Future Directions in Diesel SCR Systems

2012 CLEERS Workshop

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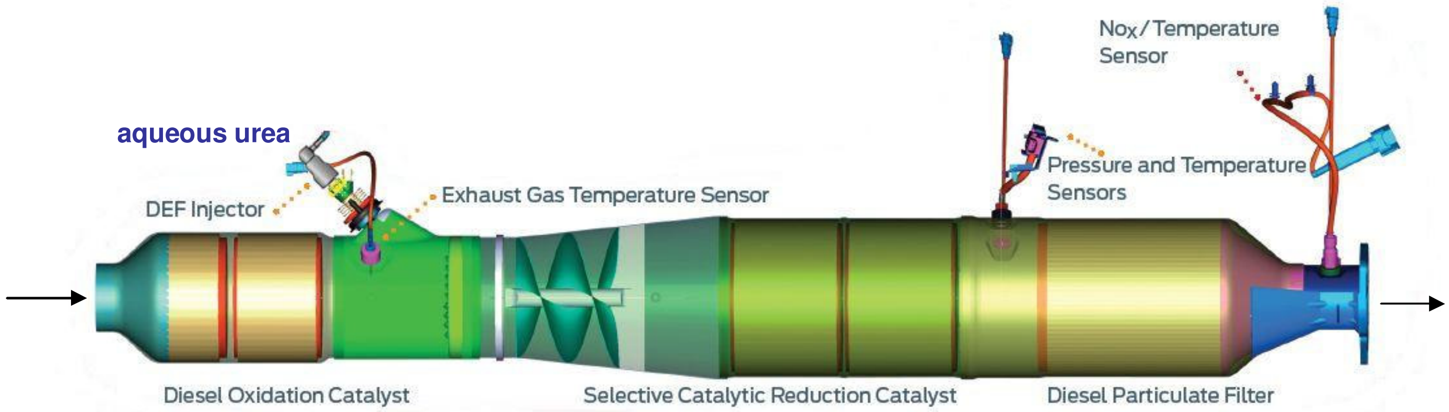
Outline

- Background of a 2010 U.S. SCR system
- Catalyst development challenges
- Catalyst and filter structures
- LEVIII catalyst system predictions
- Greenhouse gases (N_2O)
- Summary / Next steps
- Acknowledgements

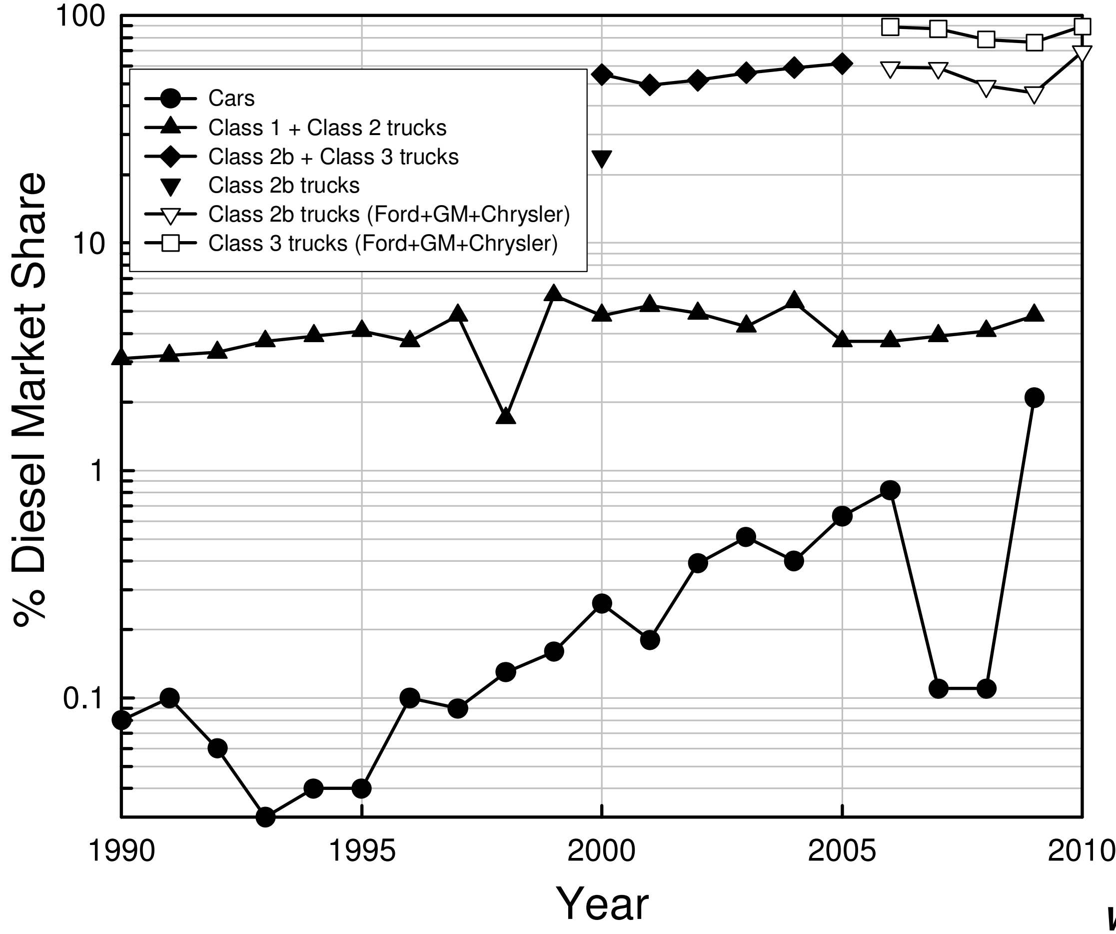
2010 U.S. Super Duty Diesel Aftertreatment



- 2011 model year trucks >8500 lbs (MDV)
- Certified as complete vehicle on LD FTP-75
- LEVII emissions (0.2 g/mi NOx)
- 120,000 mi durability

media.ford.com, 2011

Diesel Fraction of New U.S. Vehicle Sales



Trucks

Class 3: 10,001-14,000 lbs

Class 2b: 8,501-10,000 lbs

Trucks

Class 1: < 6,000 lbs

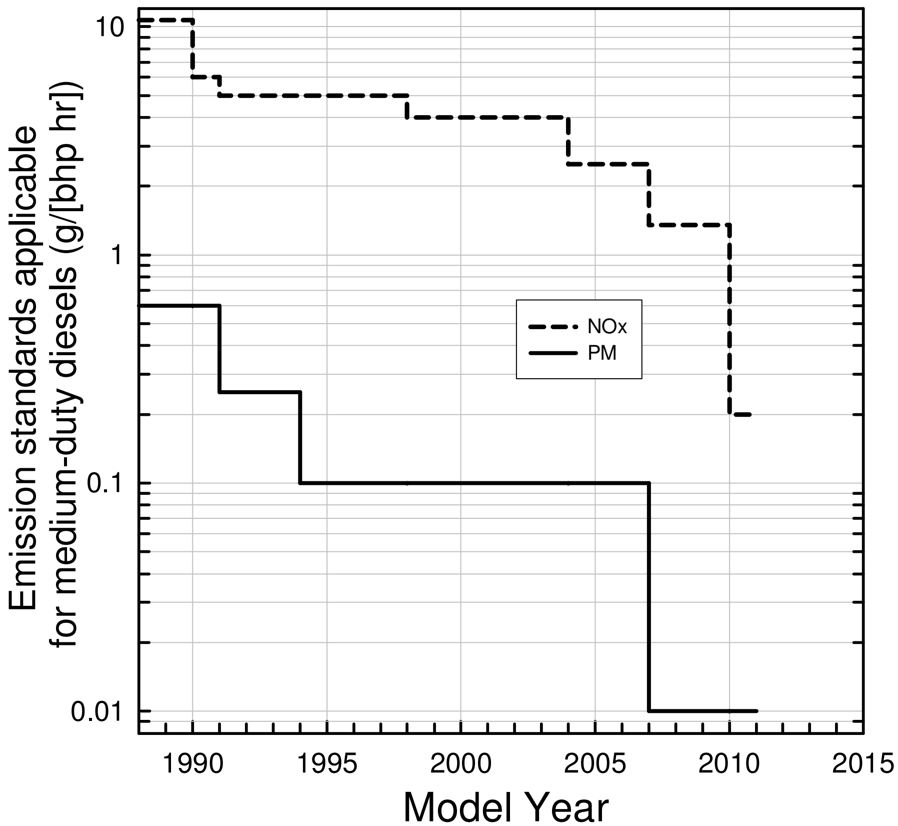
Class 2: 6,001-10,000 lbs

Cars

Wallington et al., Energy Policy, in press

A Brief History of U.S. Diesel Aftertreatment

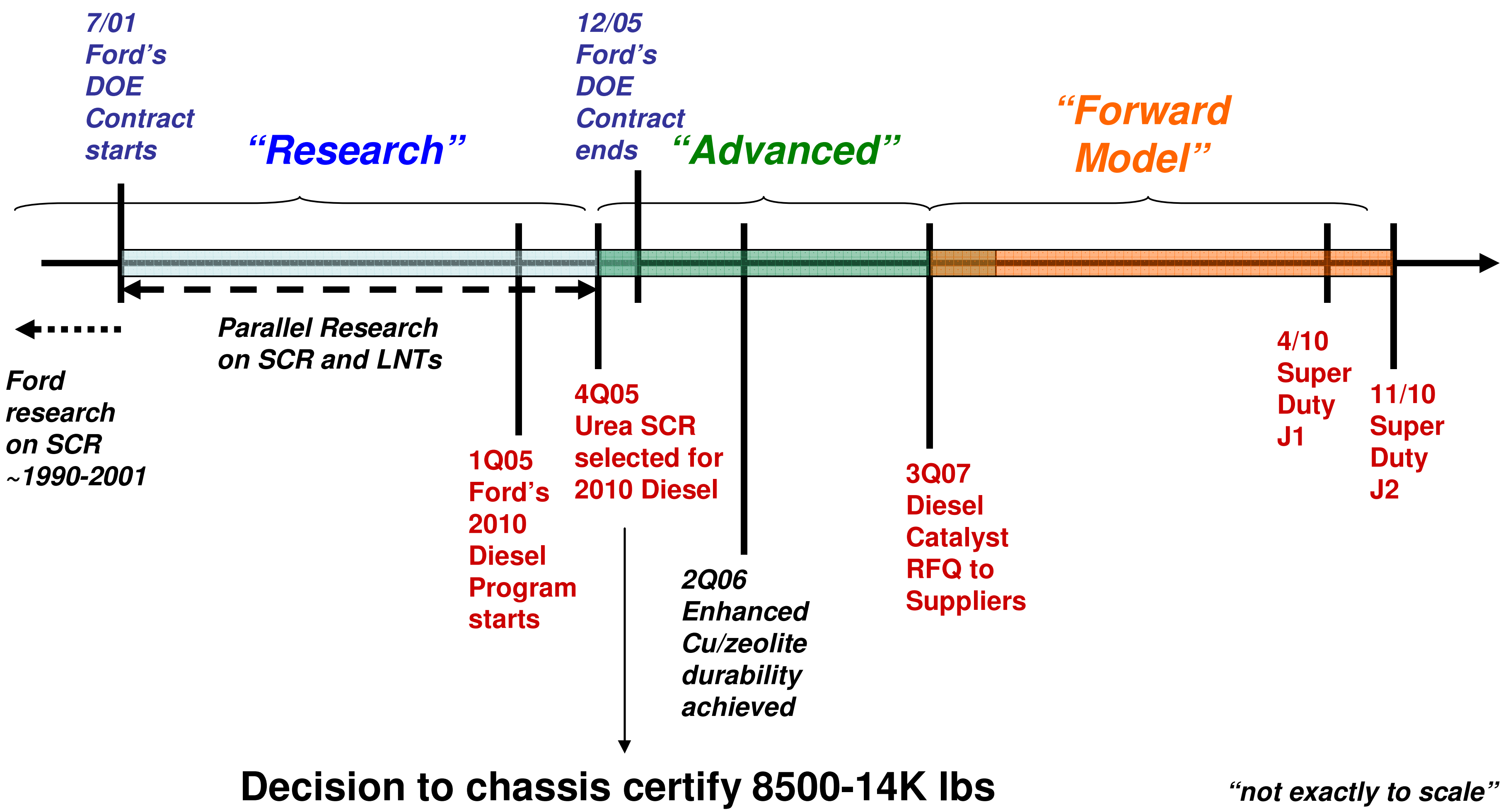
Evolution of emissions standards for NOx and PM.



