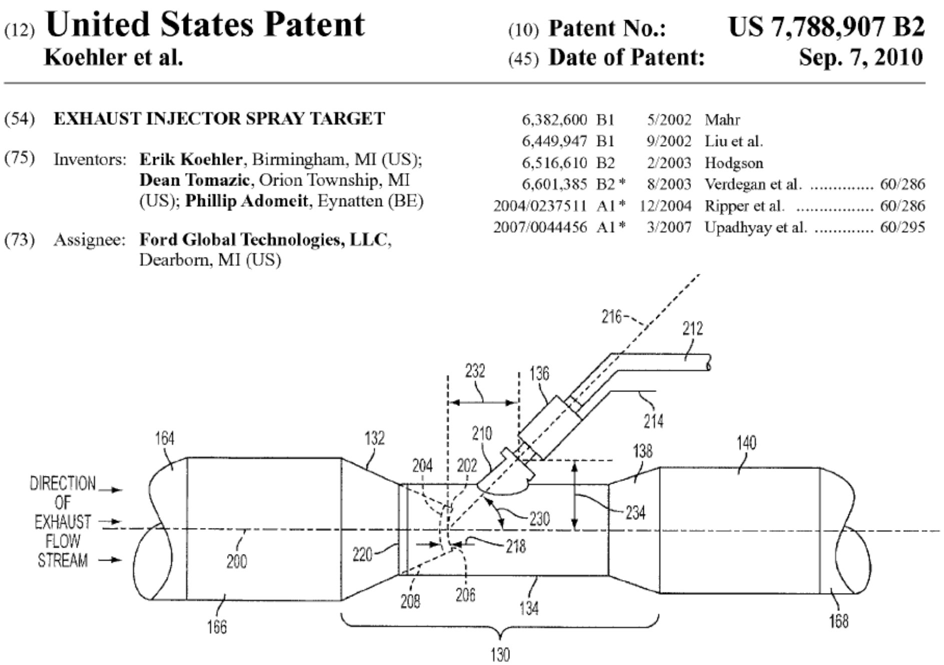
Key Accomplishments (con't)



(12) **United States Patent**
Koehler et al.

(10) **Patent No.: US 7,788,907 B2**
(45) **Date of Patent: Sep. 7, 2010**

(54) **EXHAUST INJECTOR SPRAY TARGET**

(75) Inventors: **Erik Koehler**, Birmingham, MI (US); **Dean Tomazic**, Orion Township, MI (US); **Phillip Adomeit**, Eynatten (BE)

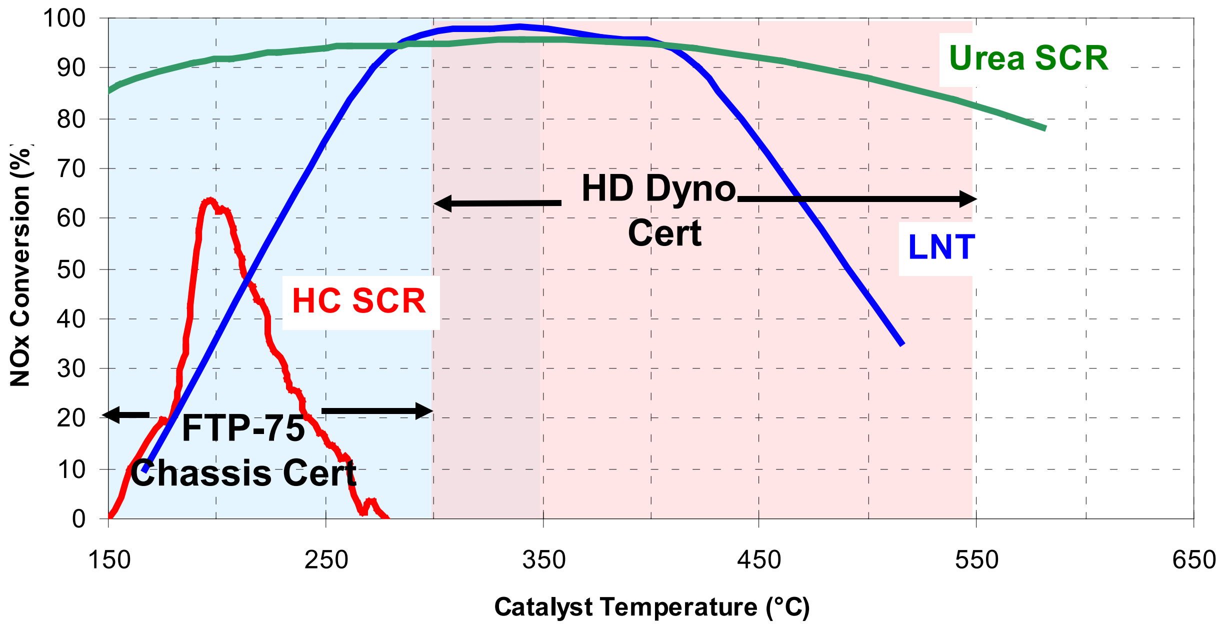
(73) Assignee: **Ford Global Technologies, LLC**, Dearborn, MI (US)

6,382,600	B1	5/2002	Mahr		
6,449,947	B1	9/2002	Liu et al.		
6,516,610	B2	2/2003	Hodgson		
6,601,385	B2 *	8/2003	Verdegan et al.	....	60/286
2004/0237511	A1 *	12/2004	Ripper et al.	....	60/286
2007/0044456	A1 *	3/2007	Upadhyay et al.	....	60/295

- Urea mixing in the exhaust found to be critical for high NOx conversion

- Developed urea/diesel cofueling dispenser
- Predicted long term bottled urea cost of $3.66/gal
- Long term cofueled urea price ~$1.50/gal

