

# Rapid Aging and Poisoning Protocols to Assess Fuel and Lube Effects on Diesel Aftertreatment (Agreement 13415)



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Technology Program, Kevin  
Stork and Dennis Smith are  
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# Outline

- **Purpose**
- **Goals**
- **2007 reviewer feedback**
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- **Approach**
- **Accomplishments**
  - **DOC, DPF, LNT, SCR**
- **Technology transfer**
- **Summary**
- **Future work**

# Goals and objectives

- **Help enable high efficiency engines through:**
  - **Implementation of accelerated aging and poisoning protocols**
    - **Currently, industry lacks widely accepted methods for rapid evaluation of diesel emissions control devices**
  - **Provide deeper understanding of the mechanisms and chemistry of deactivation**
  - **Provide input for modeling of deactivation and impact on performance**
  - **Protocols include:**
    - **Analysis of application and means to accelerate**
    - **Extensive materials characterization**
    - **Verification by comparing to high mileage units**

# 2007 reviewer feedback

- **Link observations from field parts to elementary degradation mechanisms .... Place more emphasis on fundamentals of performance, not just aging .... Need better understanding of chemistry vs. catalyst impacts**
  - *We have increased performance and materials characterization in protocols to gain a better understanding of fundamentals*
  - *We have begun a modeling task to help define kinetics of deterioration and better understand the link between materials changes and deterioration*
- **Positive feedback**
  - *“Focus on improved efficiency and reduced emissions is consistent with DOE goals ..... essential work to support clean diesel development ..... good combination of characterization, reactors, engines, and modeling ..... well integrated with OEMs ..... good access to field aged parts ..... all work is essential and makes use of ORNL materials characterization capabilities ..... broad interactions with relevant industry ..... good linkage to catalyst suppliers and OEMs ..... recent emphasis on linked systems and modeling is essential”*

# Barriers addressed

- **New emissions regulations and durability requirements are very tight and have lead to some loss in fuel economy**
- **More efficient and durable aftertreatment will enable more fuel efficient engine calibrations**
- **Accelerated aging techniques allow evaluation of more options and can enable earlier decision making**
- **Our research helps develop more fundamental understanding by linking aging and poisoning to detailed materials changes**

