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Heavy Vehicle Propulsion Materials (HVPM) Exhaust After-treatment

Materials for Exhaust Aftertreatment –

Filter Substrate & Catalyst Durability

Herbert DaCosta, Ronald Silver, & Paul Park

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This presentation does not contain any proprietary or confidential information

Project ID # PM_9087

21ST CENTURY TRUCK PARTNERSHIP

Materials for Exhaust Aftertreatment

21CTP

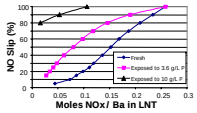
21CTP Technical Goal: Develop and demonstrate an emissions compliant engine system for Class 7-8 highway trucks that improves the engine system efficiency from ~42% today to 50% by 2010.

Project Objectives
Materials research and development that will be applied in advanced diesel engine aftertreatment systems to comply with future emission regulations with minimum fuel penalty.

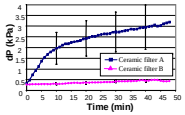
FY 2005 Focus
1. Evaluate new materials for particulate matter filtration efficiency & back pressure. 2. Assess impact of phosphorus on oxidation, NOx adsorber (LNT) and urea-SCR catalysts.

Planned Duration
Jan 2005 to December 2006

DOE Funding/Industry Cost Share
FY04: $300K/$300K; FY05: $250K/$250K



1. The effect of phosphorus exposure on LNT NOx storage for three different P exposures



2. Backpressure change during the soot-loading process of two uncatalyzed high filtration efficient DPF materials.

Principal Investigator(s)
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Accomplishments
1. Various catalyzed and uncatalyzed DPF materials were obtained from suppliers and screened for filtration efficiency and back pressure. A promising material was identified.
2. The cause of LNT deactivation by phosphorus poisoning was identified. For LNTs, the NOx storage capacity function is affected first and more severely than NO oxidation and NOx reduction. (June 2005)

Significant Future Milestones
1. Study durability of selected filter materials (Dec. 2006)
2. Assess impact of combination of phosphorus, sulfur and thermal deactivation on OXICAT, LNT and SCR catalysts. (Dec. 2006)

Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
PM_9087	Materials Technology	HV Propulsion Materials	Applied Research	8-11-05

Project Objectives

- Materials research and development for diesel aftertreatment systems
  - Evaluate new materials for particulate matter filtration
    - Identify promising materials
    - Develop test protocols
    - Assess filtration efficiency of the substrate materials
    - Determine impact on engine performance
  - Assess impact of phosphorous on aftertreatment systems
    - Develop rapid aging protocol
    - Establish correlation between catalyst aging in laboratory and engine
    - Determine phosphorus (P) effect on oxidation catalyst (oxicat), Lean-NOx trap (LNT) and urea-Selective Catalytic Reduction (SCR)
    - Determine fuel penalty vs. catalyst aging due to P

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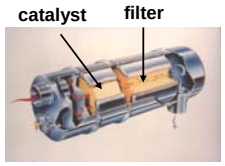
Technical Approach

- Evaluate new materials for particulate matter filtration
  - Modify diesel burners
  - Measure particulate filtration efficiency
  - Measure pressure drop
- Assess impact of phosphorous on aftertreatment systems by comparing fresh and aged catalyst performance using fuel burner and bench test system
  - LNT: P impacts on NO→NO_2 Oxidation, NOx storage and reduction functions
  - SCR: Zeolite based and vanadia based samples were evaluated using temperature and NH_3/NOx ratio sweeps
  - Oxidation catalyst: developing correlation between bench and field

Relevance to 21 CTP Goals

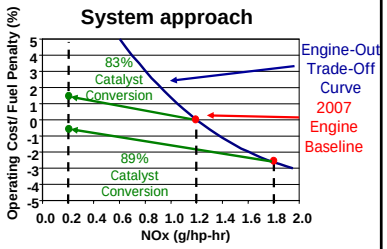
21 CTP Goals: improve fuel efficiency, reduce emissions, enhance safety, reduce owning/operating costs, maintain/enhance performance

HVPM Vision: to identify and provide improved and new materials to enable cost-effective, high energy-efficiency, heavy-duty engines with high durability and reliability and substantially lower emissions.