- mid-1990s: Diesel oxidation catalysts (DOCs) with ceria and alumina for PM oxidation
- 2007:
  - ultra-low sulfur diesel,
  - particulate filters for PM control
  - high precious metal DOCs
  - lean NOx control (NOx traps)
- 2010:
  - lean NOx control (urea SCR)

Wallington et al., Energy Policy, in press.

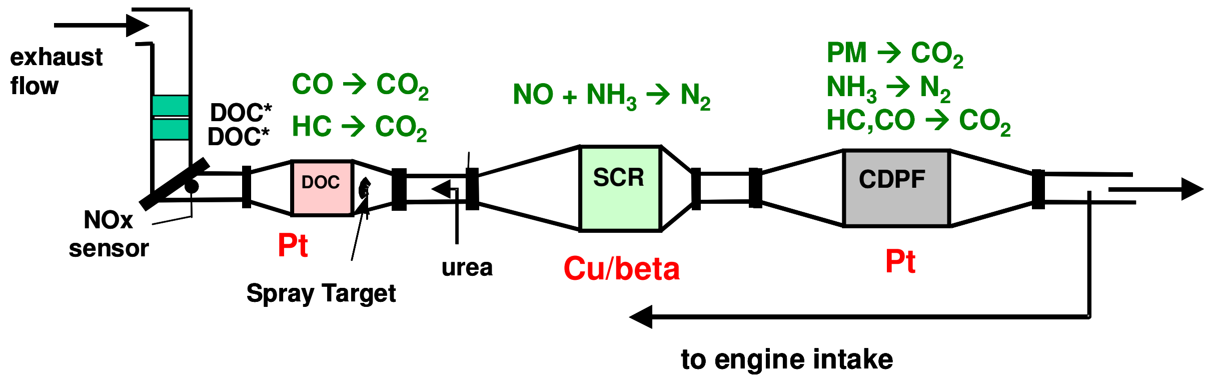
Timeline for 2010 Diesel Aftertreatment



Diesel Aftertreatment Layout

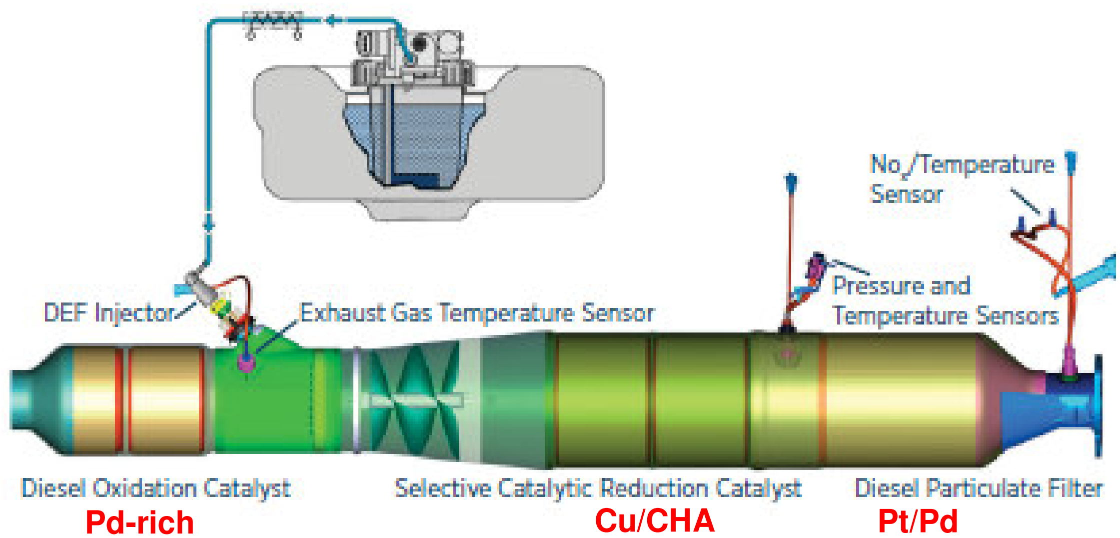
DOE Program Truck
6000 lbs LDDT

- Pt DOC
- Cu/beta SCR
- Pt CDPF



2011MY Super Duty
8,500 – 14,000 lbs

- Pd-rich DOC
- Cu/CHA SCR
- Pt/Pd CDPF

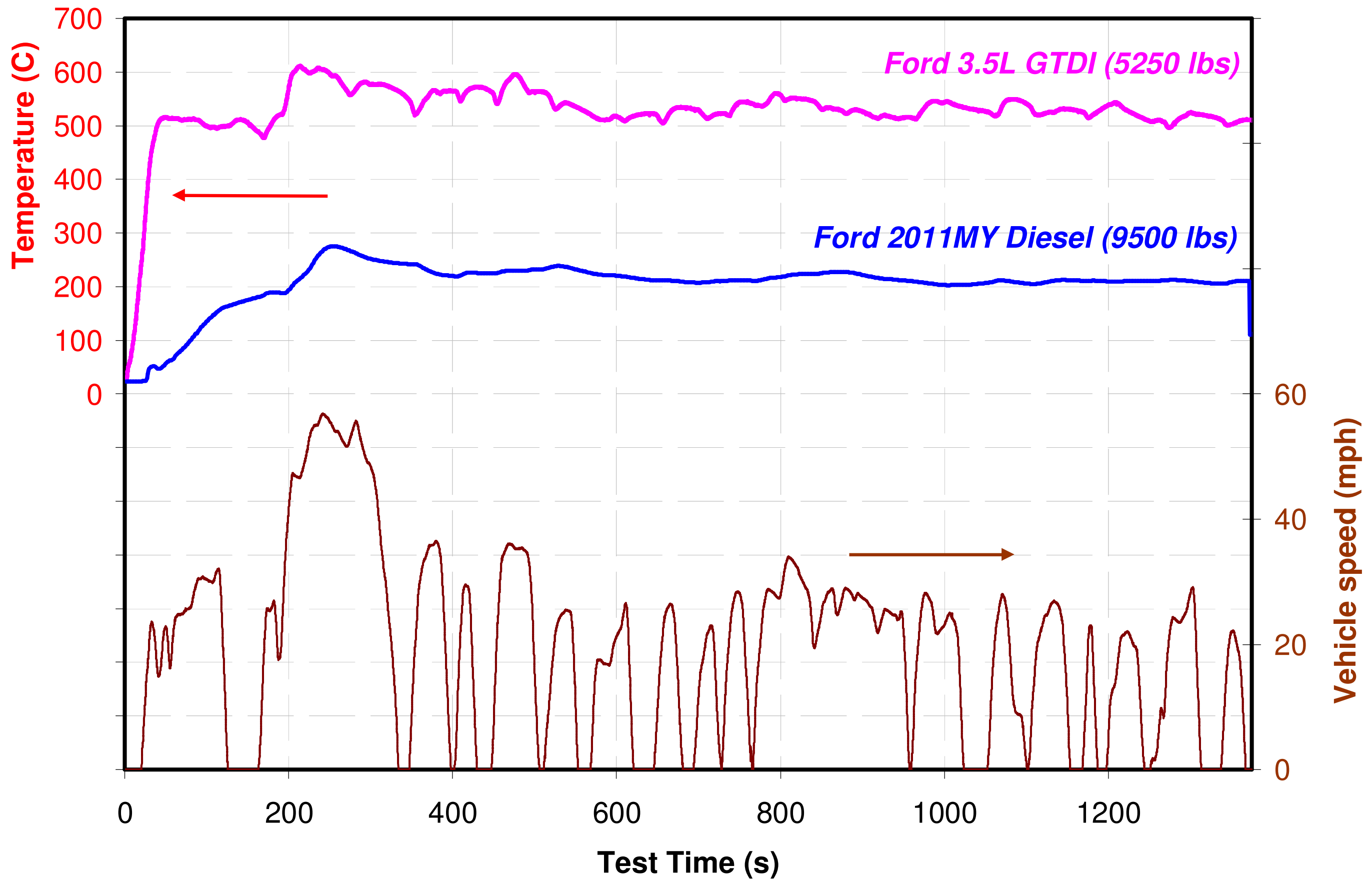


A Few Challenges Faced During Commercial Urea SCR System Development

- Low exhaust gas temperatures
- Catalyst thermal stability
- HC poisoning/coking of SCR
- Precious metal poisoning of SCR
- Catalyst deterioration by sulfur
- Catalyst system cost

Temperature Operating Windows

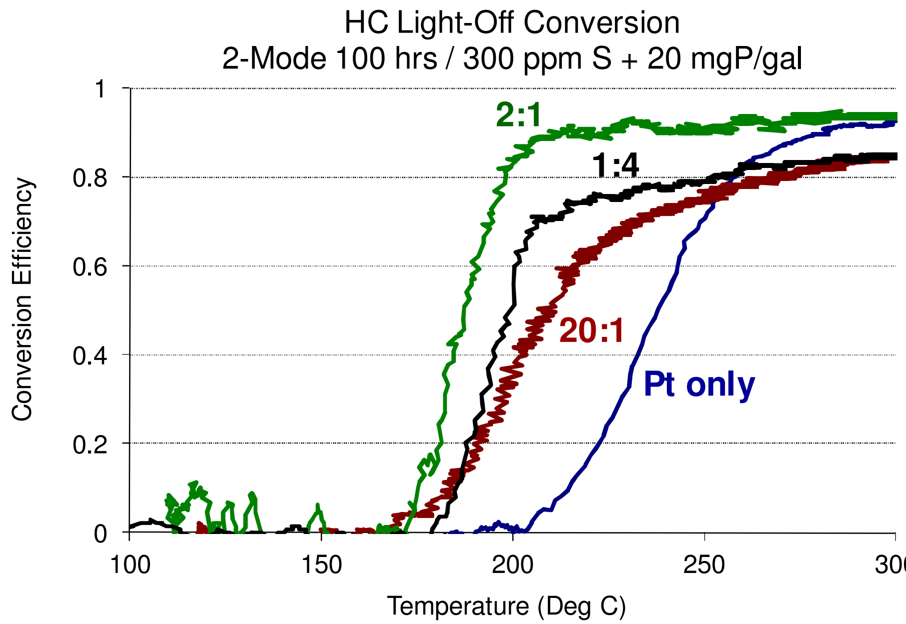
SCR Inlet Temperature on FTP-75



Diesel truck has very low exhaust gas temperatures.