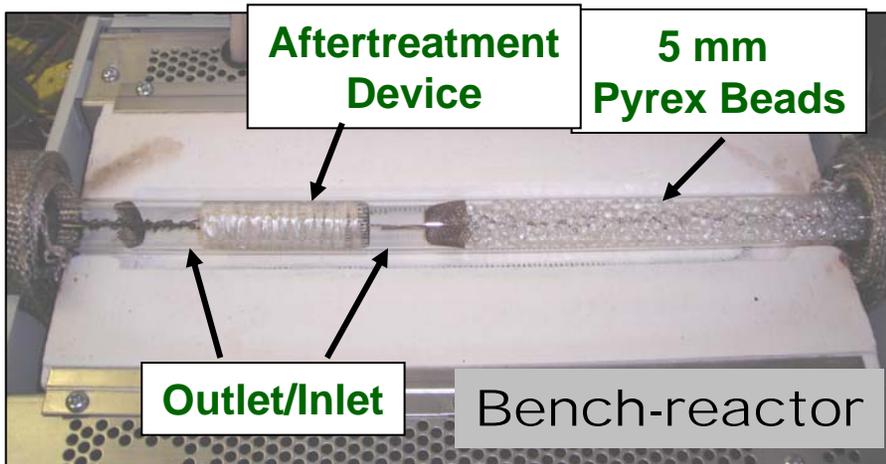
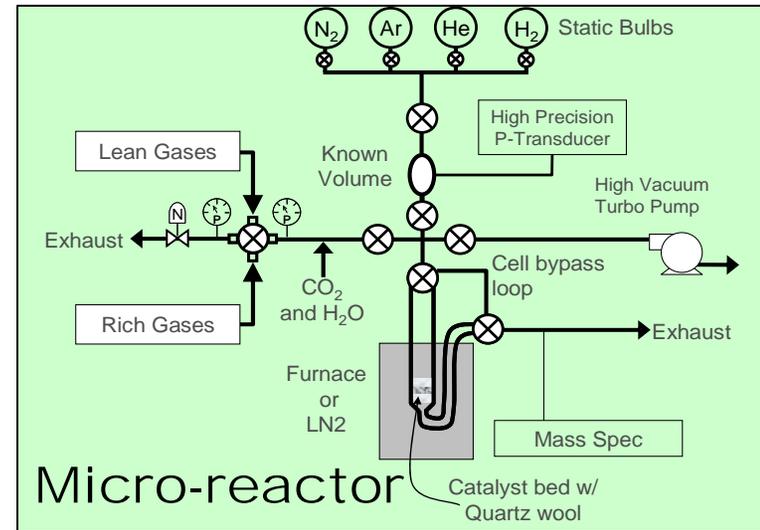
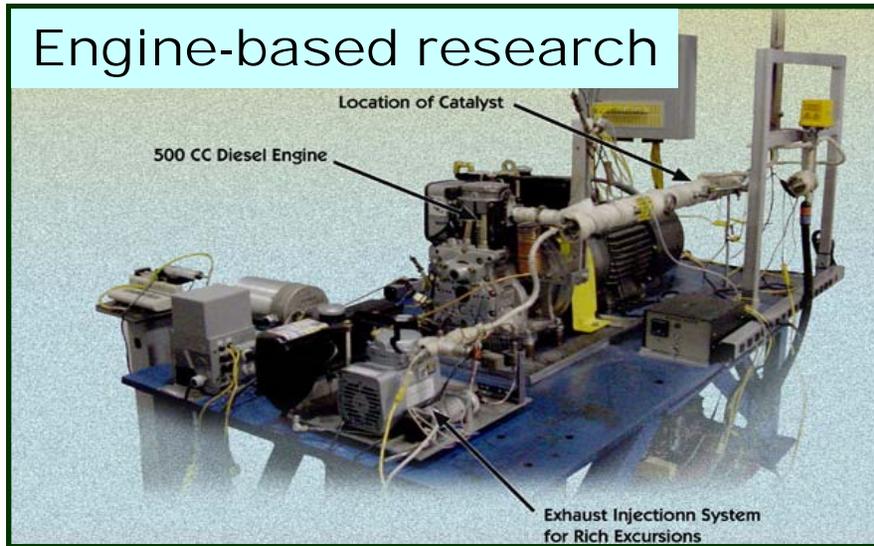
# Approach

- **Protocols developed with industrial input to ensure relevance**
- **Use industrially supplied emissions control devices**
  - **Multiple functions, formulations, and suppliers (NGK, Corning, Catalytic Solutions, BASF, Umicore, JMI, and Cummins)**
- **Protocols developed for bench-flow reactor and small diesel engine**
  - **Low sample cost for destructive analysis**
- **Current areas of focus:**
  - **Phosphorus poisoning of DOC**
  - **Lean-rich thermal aging of LNT**
  - **Rapid ash loading of DPF**
  - **Thermal aging of DOC-SCR-DPF system.**
- **Materials characterization used to understand changes**
  - **Relate materials changes to performance changes**
- **Research conducted at ORNL and UTK**
  - **Optimizes resources, provides multi-disciplinary graduate work**

# Accomplishments / progress / results

- Phosphorus poisoning of DOC
  - Method of oil introduction leads to different phosphorus chemistry
  - Loss in OSC attributed to accumulation of phosphorus
  - Soot masking as important as phosphorous
- Thermal aging of LNTs
  - Compared engine bench and bench reactor methods
  - Bench reactor protocols developed for aging at 700, 800, 900, and 1000°C
  - Excursions above ~850°C lead to significant performance deterioration
- Ash loading of DPFs
  - Developed mixed protocol to controllably deposit ash in DPFs
    - Ash gradient towards rear, similar to field parts
  - Back pressure increases linearly with ash for all substrates evaluated
  - Active regen soot light-off temperature increases with ash loading
- Thermal aging of DOC-SCR-DPF systems
  - Fresh and field aged SCR catalysts compared (iron-zeolite)
  - Front of field-aged SCR is deactivated compared to the middle and rear
    - NO performance more affected than NO/NO<sub>2</sub> mix performance
    - Characterization suggests sulfur contamination
- Modeling effort begun with MIT