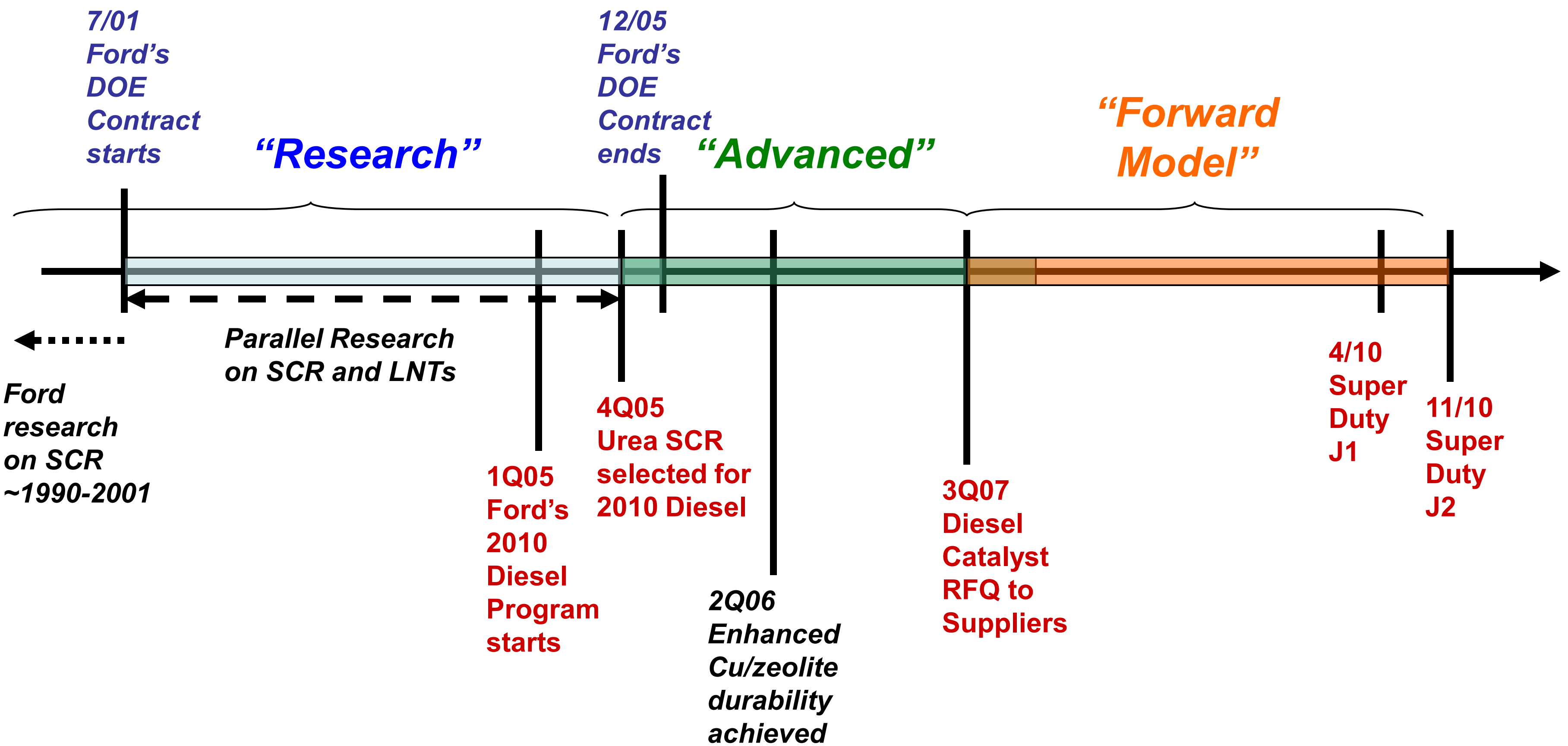
Aftertreatment Selection for 2010 Super Duty



- Ba LNT determined not capable for eng dyno cert
- K LNT had durability issues, large size, high cost
- Decision was made to certify 90% of diesel MDV fleet volume as complete chassis on FTP-75 (LEVII F250/F350 - **Class 2b** 8,501-10,000 lbs and **Class 3** 10,001-14,000 lbs)
- Desire to align chassis and dyno cert NOx control

→ Urea SCR became the prime option supported by data from Ford's DOE program

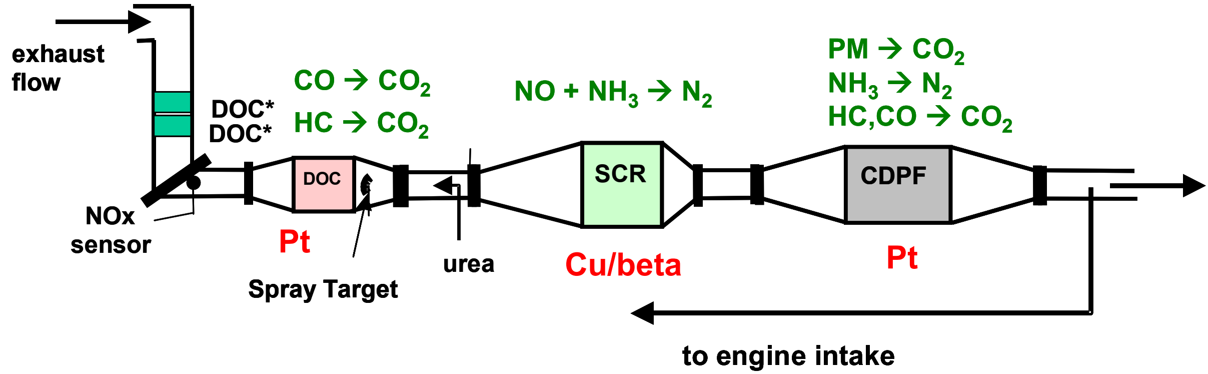
Timeline for 2010 Super Duty Aftertreatment



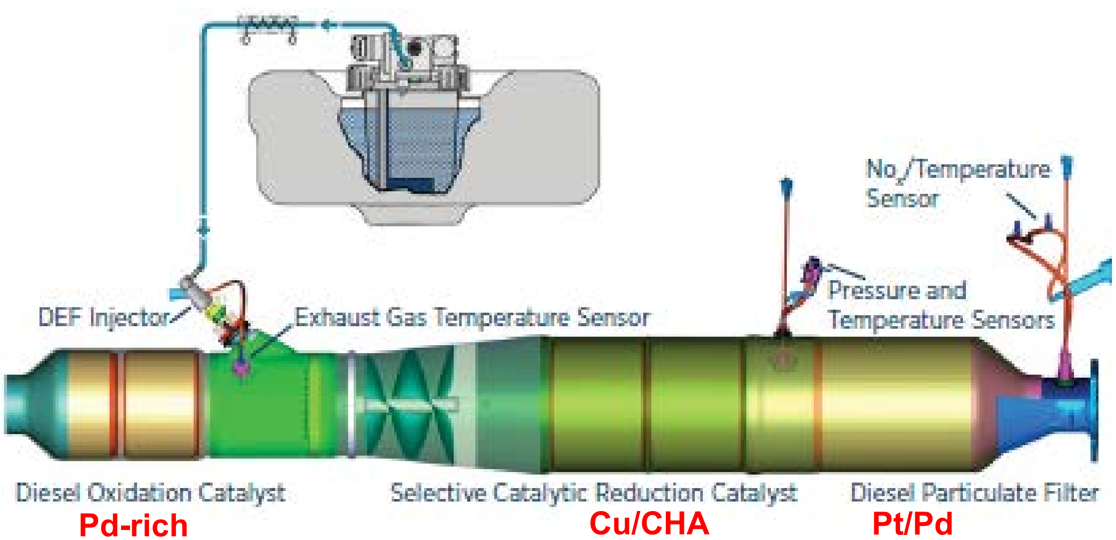
"not exactly to scale"