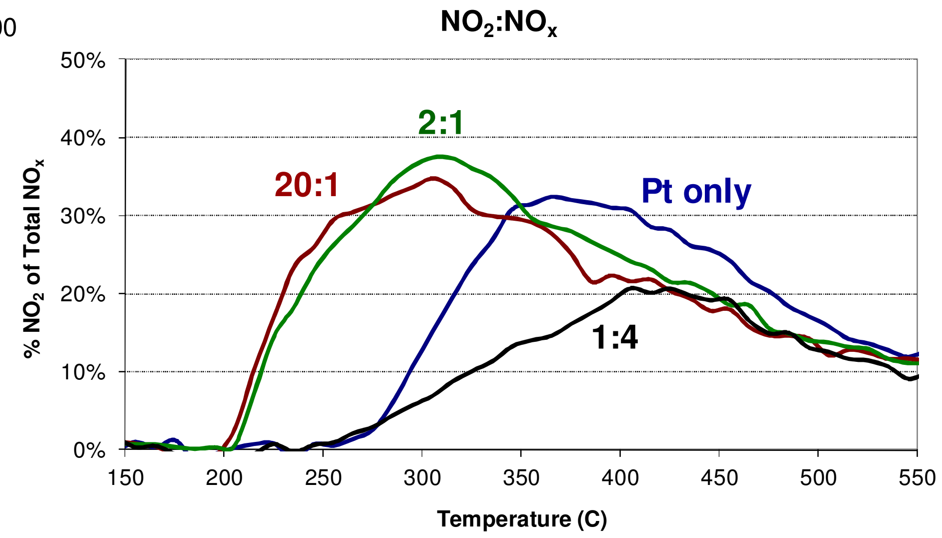
Research and Advanced Engineering

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℃ (Cu/beta → Cu/CHA)
- NO_2 no longer needed for low temp conversion
- Lower cost aftertreatment now possible

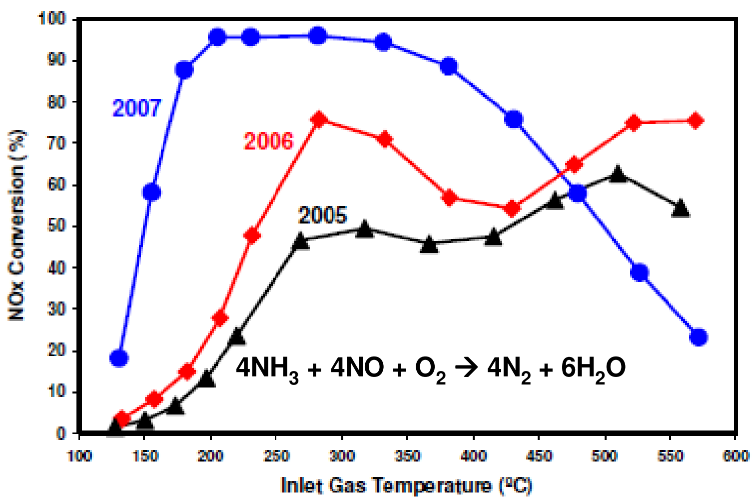


FIGURE 7. NOx conversion of best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 1 hour at 900℃.

Cavataio 2008-01-1025

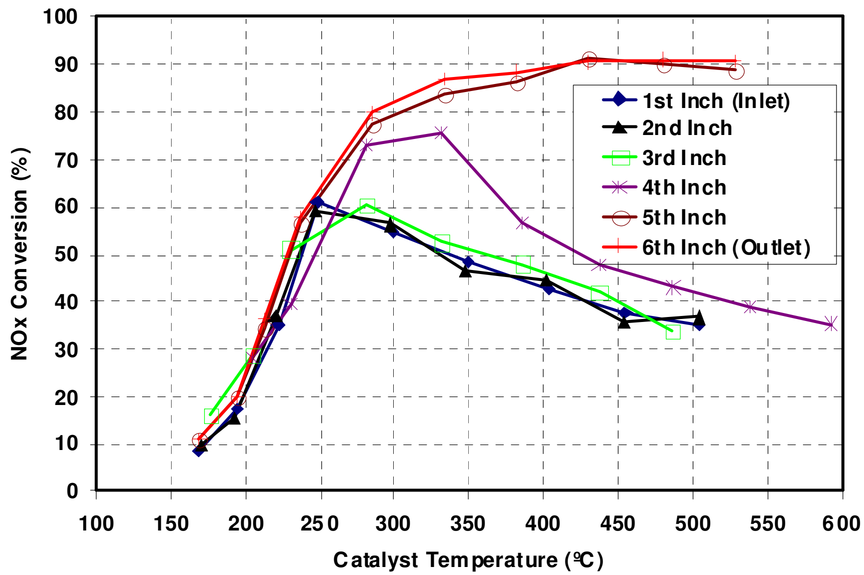
HC Poisoning/Coking of Zeolitic SCR

SCR HC/coking issue resolved by transition from Beta to CHA.

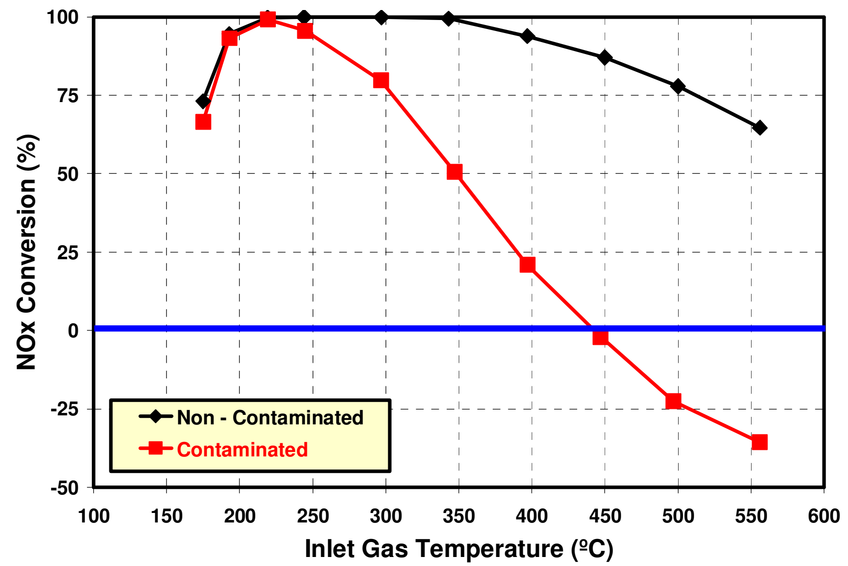
DEER 2004

Precious Metal Poisoning of SCR

EVALUATION of DYNAMOMETER AGED FeSCR CATALYST



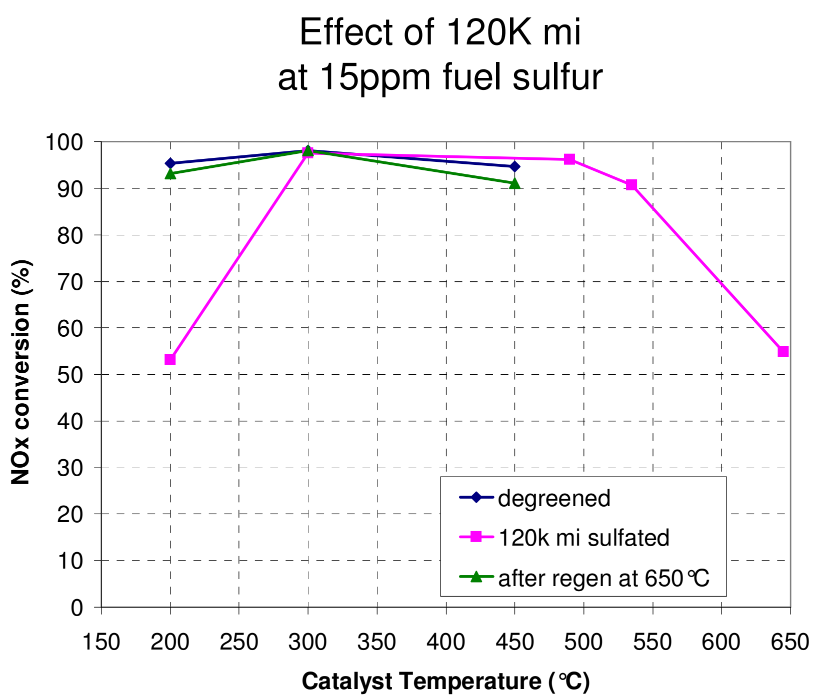
Lab flow reactor Pt poisoning of Cu SCR by upstream DOC