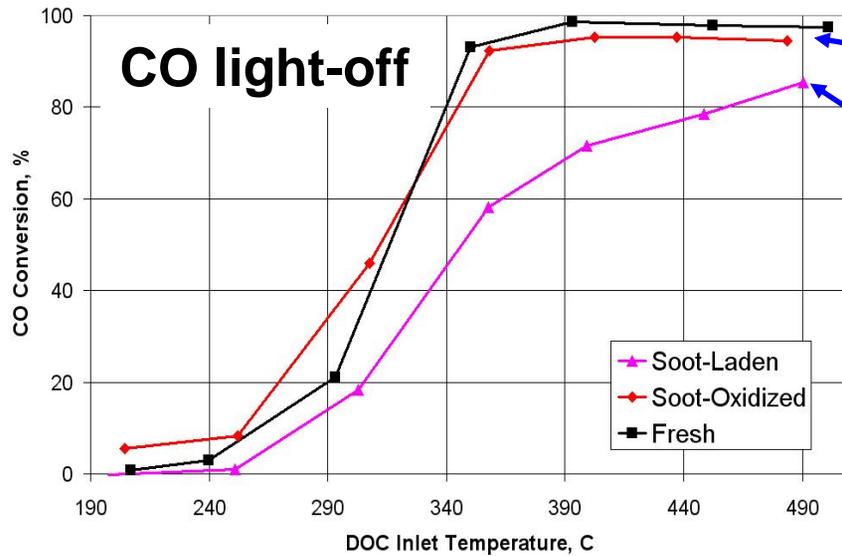
# Experimental equipment



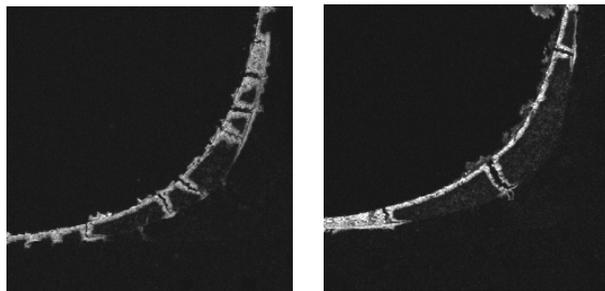
Characterization:

**SEM, TEM, microprobe, chemi and physisorption, XRD, ICP, XRF**

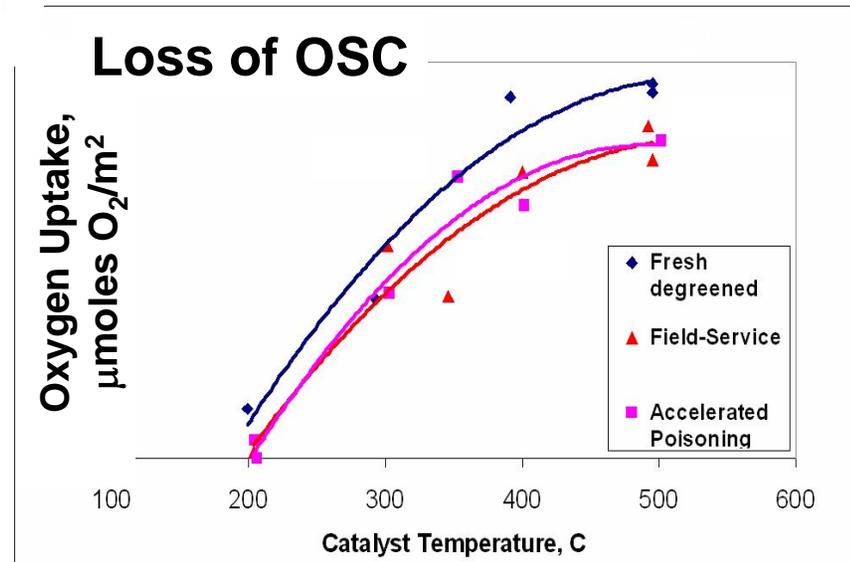
# For DOC protocol, we matched field results for soot and phosphorous effects