Diesel Aftertreatment Layouts

UCF Program Truck
6000 lbs LDDT
- Pt DOC
- Cu/beta SCR
- Pt CDPF

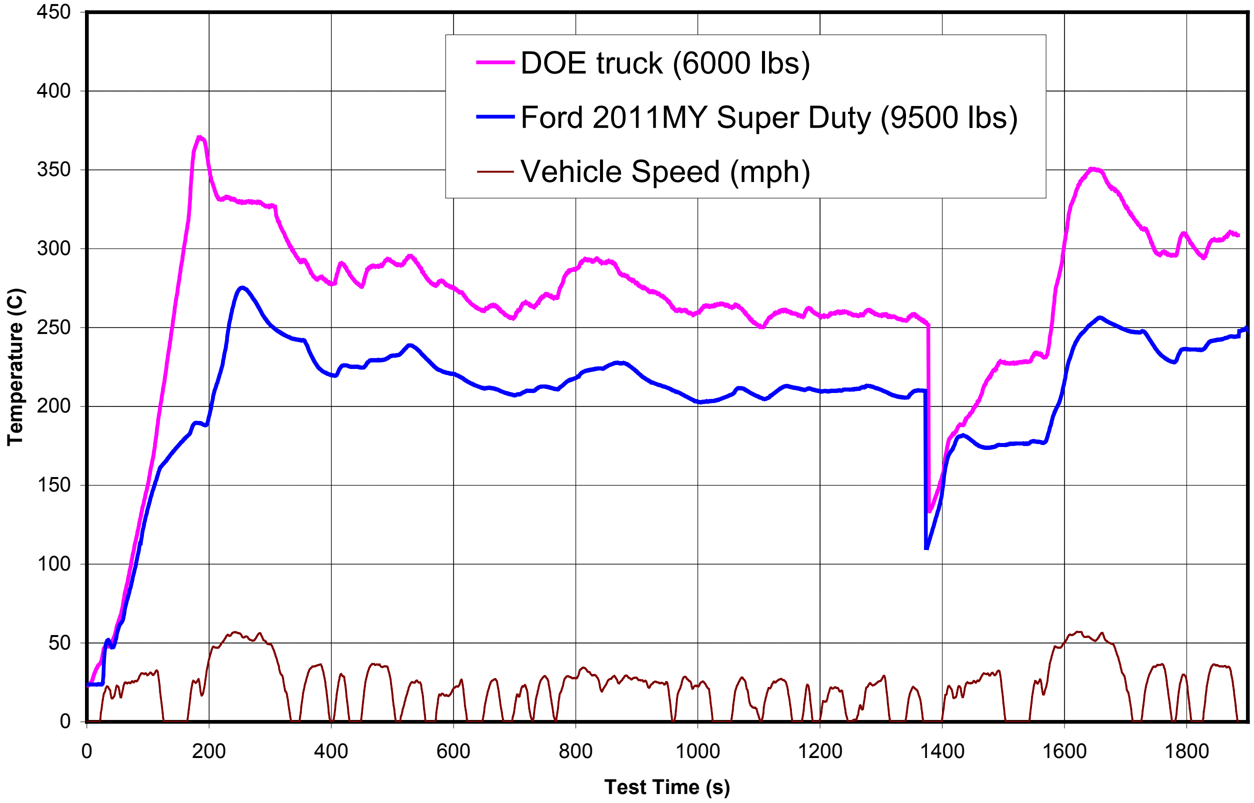


2011MY Super Duty
8,500 – 14,000 lbs
- Pd-rich DOC
- Cu/CHA SCR
- Pt/Pd CDPF



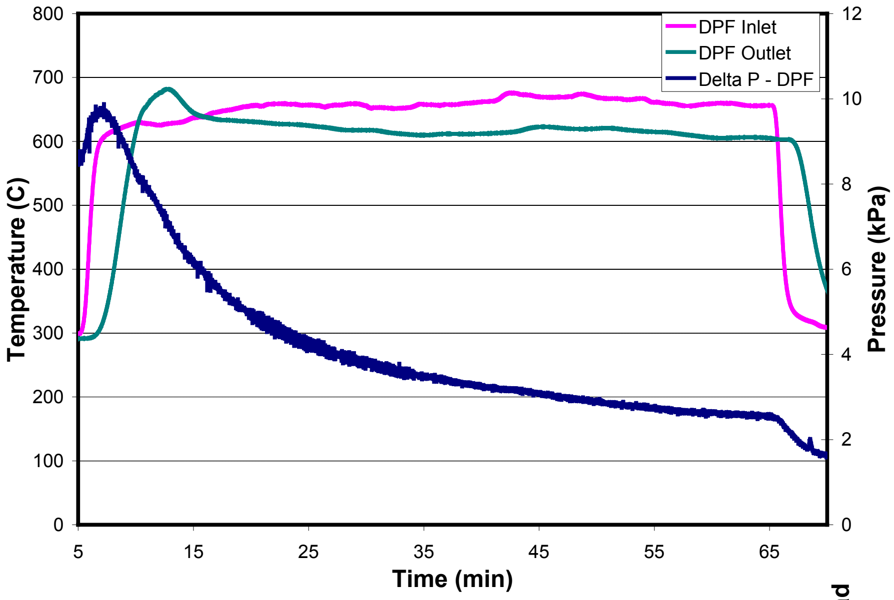
Temperature Operating Windows

SCR Inlet Temperature on FTP-75

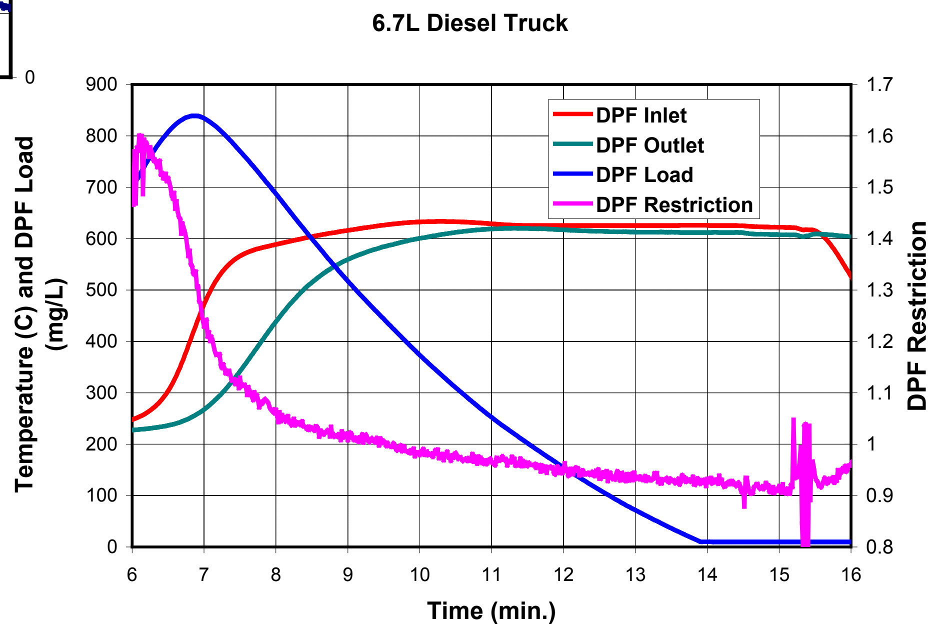


DOE truck with engine < 6.7L resulted in higher temperatures than production truck.

Filter Regeneration Strategies



UCF program truck:
- Downstream fuel injector
- Long regen time studied
- 80% regen in <10 min