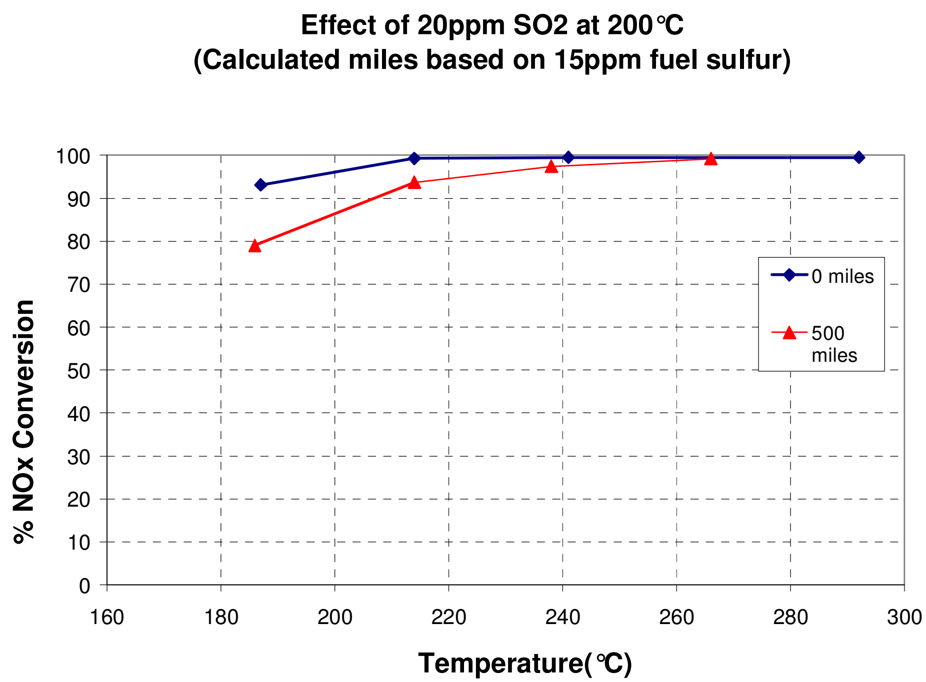


- Pt from upstream DOC can volatilize and interfere with SCR function
- Prime indicators are increased NH_3 oxidation and N_2O make
- Front section of catalyst most affected and can be regenerated
- Pt DOC may be stabilized with addition of Pd and lower exotherm Ts

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

Sulfur Effects on Cu/zeolite



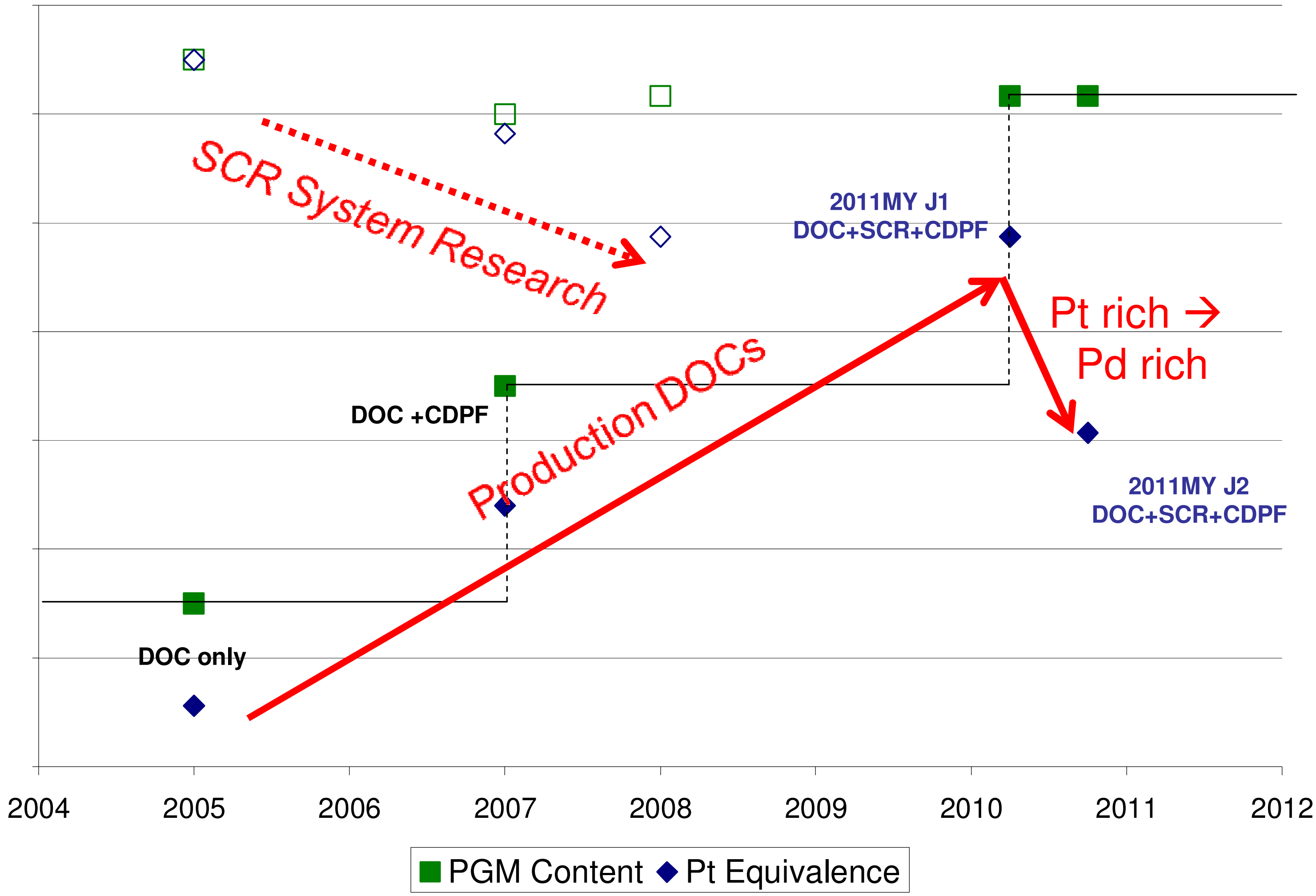


- Sulfur affects NOx activity below 300C
- Sulfur can be removed by lean filter regeneration conditions (>650C)
- Amount adsorbed between regens can be tolerated based on 15 ppm-wt S in diesel fuel

DEER 2004

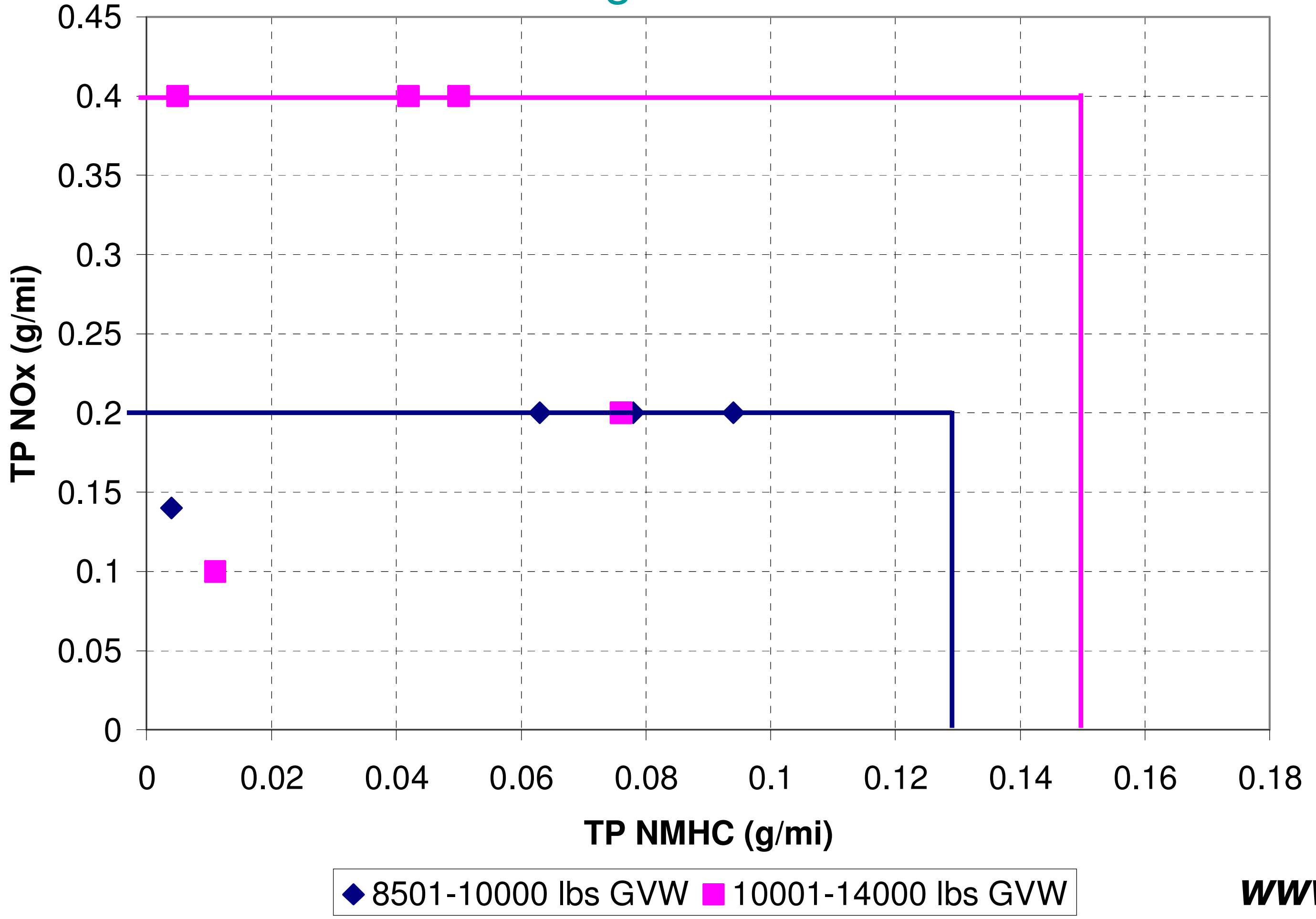
Catalyst Cost Impact

Precious Metal Usage in Super Duty DOCs



2012 MDV Cert Data

Ford, GM, Daimler, Isuzu use Urea SCR
Dodge uses LNT



www.arb.ca.gov

Future Implications for Chassis Certified Diesel MDV

- All 8501 to 10K lbs must chassis certify (~2016MY)
- FUL increased to 150,000 mi (2016MY start)
- SFTP at FUL (all emissions level lower than ULEV340 or ULEV570 require SFTP)
  - 8501-10K lbs US06 + SC03
  - 10,001 – 14K lbs: LA92 + SC03
- CO_2 reporting (2012MY)
- Greenhouse gases (CH_4, N_2O - reporting in 2012MY, regulated in 2013MY)