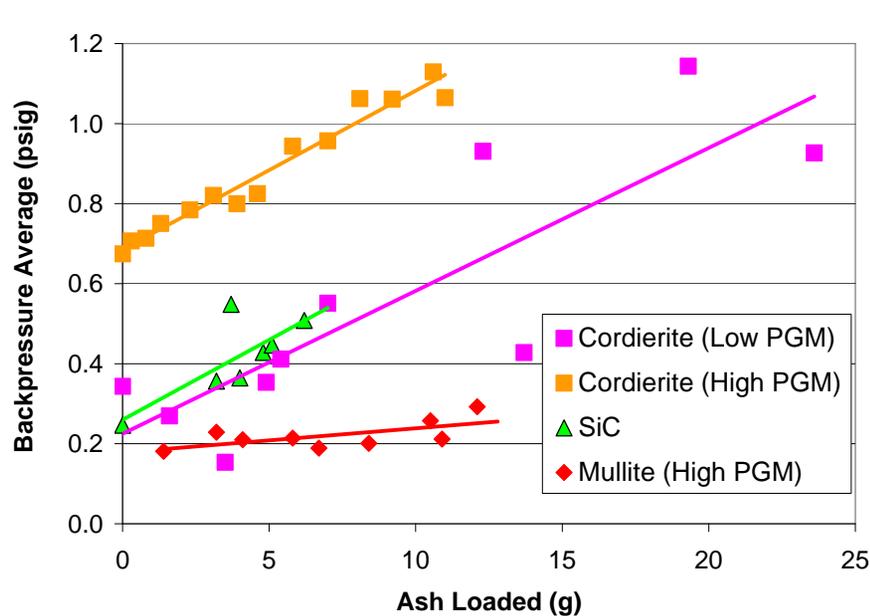
**Soot masking**



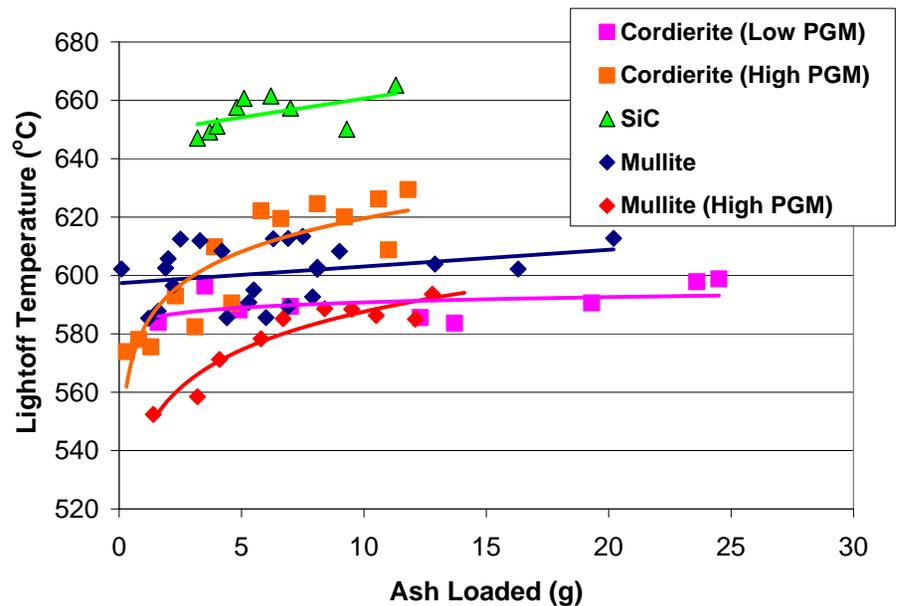
**Phosphorous surface layer unaffected by soot removal**