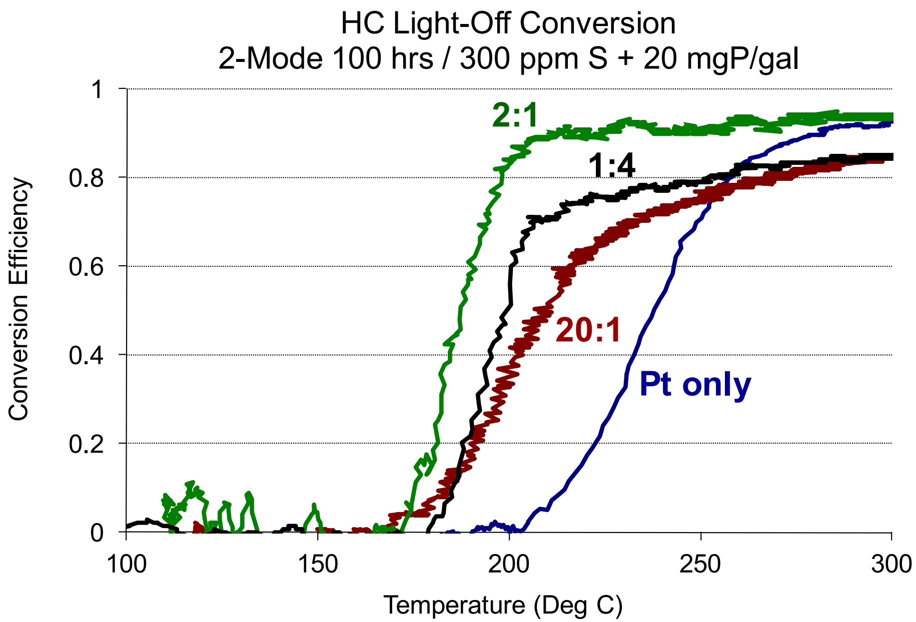


2010 Super Duty:
- Post injection in cylinder
- Shorter regen times
- Similar temperatures
- Refined variables

A Few Challenges Faced During Commercial Urea SCR System Development

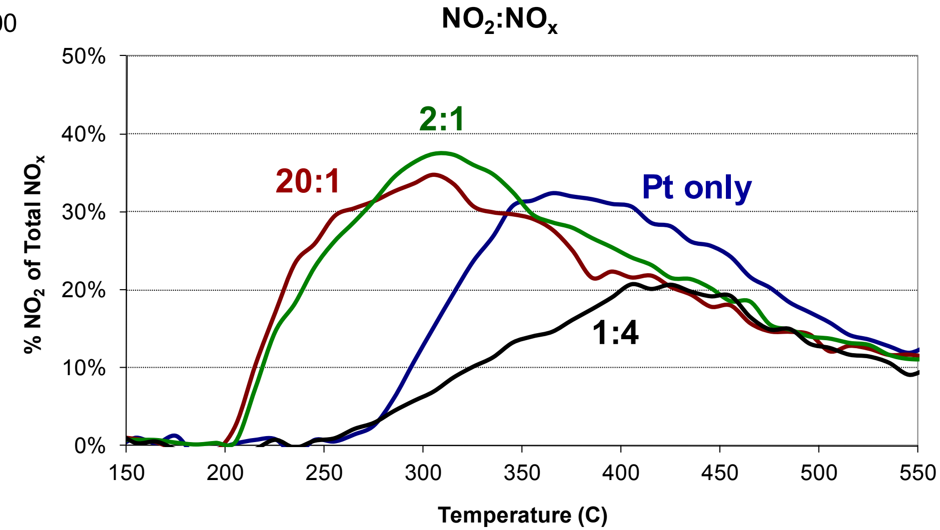
- Thermal stability
- Ammonia storage
- Washcoat adhesion
- HC poisoning/coking
- Precious metal poisoning
- Sulfur effects
- Urea specifications and refill

Thermal Stability of DOC



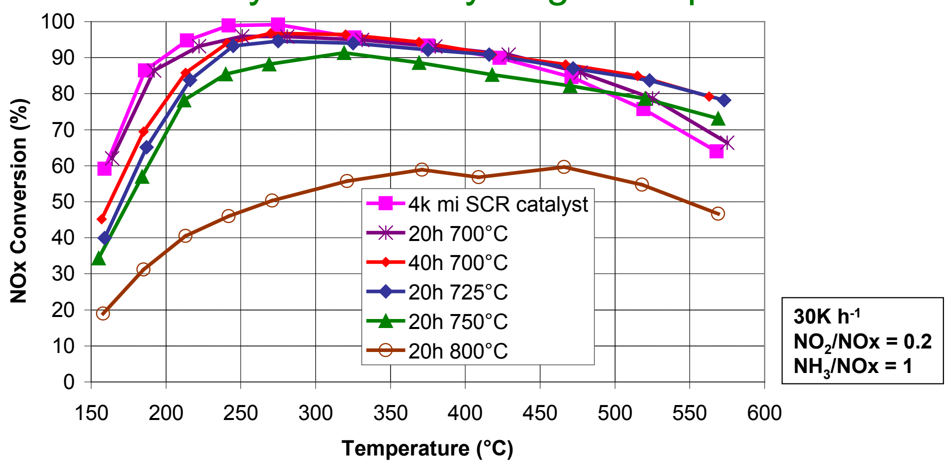
- Addition of Pd to Pt has a stabilizing effect for HC oxidation during cold-start

- Pd also stabilizes Pt for NO oxidation but has no inherent activity itself



Thermal Stability of SCR Catalyst

- Thermal stability of Cu/zeolite recently improved from 750 to 900 C (Cu/beta → Cu/CHA)
- NO_2 no longer needed for low temp conversion
- Lower cost aftertreatment now possible



- With 20% NO_2/NOx feed, the catalyst is durable to 750°C

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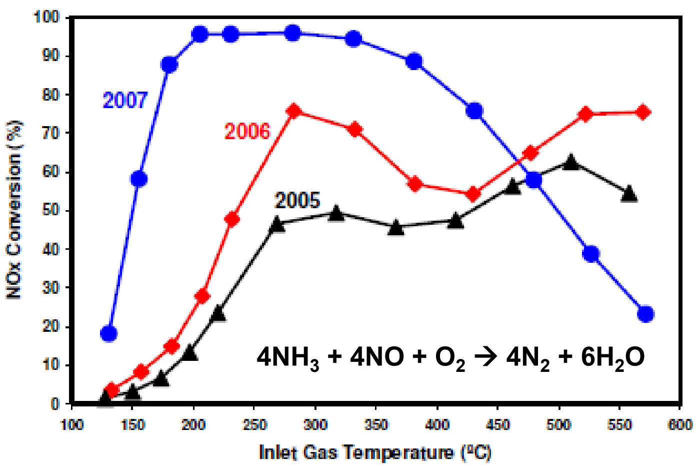
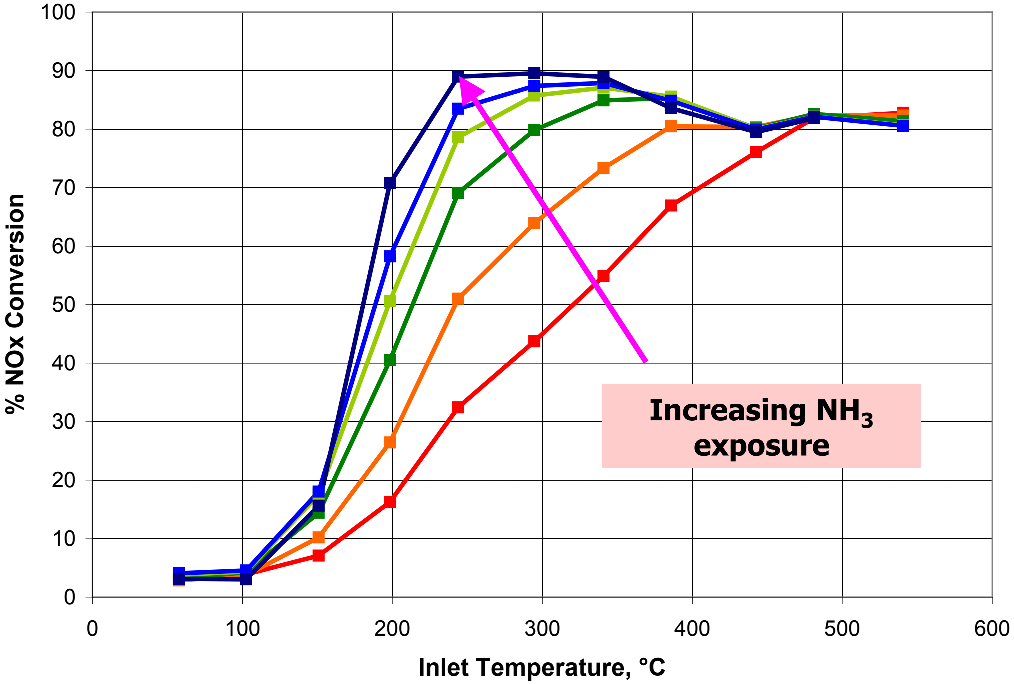


FIGURE 7. NOx conversion of best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 1 hour at 900°C.