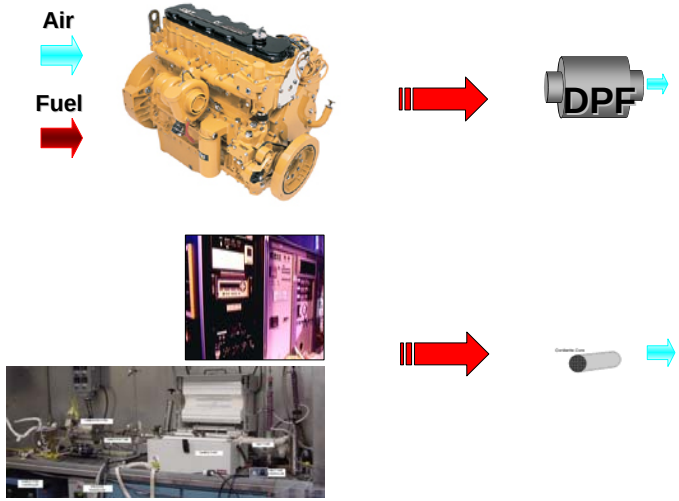


Johnson Matthey CRT® Particulate Filter

Critical factors
- Back pressure
- Durability (DF)
- Size/weight
- Regen cycles



Engine Conditions vs. Test Bench



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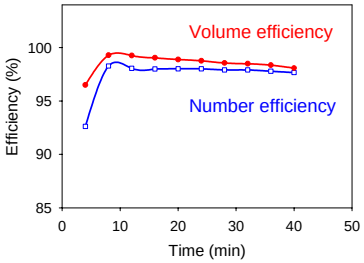
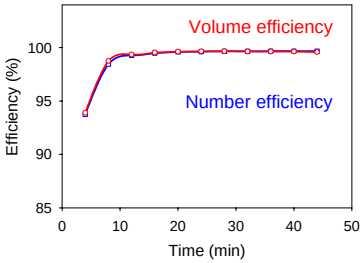
Filtration Efficiency of Substrates

New material substrate



(average of 6 uncatalyzed fresh samples)

Cordierite substrate



(average of 3 uncatalyzed fresh samples)

- The filtration efficiency of fresh samples of both substrates is higher than 95%

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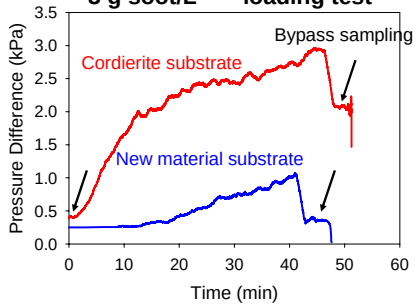
Pressure Drop in Substrates

(single uncatalyzed fresh sample)

3 g soot/L$^{(DPF)}$ loading test



Cordierite substrate

- Exponential increase ΔP
- Higher ΔP for catalyzed DPF

New material substrate

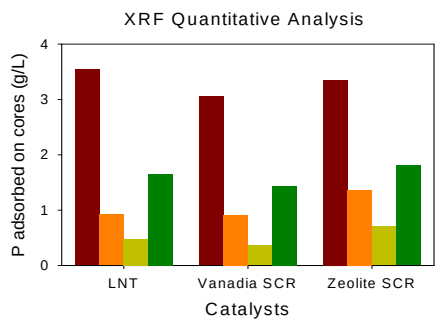
- Linear increase ΔP
- Similar ΔP for catalyzed DPF

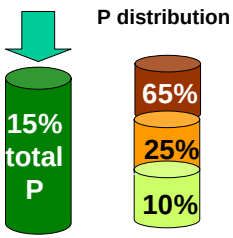
- The filtration efficiency of both fresh substrates is higher than 95%.
- The pressure drop of the new material is significantly lower than cordierite.
- The new material has the potential to yield more efficient DPFs.

Technical Accomplishments – DPF Substrates

- Various catalyzed and uncatalyzed DPF materials were obtained from suppliers and screened for filtration efficiency and backpressure (ΔP).
- A promising material was identified.
- It provides filtration efficiency higher than 95 % with reasonably low ΔP.
- Catalyst coating does not affect ΔP on selected material.

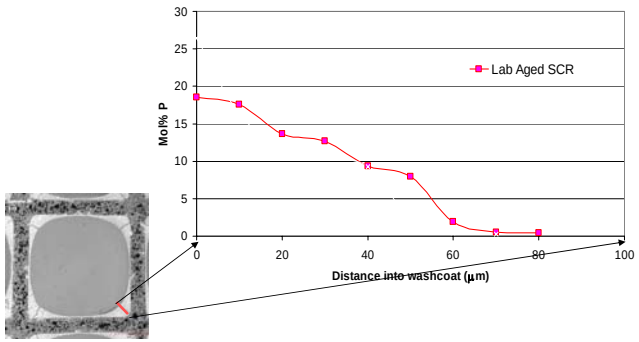
Phosphorus Distribution on Catalyst





- Similar distribution of P adsorbed on each catalyst type
- Conclude: P is a non-selective deactivator.