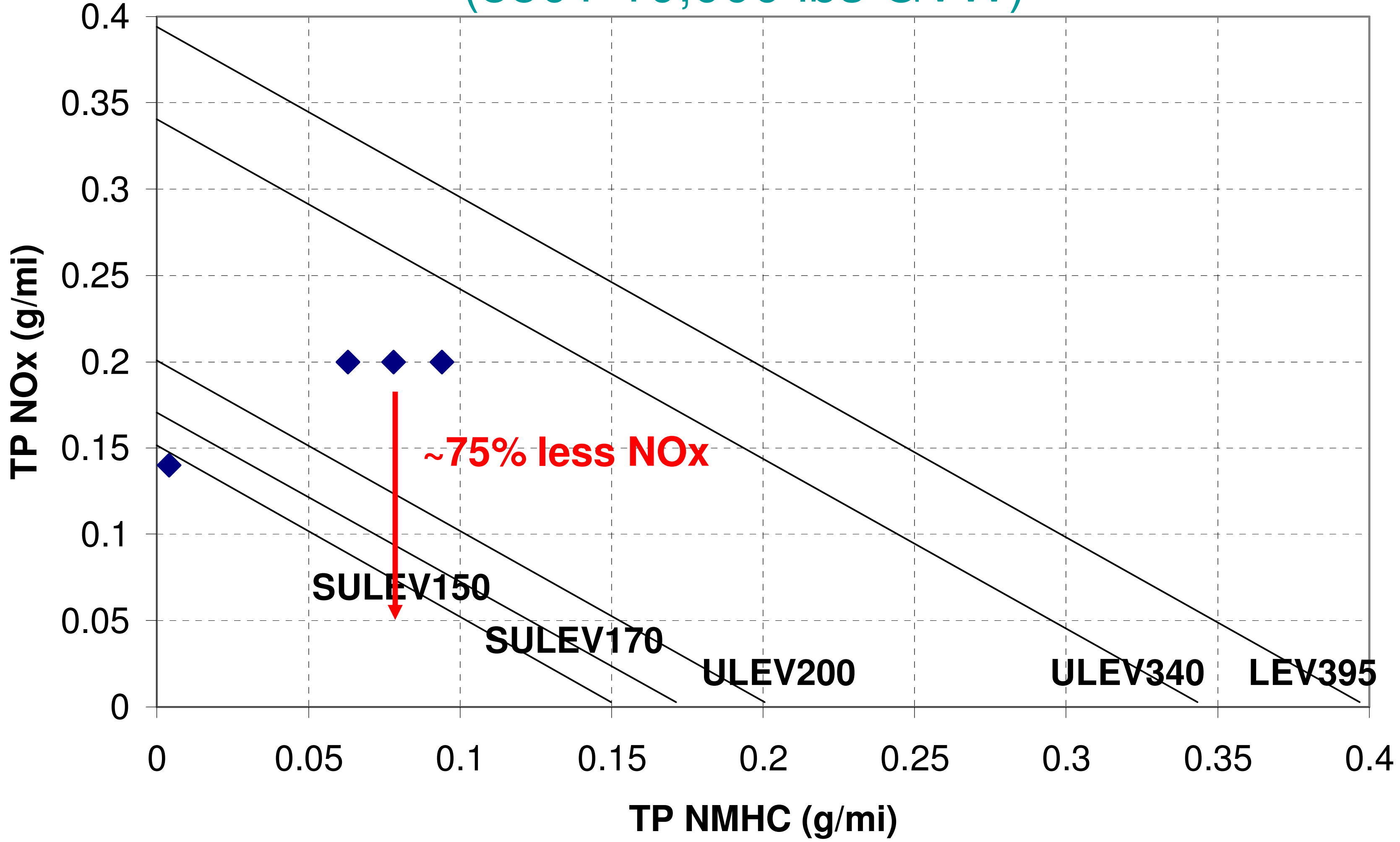
Accelerated Aging Conditions Equivalent to 150K mi

- Hydrothermal Oven:

DOCs	900°C, 80hrs
SCR catalysts	800°C, 80hrs
SCR filter	800°C, 80hrs
Slip catalyst	750°C, 80hrs

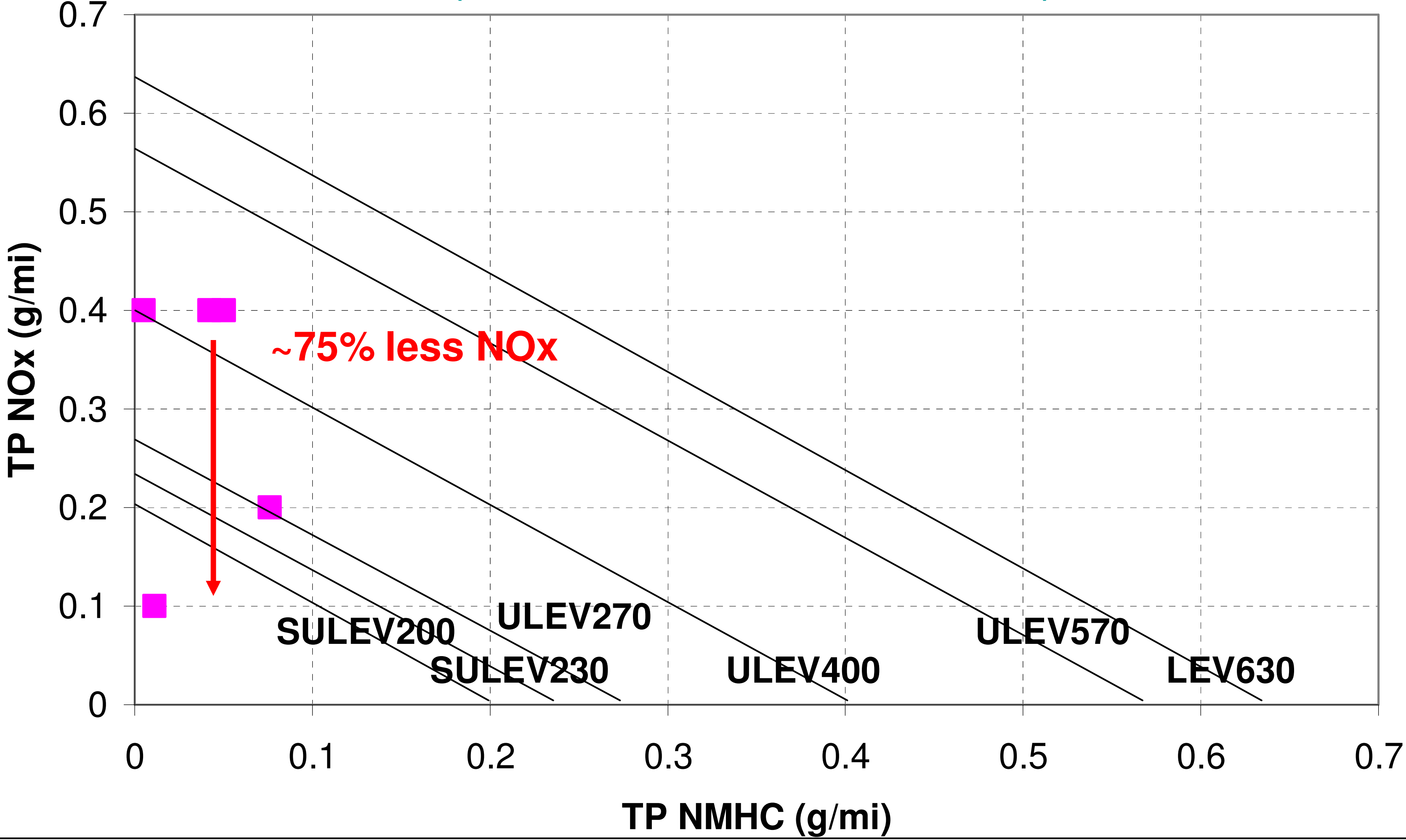
2012 Chassis Cert Data

(8501-10,000 lbs GVW)