Cavataio 2008-01-1025

Urea Dosing Strategy



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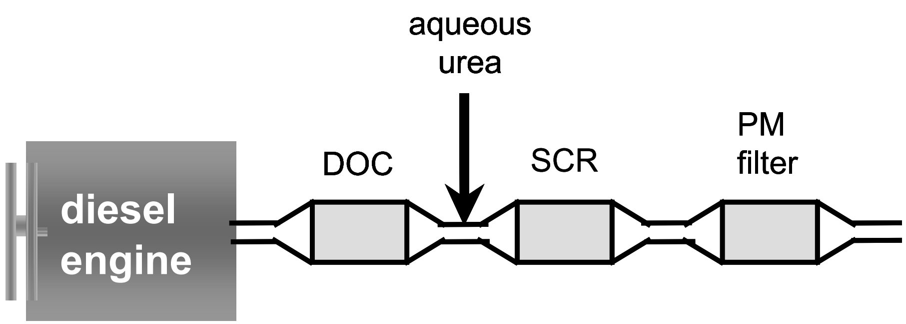
- SCR catalysts can store a large amount of ammonia
- A certain amount of ammonia on the catalyst surface is required for a given NOx conversion
- Data at different NH_3 load are fed into the urea dosing strategy

Washcoat Adhesion of DOC and SCR

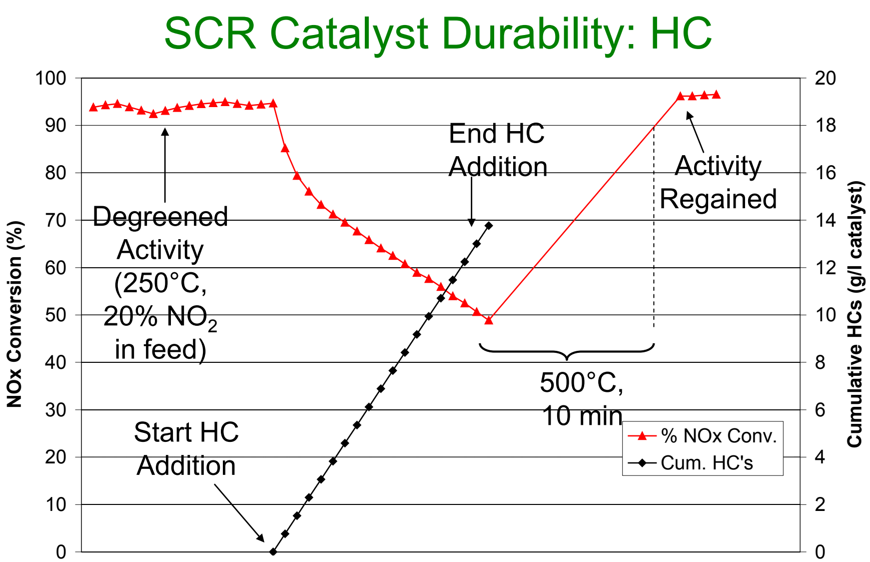


Main concerns for pre-filter catalysts:

- **Loose debris will create backpressure issues in the filter**
- Precious Metal loss to downstream components (primarily SCR)

→ Result was DOC and SCR Washcoat Loss Targets **one order of magnitude lower** than for TWC coatings

HC Poisoning/Coking of Zeolitic SCR



- HC poisoning is reversible after 500°C, lean

HC Inhibition

HC Storage/Exotherm

Both issues were resolved by transition from Cu and Fe/beta to Cu/CHA

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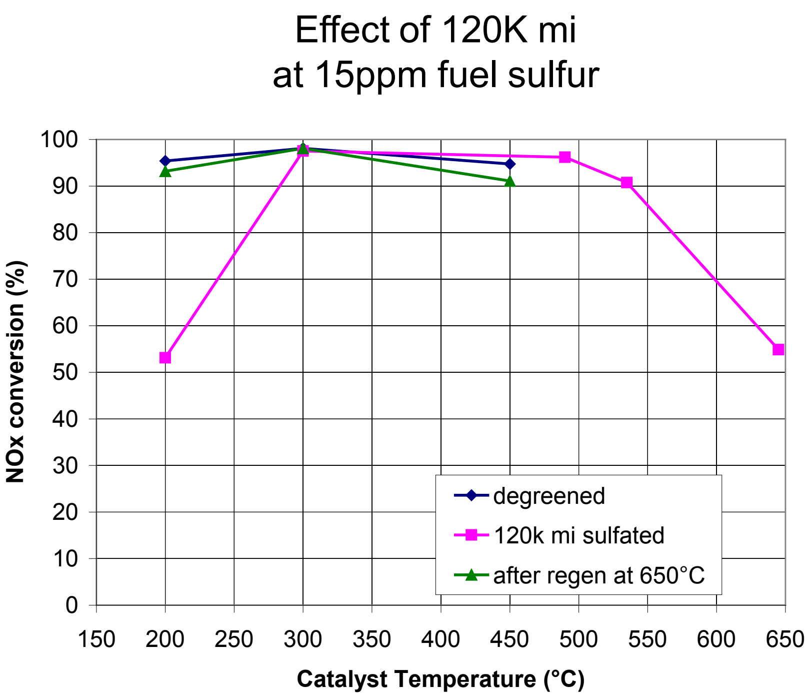
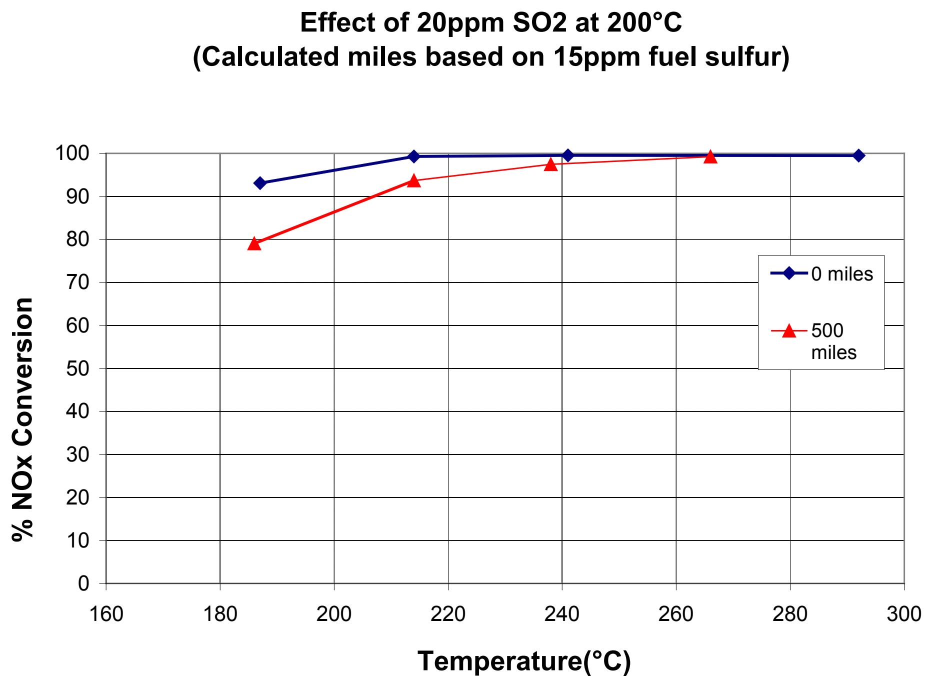
Sulfur Effects on Cu/zeolite