# DPF ash protocol provided consistent results with wide range of soot filters

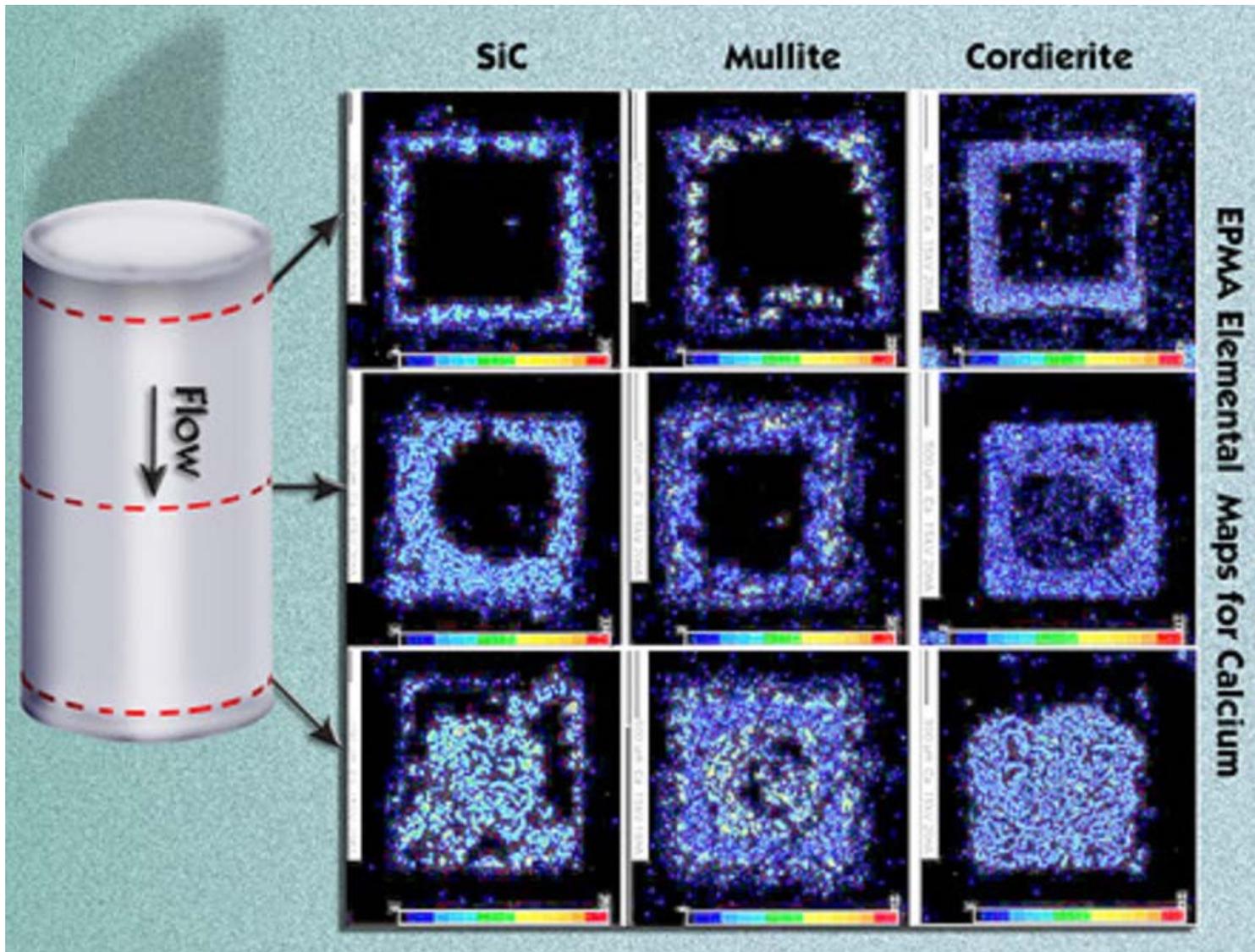


Backpressure increases linearly with ash, mullite has a lower rate compared to cordierite and SiC