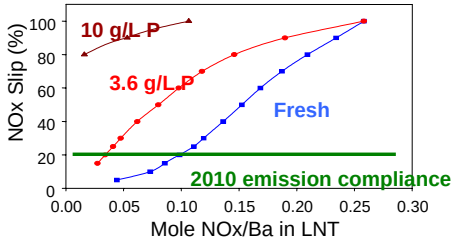
Phosphorus penetration profile in catalyst washcoats



Phosphorus Effect on LNT Storage

Amount of P exposure/unit volume catalyst	Time* on engine	Mileage*
3.6 (g/L)	4000 hrs	200K
10 (g/L)	10000 hrs	500K

*Assuming 800 ppm P in oil, 20L catalyst volume, 50 mph avg. speed



- Loss of Storage capacity with P exposure is primary cause of decline in NOx conversions over LNT

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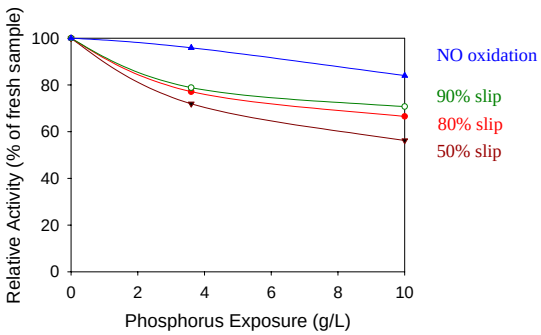
Activity Loss vs. P Exposure Level

$NO + O_2 \xrightarrow{Pt} NO_2$	NO oxidation
$NO_2 + BaO \xrightarrow{Lean} BaNO_3$	Lean Storage
$BaNO_3 \xrightarrow{Rich,Rh} BaO + N_2 + O_2$	Rich Release + Reduction



➢ Loss of Oxidation Function Less Severe than Storage Loss

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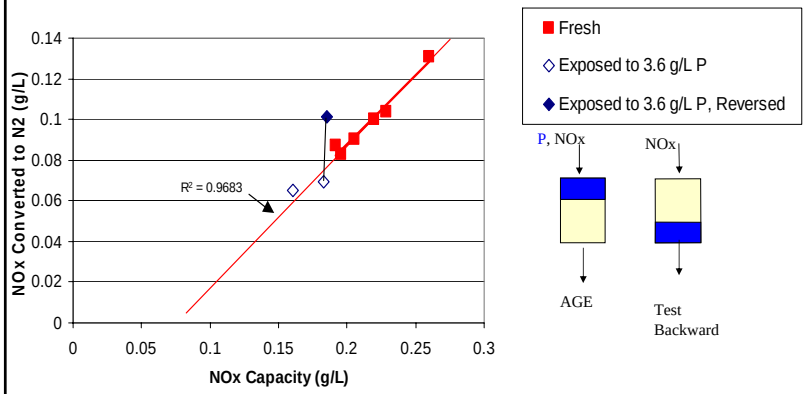
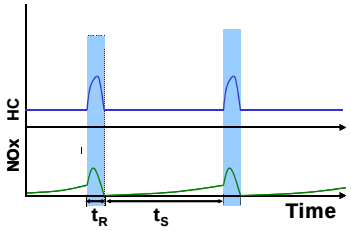
NO Reduction vs. NOx Capacity

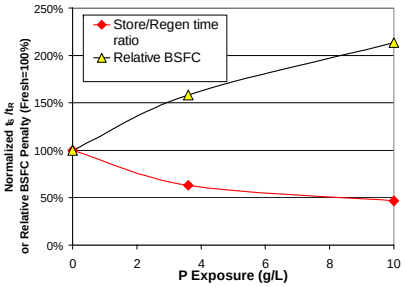


➢ Results with reverse flow suggest Rh still active in P deposited zone.

Impact of Phosphorus Exposure on BSFC of LNT



Assumptions :
- Using in-pipe HC injection to make exhaust rich
- HC injection amount is constant
- Duration of injection (t_R) is constant
- Duration of storage (t_S) decreases with LNT capacity
- Increase # of rich excursions with lost reducing function

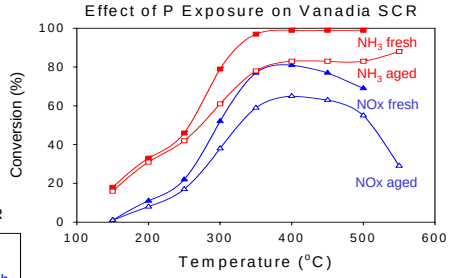


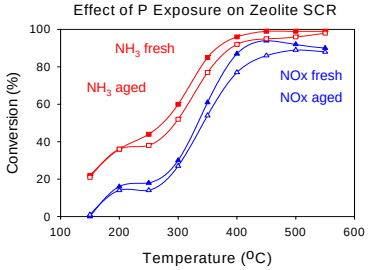
- Ratio of t_S to t_R decreases with increased P
- BSFC penalty increases with decreasing t_S/t_R
- 10g/L P > double BSFC penalty vs. baseline