- Sulfur affects NOx activity below 300C
- Sulfur can be removed by lean filter regeneration conditions (>650C)
- Amount adsorbed between regens can be tolerated based on 15 ppm-wt S in diesel fuel

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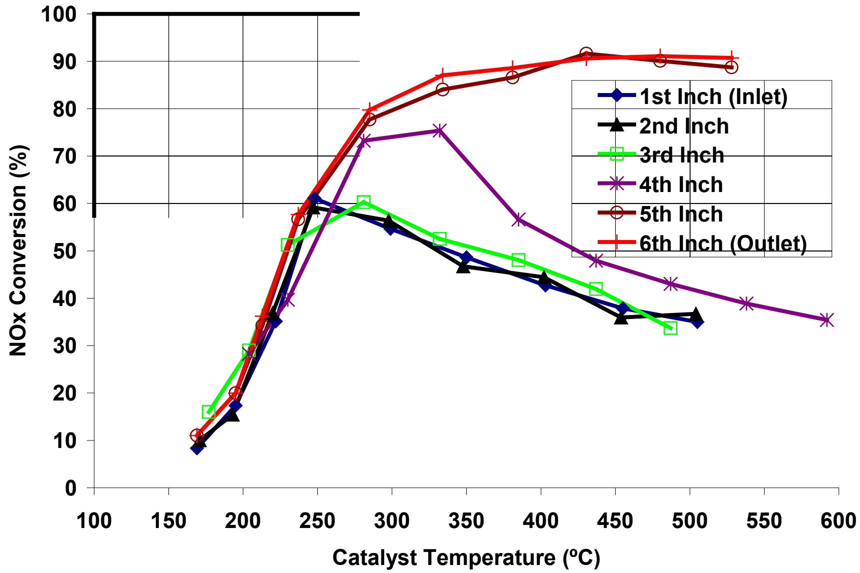
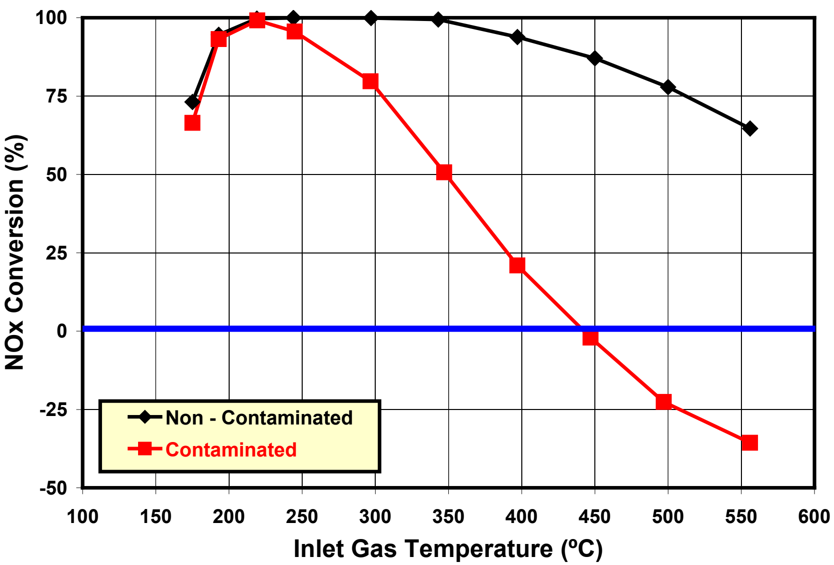
Precious Metal Poisoning of SCR

EVALUATION of DYNAMOMETER AGED FeSCR CATALYST



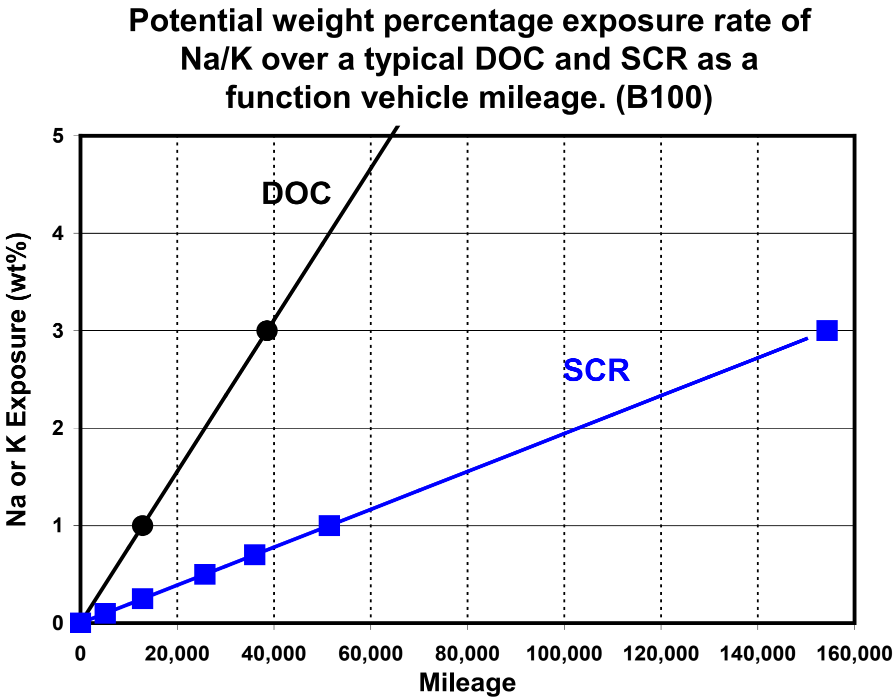
Lab flow reactor Pt poisoning of Cu SCR by upstream DOC

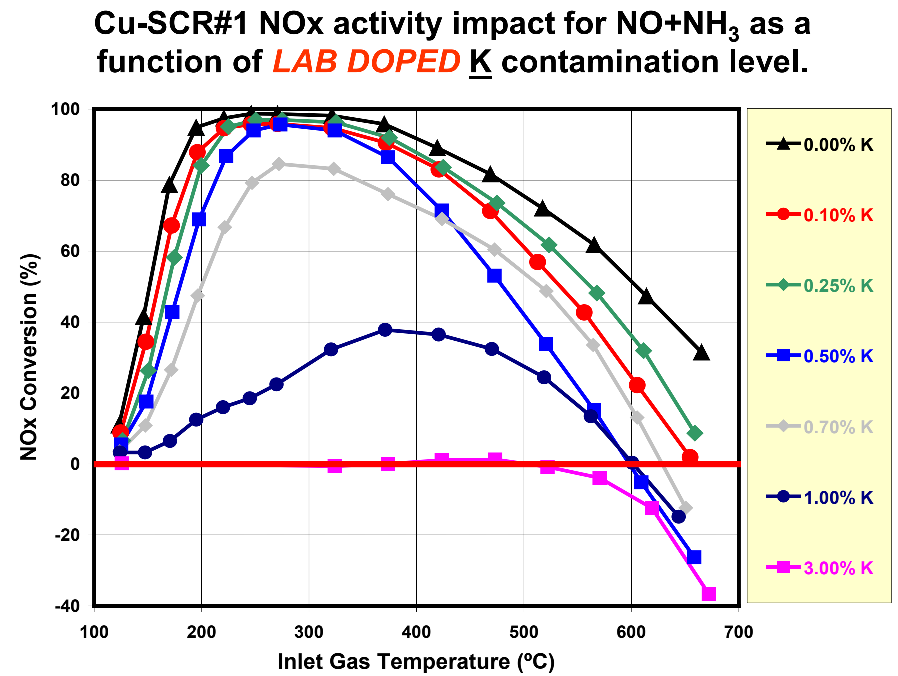


- Pt from upstream DOC can volatilize and interfere with SCR function
- Prime indicators are increased NH_3 oxidation and N_2O make
- Front section of catalyst most affected and can be regenerated
- Pt DOC may be stabilized with addition of Pd and lower exotherm Ts