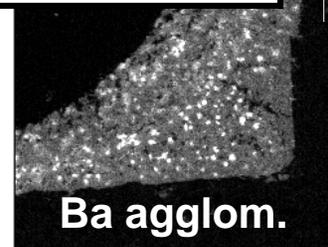
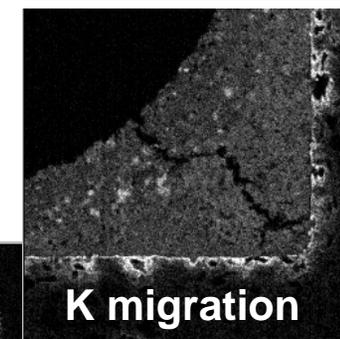
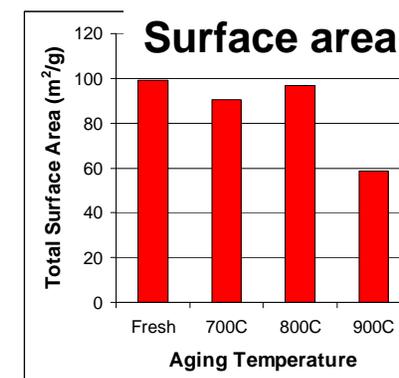
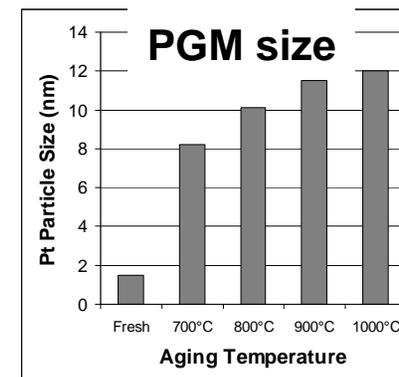
Temperature for active soot regeneration (active balance point) increases with ash loading, partially offsetting benefits of catalyst

# DPF ash gradients mimic those found in field parts



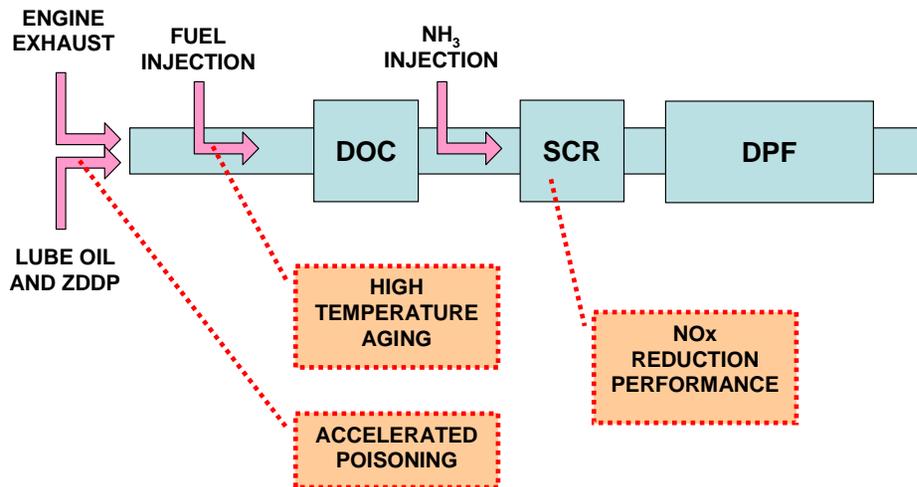
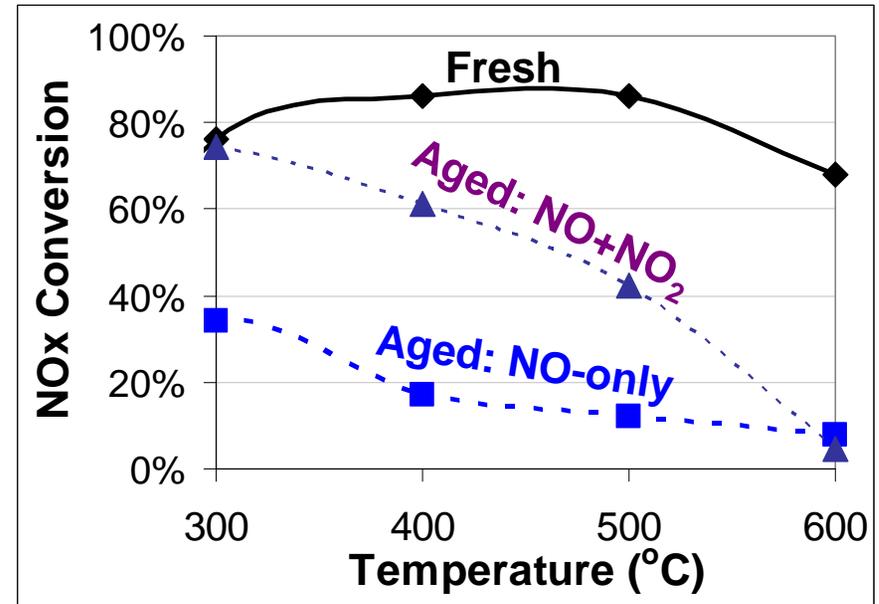
# LNT materials changes and effects