P Impact on SCR Catalysts

$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$

- P impacts strongly at high temperature
- P impacts both NOx and NH_3 conversions
- Ammonia oxidation decreases NOx reduction





- P impacts less on zeolite than vanadia catalyst
- P impacts similarly in broad temp range
- No drop off in activity at high temp

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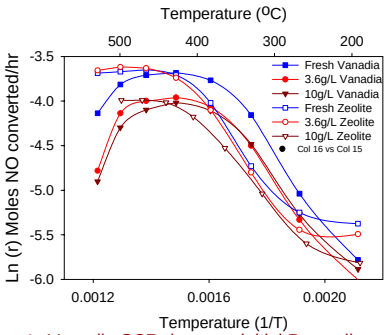
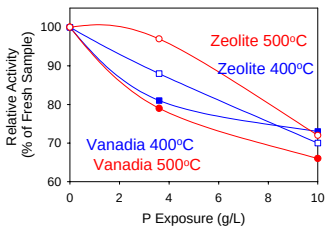
Kinetics provide insights on effect of P



- Vanadia SCR drops on initial P, smaller decline on further exposure
- Zeolite less affected by initial P, bigger decline on further exposure
- Increased Temperature on P exposure helps zeolite, hurts vanadia

- Similar kinetics on both catalysts
- < 400°C, P impact less since some SCR occurs in bulk
- > 400°C, P impact increased as more SCR occurs on outer surface
- Δ curves typical of activity loss due to physical blockage of active sites



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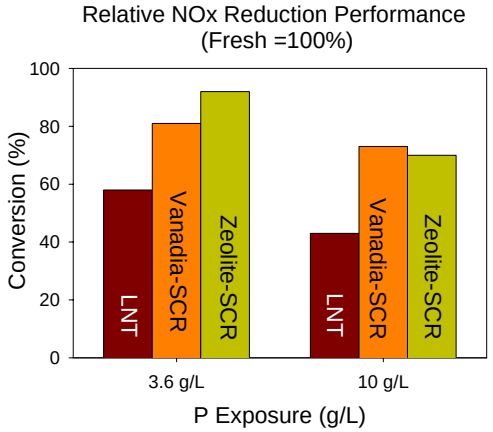
Comparison of P Impact on LNT vs. SCR



- Zeolite SCR has best durability initially; SCRs similar after extended exposure.
- Phosphorus impacts LNTs > SCRs
- P deactivation is a challenge for both strategies.

Technical Accomplishments - Catalyst Deactivation by Phosphorous (P)

- **Evaluated vanadia and zeolite based SCR catalysts**
  - P similarly impacts both NH_3 and NO conversions.
  - Zeolite catalyst shows higher P tolerance initially, but both catalysts had similar deactivation after extended exposure.
  - Speculate that P blocks NH_3 adsorption sites which prevent NO reduction.
- **Evaluated LNT catalyst**
  - P impacts NOx storage leading to decreased NO conversion.
  - P impacts NOx storage more at low NOx slip than at high slip.
  - P impacts NO oxidation and reduction functions less than storage.
- **P reduces NOx catalyst performance and increases BSFC penalty.**
- **P impacts LNTs more than SCRs; presents a challenge for both**

Technology Transfer

Diesel Particulate Filter

- Scale-up engine tests with DPFs made of the new substrate material

Catalyst durability

- Provide engineering margin for catalyst sizing estimates.
- Work with catalyst suppliers to improve catalyst durability
- Suggest options for mitigation strategy

Future Work (2006)

- Test thermal deactivation of DPF substrate materials
- Assess impact of combination of phosphorus, sulfur and thermal deactivation on aftertreatment catalysts.
  - Complete work on oxidation catalyst
  - Combine effect of P exposure with S and thermal aging and compare to engine aging
  - Explore 1 or 2 mitigation strategies

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Questions?

Publications/Presentations

- R. G. Silver, M. Stefanick, J. M. Faas and S. Zemskova, "Impact of Phosphorus Exposure on Lean NOx Trap Performance," presented at 19th Catalysis Society Meeting in May 2005.
- R.G. Silver, M. Stefanick, and A. Alletag, "Impact of Phosphorus on NOx Aftertreatment Catalysts," poster presentation at 2005 DEER meeting.