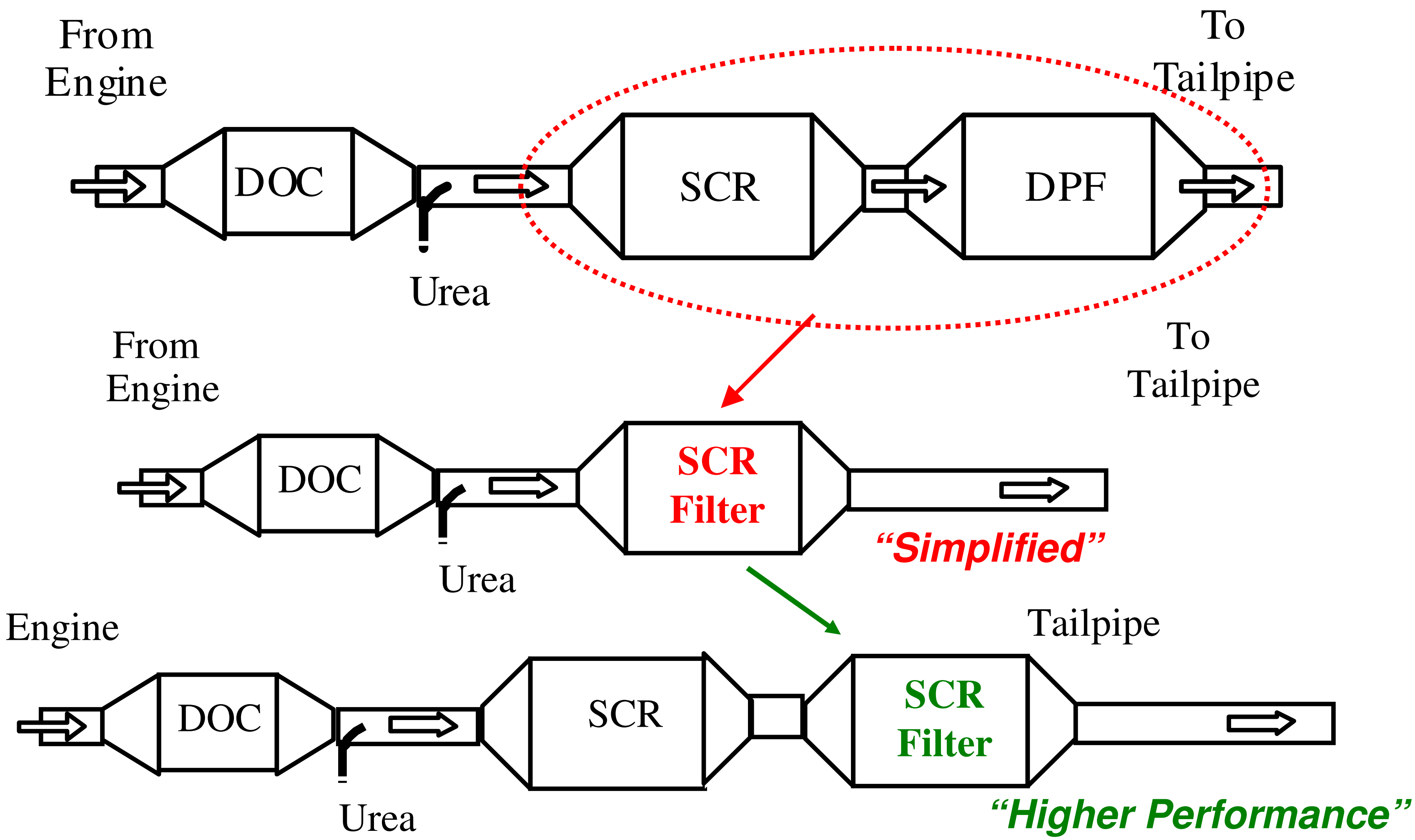


2012 Chassis Cert Data

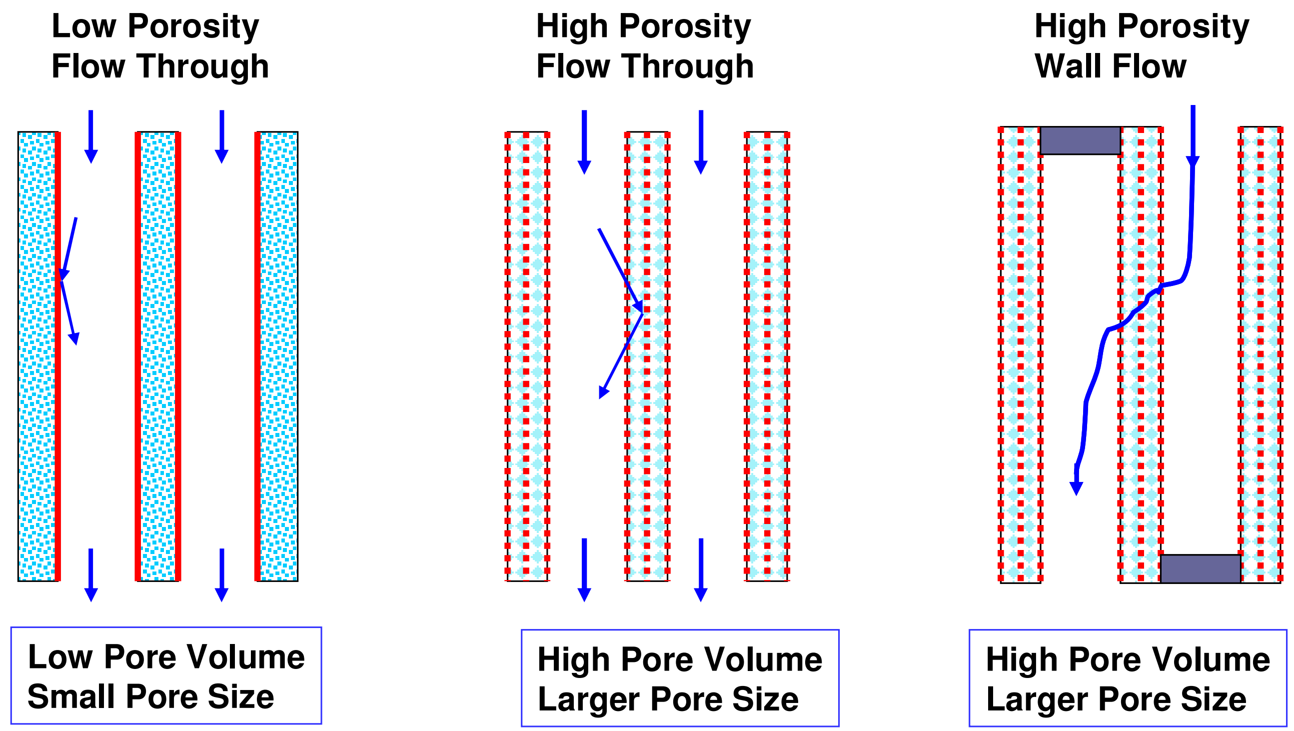
(10,001-14,000 lbs GVW)



Potential SCR Technologies: SCR Filter

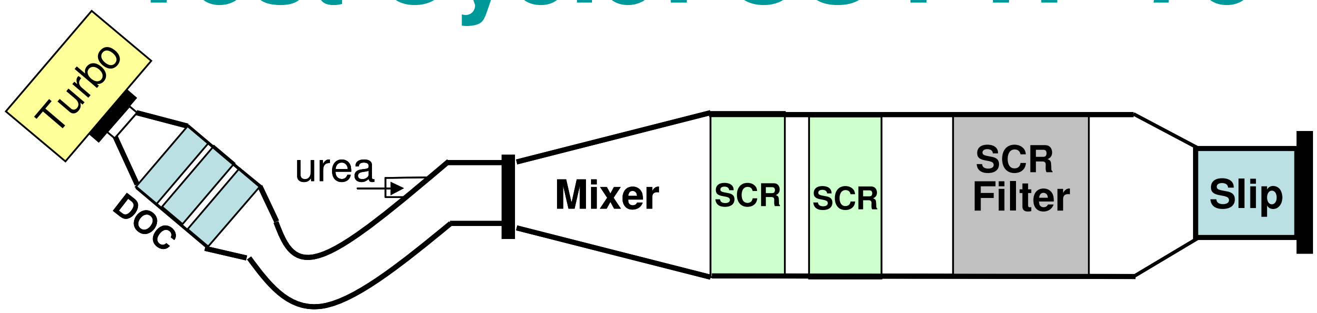


Modeling Implications of SCR Filter Technology

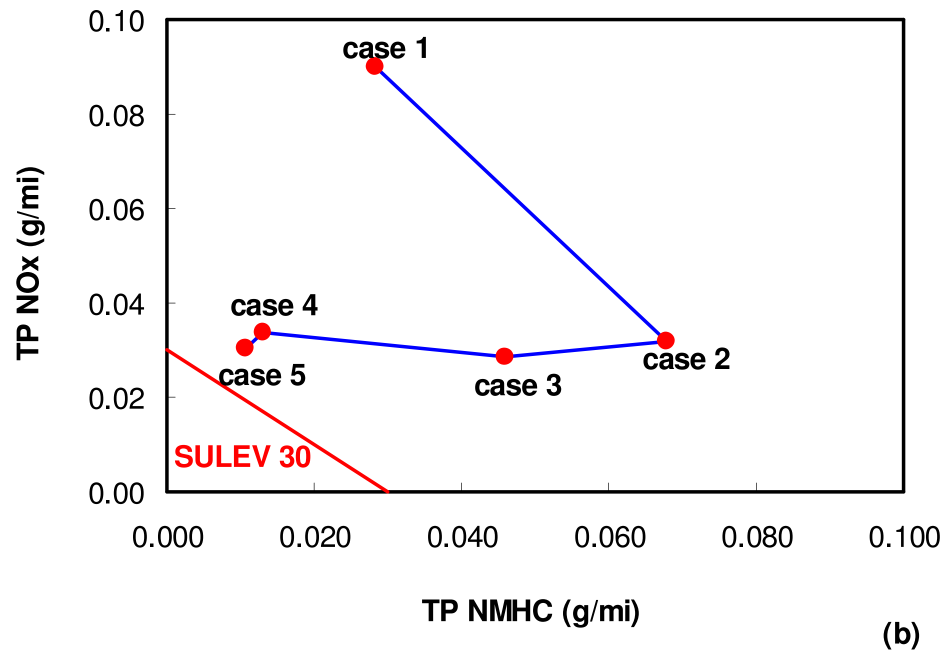


- Wall flow vs channel flow
- Lower washcoat loading per volume
- Backpressure sensitive

4.4LPrototype Light Duty Diesel Test Cycle: US FTP-75



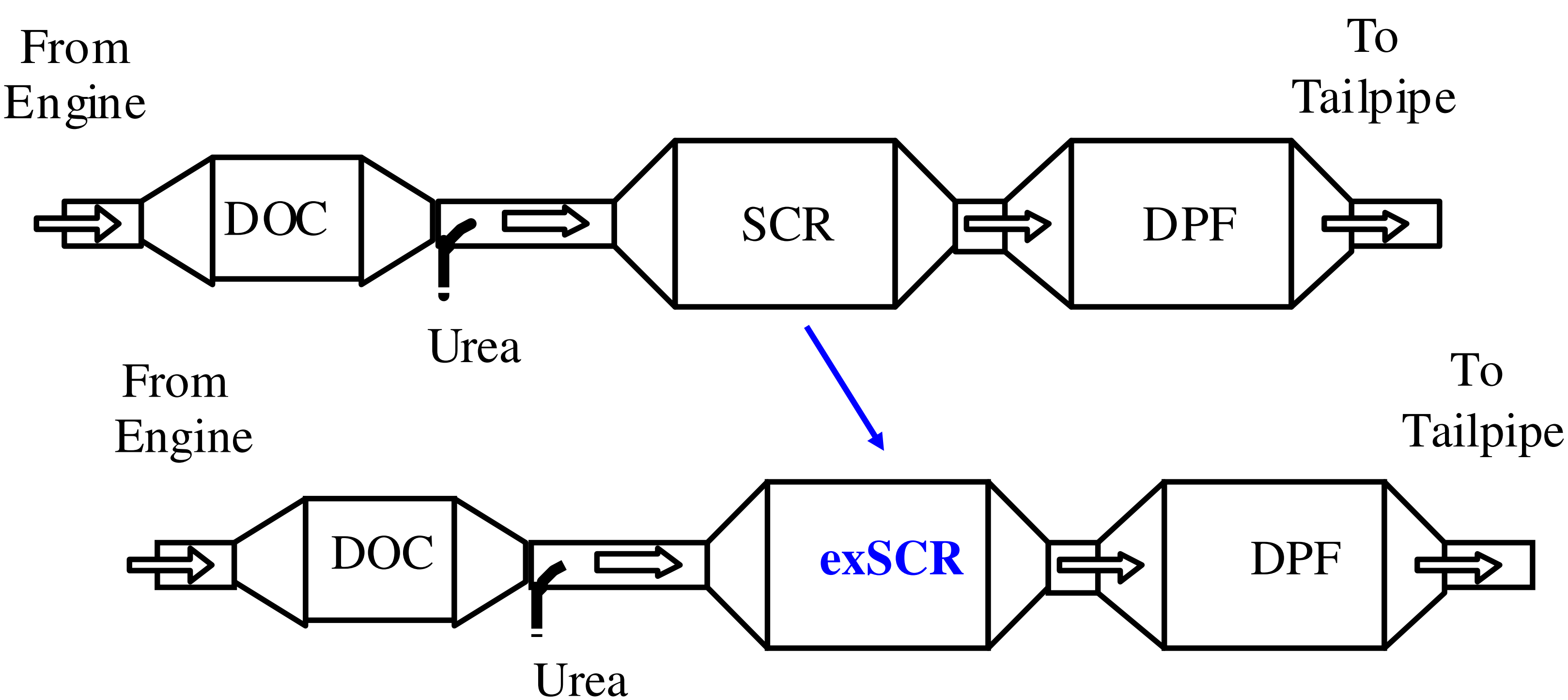
- **Engine calibration changes**
- **Urea calibration changes**
- **Heating strategies ~1.8% FE**
- **Increased PGM**
- **SCR filter helps at higher SV**



Future SCR Technologies

Extruded zeolite offers higher density of active material

- **Replace one or more bricks for higher performance**
- **Downsize the SCR System**

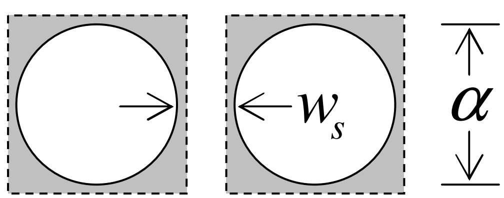


Modeling Implications of Extruded SCR Technology

- Higher backpressure due to thicker walls
- Slower warmup due to greater mass
- Higher SV if downsizing
- Different cell geometry

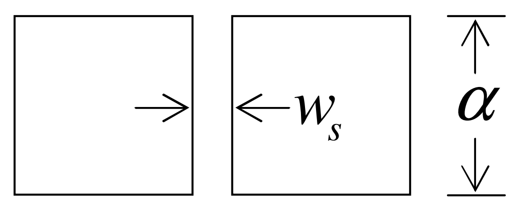
Washcoated

Washcoat collects in corners, resulting in circular flow channels.