THRESHOLD TEMPERATURE	MATERIALS CHANGE	HOW MEASURED	PERFORMANCE EFFECT
700°C	PGM sintering	TEM, chem-adsorp	Little, at this PGM loading
750°C	K migration	Microprobe, ICP	Loss of conversion
850°C	Ba agglomeration	SEM	Unknown
850°C	Overall surface area loss (alumina)	Phys-adsorp	Loss of conversion
950°C	Solid state reactions (aluminides, etc.)	XRD	Loss of conversion



# SCR: thermal aging

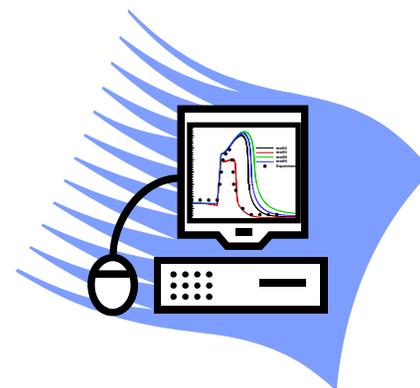
- Recently started
- Fe and Cu-zeolite
- Thermal aging of SCR from active DPF regeneration
- Engine aging → bench evaluation
- DOC/SCR/DPF, DOC/DPF/SCR



- On front section of field aged catalysts:
- NO performance degraded
- NO/NO<sub>2</sub> performance less affected
- Overall vehicle performance maintained

# Modeling of catalyst aging and poisoning – with MIT

- Develop model for DOC bench reactor
  - surface chemistry mechanisms
  - CO and HC light-off curves
- Parametric study to reflect changes in PGM dispersion, OSC, surface area, and masking
  - Use characterizations of aged catalysts
  - Determine best methods for altering catalyst model to reflect changes from aging and poisoning
- Estimate rates of change based on lab and field results
- If methodology shows promise, apply to other catalyst technologies



$$k_{1,k} = k_k T \exp \left[ -\frac{E_k}{RT} \right]$$



# Technology transfer

- **Good success in obtaining commercial type samples**
  - **BASF, Umicore, Catalytic Solutions, NGK, JMI, Corning, Dow**
- **Presentations and discussions to multiple companies**
  - **Cummins, ITEC, DDC, Electromotive Diesel, Umicore, BASF, Catalytic Solutions, MECA, Cleaire**
- **Building data base of material changes for comparison to field aged samples**
- **Large funds-in project: DPF**
- **Small funds-in projects: substrates, HC/CI catalysts**
- **Modeling work in partnership with MIT through lube oil / aftertreatment consortium**