SAE 2008-01-2488
SAE 2009-01-0627

Potential Biodiesel Effects





SAE 2009-01-2823

- ASTM D6751-08 limits Group I metals (Na+K) < **5 mg/kg** for biodiesel component
- The actual deposit amount on the catalysts will depend on the capture efficiency
- Real-world biodiesel may have much lower Na & K than the spec

Urea Specifications and Refill

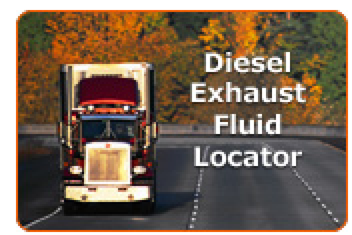
- OEMs and suppliers formed USCAR working group to define specifications
- Aqueous urea is sold as “Diesel Exhaust Fluid” or “DEF”
- Current refill uses bottles, drums, totes, and bulk dispensers
- ~ $2.79/gal in bulk
- ~ $4.65/gal in bottles

  http://www.dieselexhaustfluid.com/

  Mattina, 16th Annual Fleet Fueling Conference, Sept 2010.
- Websites offer DEF locations

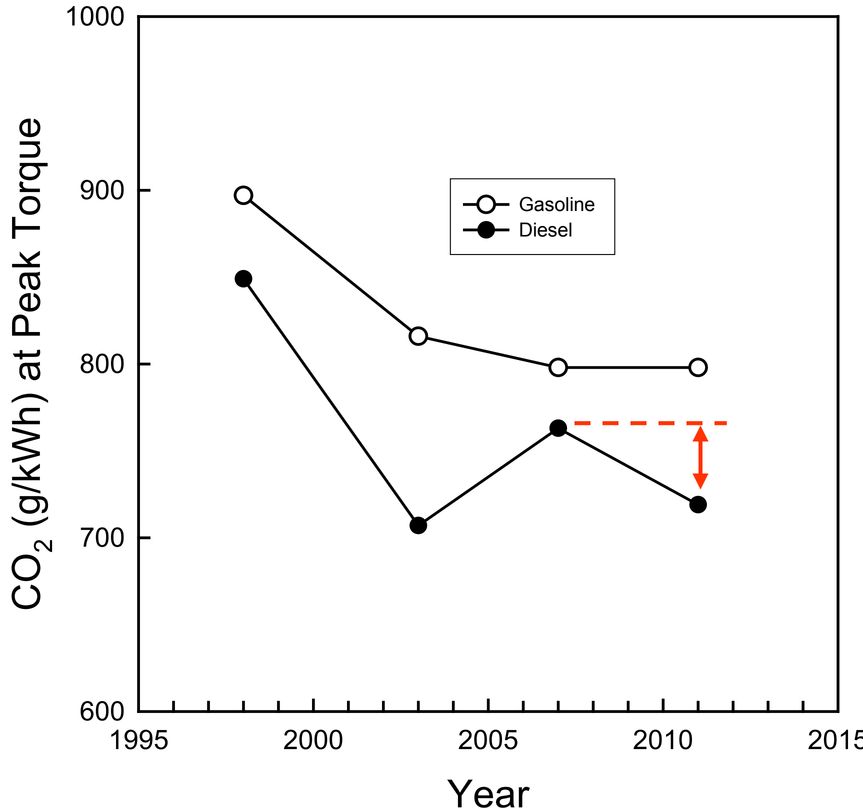
http://www.factsaboutscr.com

DISCOVER DEF .COM



Diesel MDV Impact on Sustainability

Comparison of Class 2b / Class 3 peak torque brake specific CO_2 for medium-duty vehicles 1998 - 2011 calendar years.



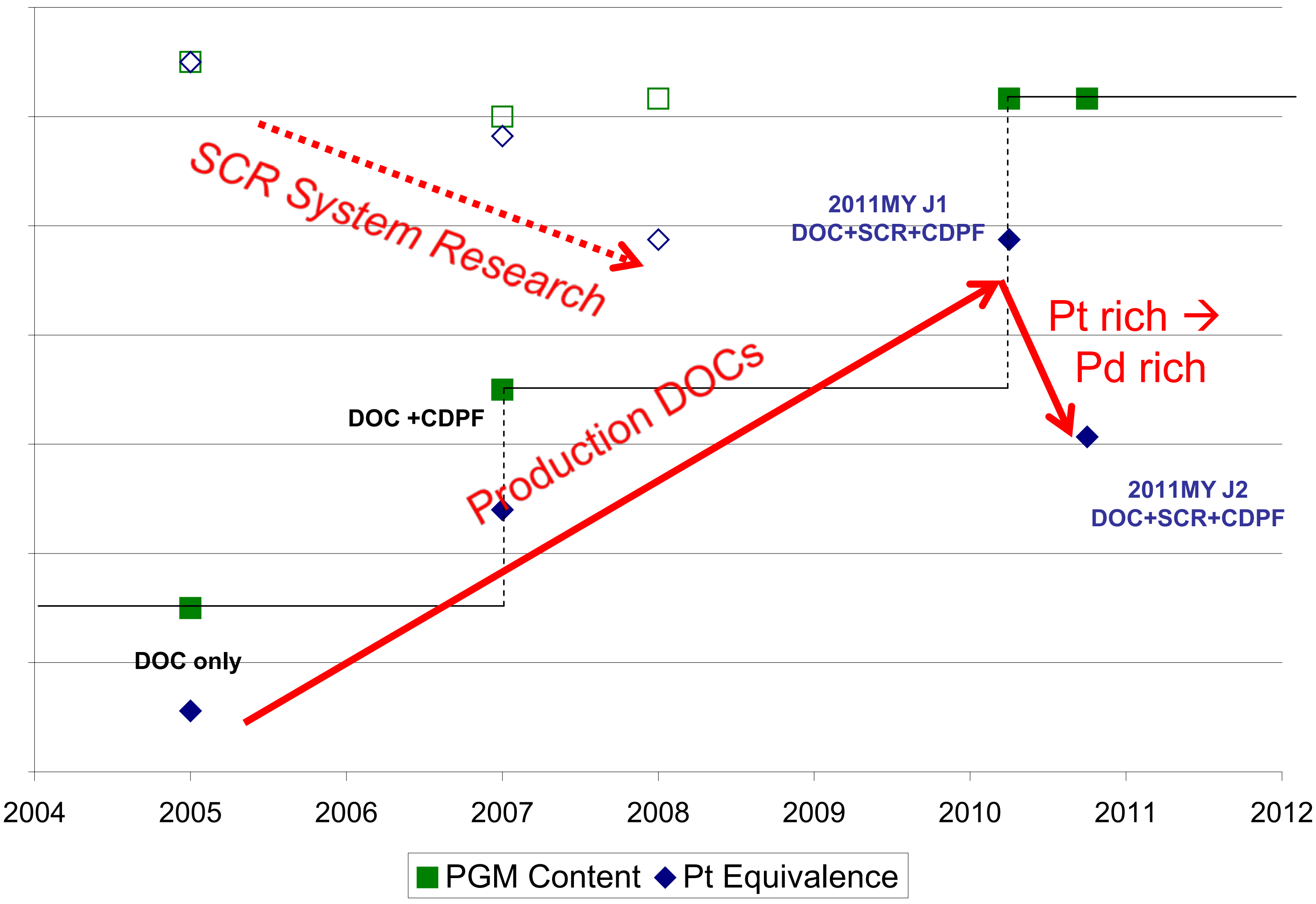
- ***Data from EPA HD database.***
- ***Figure from T.J. Wallington, C.K. Lambert, W.C. Ruona, Energy Policy, in review.***

Urea SCR used on majority of diesels in 2010+.