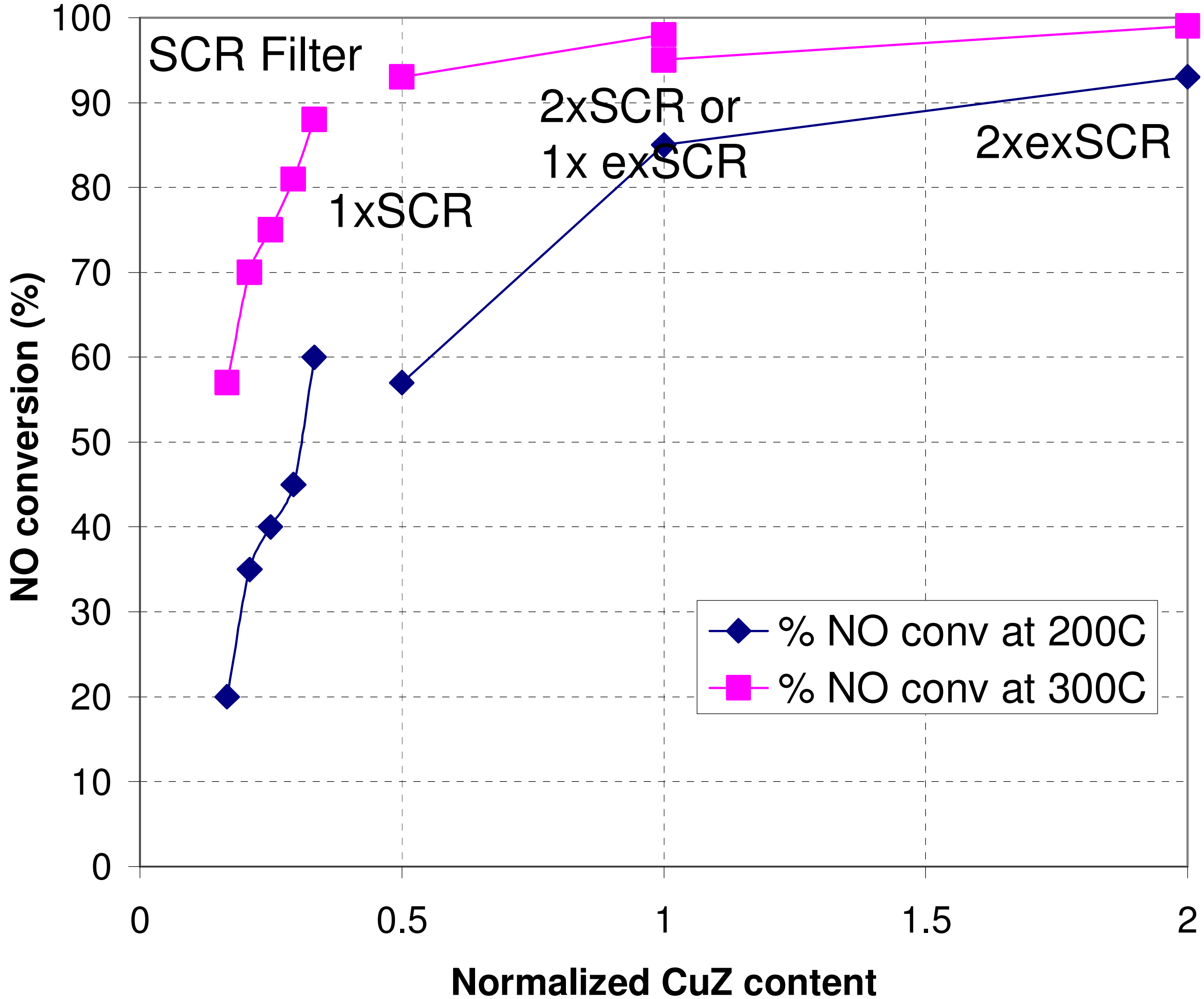


Extruded

Flow channels are assumed to be square.