# 2007 Publications and presentations

- Toops, Bunting, Nguyen, and Gopinath, “Effect of Engine-Based Thermal Aging on Surface Morphology and Performance of Lean NOx Traps”, *Catalysis Today* 123 (2007) 285.
- Toops, Bunting, Nguyen, Kim, and Gopinath, “Effect of Thermal Aging on Catalyst Morphology and Performance of Lean NOx Traps”, 20th North American Catalysis Society Meeting, Houston, TX, June 2007.
- Eaton, Nguyen, Bunting, and Toops, “Effect of Soot Accumulation on Light-Off Performance of Field-Aged and Accelerated Phosphorus Poisoning Diesel Oxidation Catalysts”, 20th North American Catalysis Society Meeting, Houston, TX, June 2007.
- Bunting, Toops, Nguyen, and Kim, “Rapid Thermal Aging of Lean NOx Traps”, 10th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Detroit, MI, May 2007.
- Nguyen, Kim, Bunting, Toops, and Yoon, “Rapid Aging of Lean NOx Traps by High-Temperature Thermal Cycling”, SAE paper 2007-01-0470.
- Bunting, Toops, Foster, Ottinger, and Nguyen “Rapid Aging/Poisoning Protocols for Diesel Aftertreatment Devices: NOx Abatement Catalysts”, Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, August 2007.
- Bunting, Toops, Youngquist, and Nguyen “Accelerated Testing Protocol for Rapid Poisoning of Diesel Particulate Filters”, Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, August 2007.
- Eaton, Bunting, Toops, and Nguyen “Impact of Lube-oil Phosphorus on Diesel Oxidation Catalysts”, Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, August 2007.

# Summary to date

- **Multiple material changes occur during aging and poisoning**
  - Performance losses must be related to specific material changes
  - Time-temperature rates of material changes can be modeled
- **DOC performance largely dominated by soot layer in our studies**
  - Sulfur and phosphorus have a measurable impact on OSC
- **LNTs show significant performance degradation above 850°C**
  - NO<sub>x</sub> reduction performance largely relates to total surface area losses
- **Rapid ash loading can reproduce a field pattern of ash tubes and plugs**
  - Ash-driven backpressure characteristics are substrate specific
  - Ash accumulation has an effect on soot light-off behavior
- **Field-aged SCR catalysts show deactivation in front section**
  - NO only performance affected, NO/NO<sub>2</sub> mix less affected
  - Significantly more sulfur observed in front section.
  - Overall system performance maintained

# Activities for next year

- **Phosphorus poisoning of DOCs**
  - Continue modeling of deactivation mechanisms
  - Determine relative effects of soot, phosphorus, and sulfur
- **Thermal aging of LNTs**
  - Complete aging study on LNT samples (HT and LT)
  - Determine materials changes and effects on performance
  - Model rate kinetics of material changes
- **Ash loading of DPFs**
  - Apply experience to bio-diesel study
- **Thermal aging of DOC-SCR-DPF system**
  - Study copper-zeolite (currently iron-zeolite)
  - Study effects of sulfur, phosphorous, and/or biodiesel
  - Study other system configurations (DOC-DPF-SCR)

# Reviewer summary

- Support goal of petroleum displacement
  - *Efficient, durable aftertreatment needed to enable fuel efficient engine calibrations*
- Approach
  - *Bench and engine aging, field comparisons, small parts, extensive materials characterization, use grad students*
- Technical accomplishments and progress
  - *Defined protocols for phosphorous, thermal aging, and ash, beginning modeling effort*
- Tech transfer / market transformation
  - *Received help from industry, numerous presentations and discussions, building data base of material changes*
- Next year's plans
  - *DOC modeling and soot vs. P effects*
  - *LNT material changes and kinetics of these changes*
  - *DPF bio-diesel ash effects*
  - *DOC-DPF-SCR system performance, S and P effects*
- Noteworthy aspects / barriers
  - *Leveraged small project to large results by partnering with industry and universities and developing efficient research methods*