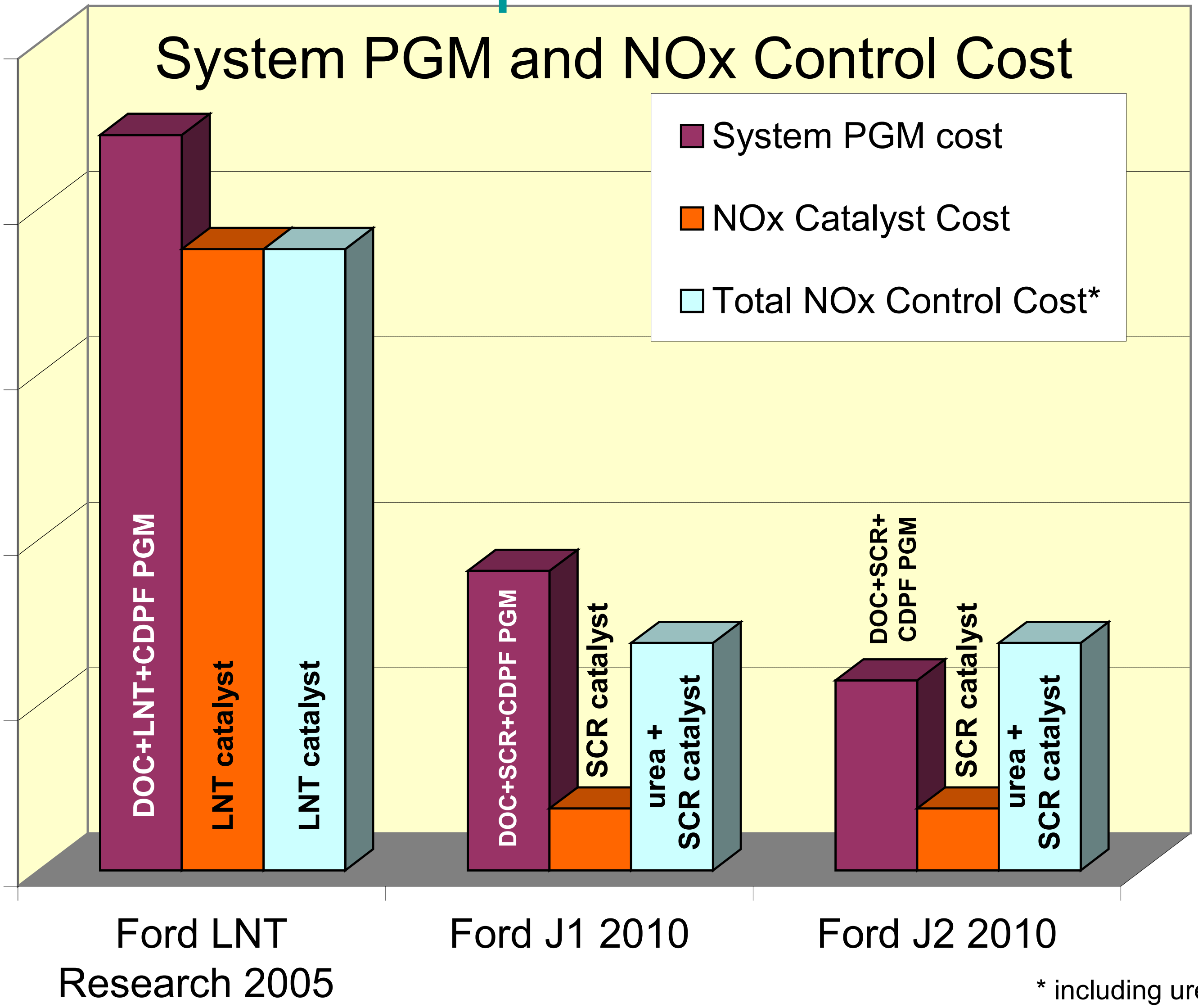
- At light/moderate loads the CO_2 advantage for SCR-equipped diesel will be > 10%.

Diesel MDV Impact on Sustainability

Precious Metal Usage in Super Duty DOCs



Diesel MDV Impact on Sustainability



* including urea hydraulics

Conclusions

- Strategic DOE tech funding can lead to production components and systems
- Important to assess potential early
- General focus on saving and/or replacing critical resources is effective
- Tech may be used in products/ways you did not initially envision

Next Steps for Diesel MDV

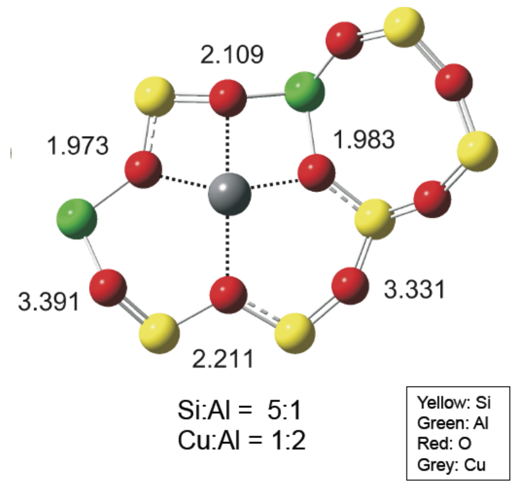
- Materials cost reductions continue
  - PGM reductions
  - substitution of Pt with Pd
- Aftertreatment efficiency improvements
  - catalyst durability improvements
  - catalyst structure improvements
  - heating strategies
  - understand non-uniform SCR aging

Further Research Needed on Small Pore Zeolite Catalysts

- Cu/CHA development enabled Cu/zeolite for automotive use
- Related patents and publications:
  - **Zones** "*Zeolite SSZ-13 and its method of preparation*" US4544538, 1985
  - **Bull et al.**, "*Copper CHA zeolite catalysts*", US7601662, 2009
  - **Kwak et al.**, "*Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NOx with NH_3*", J. Catal. 275 (2010) 187-190
  - **McEwen et al.**, *"Integrated operando X-ray and DFT characterization of Cu-SSZ-13 exchange sites during the selective catalytic reduction of NOx with NH_3*", Catal. Today, in press.

Basic experimental and computational research needed to guide rational improvement of small pore zeolites:

- wider temperature window → Fe analog?
- lower ammonia storage per unit volume
- smaller catalyst size per unit volume



Schneider, CLEERS Telecon, Sept 2011

Acknowledgments

DOE: DE-FC26-01NT41103 (2001-2005)

PNNL-Ford CRADA – Freedom Car (2006-2011)

Ford: Kevin Guo, Yisun Cheng, Cliff Montreuil, James Girard, Hungwen Jen, Scott Williams, Dave Kubinski, Brendan Carberry, Rick Soltis, Devesh Upadhyay, Michiel van Nieuwstadt, Mike Levin and many others

FEV: Erik Koehler, Dean Tomazic, Phillip Adomeit

ExxonMobil: Mike Noorman, Charlie Schleyer, Rich Grosser

Catalyst Suppliers: BASF, JMI, Umicore

And many, many more …

References

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