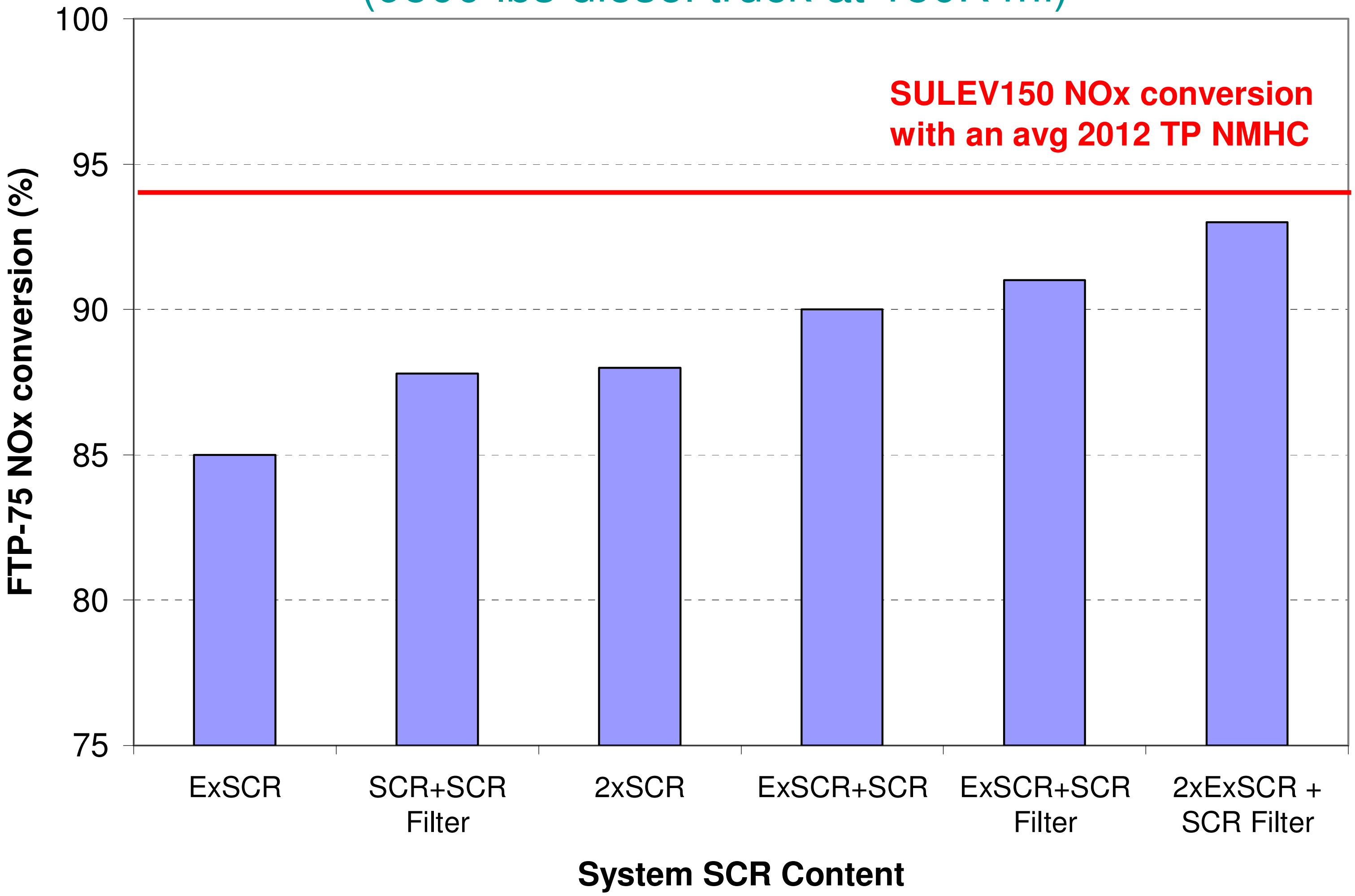


NOx Conversion vs. CuZ Content

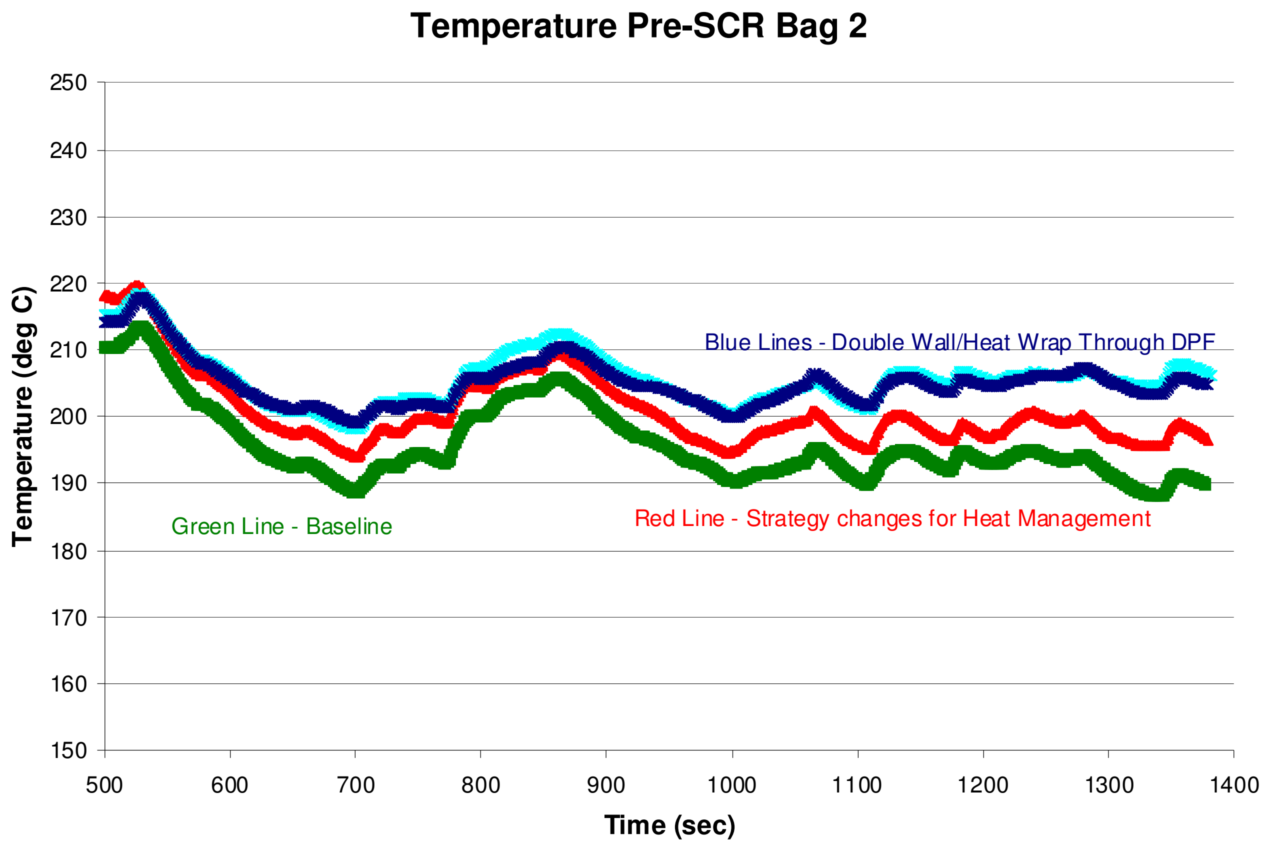


Predicted FTP-75 NOx Efficiency

(9500 lbs diesel truck at 150K mi)



Passive and Active Heat Management: FTP-75 preSCR T

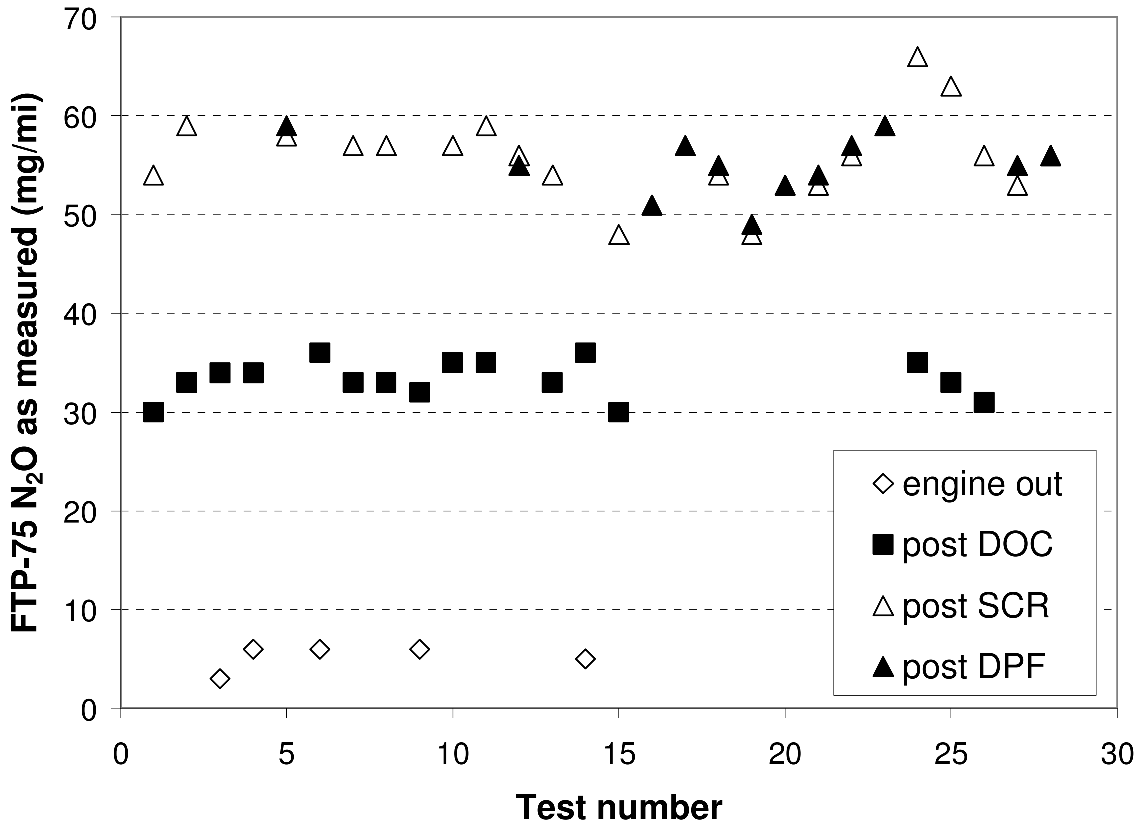


Goal: manage heat while not impacting fuel economy or HC

Greenhouse Gases (2013+)

- MDV standards
  - 50 mg/mi CH_4
  - 50 mg/mi N_2O
- Composite of FTP-75 (55%) and HWFET (45%)
- N_2O factor =298 for CO_2 equivalence

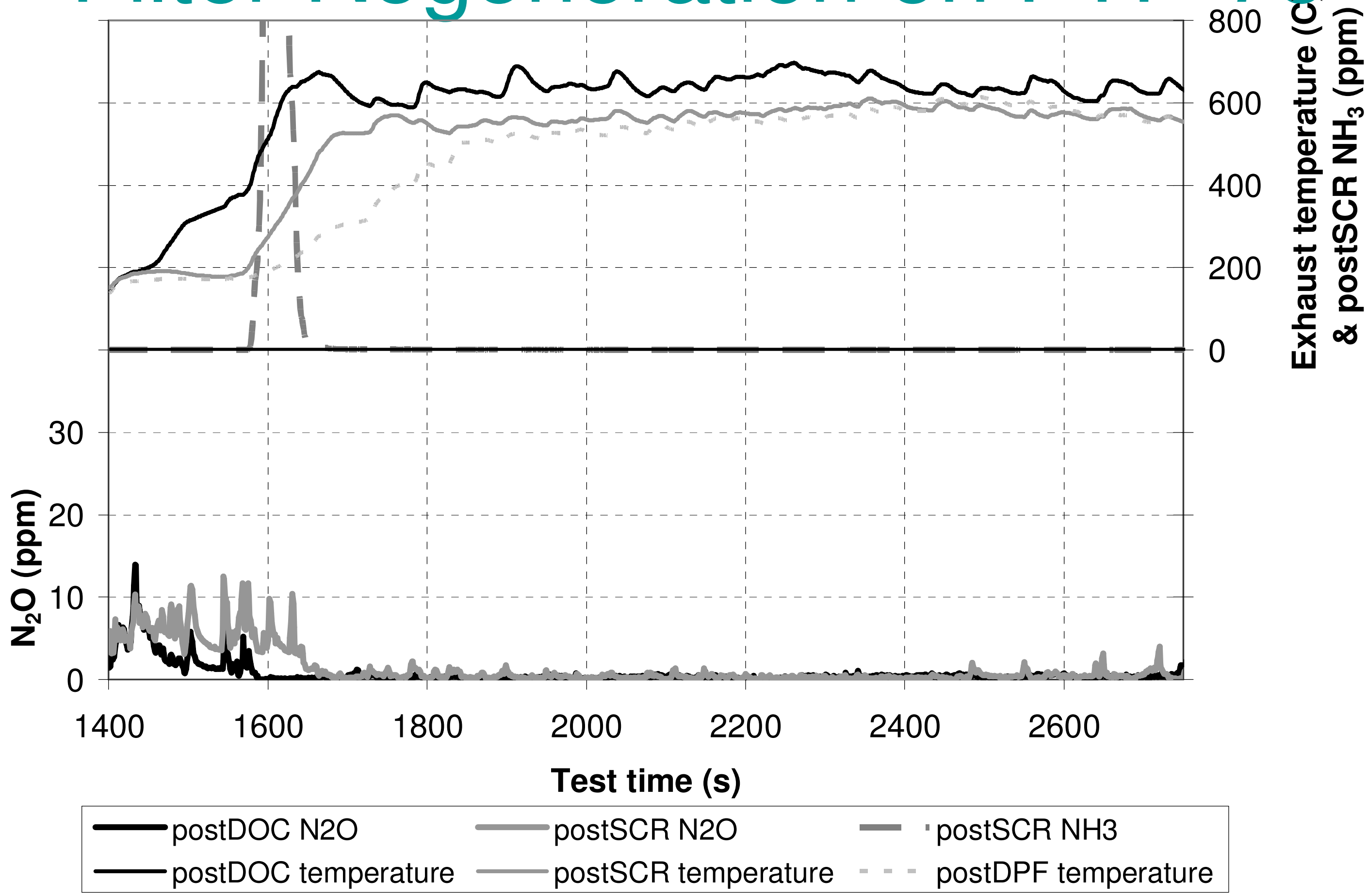
N_2O from Diesel SCR Systems on FTP-75



- Half of N_2O from HC + NOx on DOC
- Other half of N_2O from Urea SCR

Submitted to IJPT

N_2O from Diesel SCR Systems During Filter Regeneration on FTP-75



Submitted to IJPT

Composite N_2O for 9500 lbs diesel truck

	FTP-75	FTP-75 w/regen	HWFET	Composite Weighted	CO_2 equivalence
N_2O (mg/mi)	56	55	29	43	2%

N_2O formation pathways found:
Engine out HC +NOx --> DOC N_2O
DOC NO --> SCR NO_2 --> SCR N_2O

N_2O minimized by:
- low loaded, Pd-rich DOCs
- Cu/CHA SCR

Submitted to IJPT

Summary

- Diesel catalyst system development has unique challenges that were overcome
- Potential SCR technologies such as extruded SCR and SCR filter may help meet future standards
- Calibration and heat management will also play an important role
- The sources of N_2O within the diesel SCR system are understood

Next Steps for Diesel MDV

- Materials cost reductions continue
  - PGM reductions
  - substitution of Pt with Pd
- Assess future emission impacts
  - FTP-75
  - filter regen penalty
  - SFTP
  - PM
  - GHG

Acknowledgments

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Catalyst Suppliers: BASF, JMI, Umicore

And many, many more …