Development and Optimization of a Multi-Functional SCR-DPF Aftertreatment System for Heavy-Duty NO$_X$ and Soot Emission Reduction

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Pacific Northwest National Laboratory

DOE Annual Merit Review
June 7, 2017

This presentation does not contain any proprietary, confidential, or otherwise restricted information
## Timeline
- **4-yr CRADA**
  - Start date – July 2016
  - End date – June 2020
- **16.7% complete**

## Barriers
- **B. Lack of cost-effective emission control** for meeting EPA standards for NOx & PM
- **E. Durability** of the emission control system: 435,000 miles
- **G. Cost** of emission control devices … for heavy truck engines in particular

## Budget
- **Contract value** – $2.7M
  - $1.35M DOE Share
  - $1.35M PACCAR Share
- **Funding received**
  - FY16 – $200K
  - FY17 – $355K

## Partners
- **CRADA partner** – PACCAR Inc
- **PACCAR Inc** – multiple contracts in place in support of advanced aftertreatment development and engineering
RELEVANCE
Multi-Functional Aftertreatment

Current 2017 HD Aftertreatment

Future Advanced Aftertreatment

**Key:**
Enabling passive soot oxidation

**SCR-on-DPF**

- Soot trapped upstream
- Molecular diffusion to washcoat
Highly promising strategy for after-treatment integration
- Reduced thermal mass & faster warm-up – reduced cold start emissions
- Improved aftertreatment performance & increased flexibility

LIGHT DUTY – challenges
1. **Sufficient SCR performance**
   - Ultra-high porosity filter development (Corning, NGK)
     Enables more SCR catalyst at acceptable engine back pressure
   - Advanced filter coating, imaging techniques (e.g., PNNL micro-Xray-CT)
     Optimized catalyst placement and usage in the filter wall

2. **SCR catalyst durability**
   - ... to withstand **active** soot oxidation management
     Cu/SSZ-13 – more thermally durable, a key enabler

Currently being deployed for **light-duty** application

http://www.catalysts.basf.com/p02/USWeb-Internet/en_GB/content/microsites/catalysts/prods-inds/mobile-emissions/scr-filter  
http://papers.sae.org/2016-01-0915/
HEAVY DUTY – challenges

1. Sufficient SCR performance
2. SCR catalyst durability
3. Passive soot oxidation performance (via NO₂)
   - Economically attractive to manage soot passively for heavy duty
   - With incorporation of SCR phase, competition for NO₂

SOLUTION

- Modify the SCR catalyst to generate NO₂ in situ

**RELEVANCE**

**SCR-on-DPF**

fast-SCR: \[2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}\]

versus

passive soot oxidation: \[\text{C (soot)} + 2\text{NO}_2 \rightarrow \text{CO}_2 + 2\text{NO}\]

Dominates NO₂ consumption

Significantly compromises soot oxidation
FOCUS OF WORK

- Development of a novel SCR active phase for the SCRF system that exhibits sufficient passive soot oxidation and NO\textsubscript{X} reduction efficiency at acceptable ΔP to be attractive for HD diesel application.

**How?**

- An SCO-SCR binary catalyst system – incorporation of a selective catalyst oxidation (SCO) metal oxide phase with the SCR catalyst.
- The binary catalyst will yield greater availability of NO\textsubscript{2} in the system without sacrificing necessary NO\textsubscript{X} reduction performance or durability.

**PNNL and PACCAR are pursuing …**

- Advancement of the SCO-SCR binary catalyst that is achievable in the time frame proposed.
- … to make its integration with DPF a viable candidate for combined NO\textsubscript{X} and PM aftertreatment for heavy-duty.
### APPROACH

**Timeline**

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Phase 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Months</td>
<td>24 Months</td>
<td>36 Months</td>
<td>48 Months</td>
</tr>
<tr>
<td>Feasibility/approach</td>
<td>SCO-SCR development</td>
<td>2-liter scalability</td>
<td>Full-scale scalability</td>
</tr>
<tr>
<td>SCO identification</td>
<td>SCRF optimization</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### DEVELOPMENT of SCO-SCR BINARY CATALYST
- Sample screening
  - SCO phase screening
- SCO-SCR binary catalyst fundamental and aging studies
- SCO-SCR binary catalyst optimization

#### CATALYST INTEGRATION w/DPF
- Coating procedure
  - Catalyst loading/distribution
    - Substrate/porosity

#### SCR-on-DPF MODEL DEVELOPMENT
- Model platform development
  - Reaction matrix, parameter optimization, modeling aging behavior
    - Device-level model development

#### 2-L SCR-on-DPF SCALING/TESTING

#### FULL-SCALE SCR-on-DPF
# APPROACH

## Milestones

<table>
<thead>
<tr>
<th>Date*</th>
<th>Milestone and Go/No-Go Decisions</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>November 2016</td>
<td>Milestone: 1&lt;sup&gt;st&lt;/sup&gt; group of PACCAR SCO/SCR binary-phase catalyst samples delivered to PNNL for testing</td>
<td>Complete</td>
</tr>
<tr>
<td>February 2017</td>
<td>Milestone: Large-batch Cu/SSZ-13 SCR phase prepared and ready for SCO phase development</td>
<td>In-progress</td>
</tr>
<tr>
<td>May 2017</td>
<td>Milestone: Structure of integrated SCR-DPF single-wall model complete</td>
<td>In-progress</td>
</tr>
<tr>
<td>August 2017</td>
<td>Milestone: 1&lt;sup&gt;st&lt;/sup&gt; group of SCO/SCR binary-phase catalysts with candidate SCO phases (preferably &lt;3) ready for fundamental study</td>
<td>On-track</td>
</tr>
<tr>
<td>November 2017</td>
<td>Milestone: 1&lt;sup&gt;st&lt;/sup&gt; group of optimized SCRF samples with candidate SCO/SCR binary catalyst ready for detailed testing</td>
<td>On-track</td>
</tr>
<tr>
<td>February 2018</td>
<td>Go/No-Go decision: Identify candidate SCO/SCR binary phase catalyst with improved soot oxidation performance with competing SCR</td>
<td>On-track</td>
</tr>
</tbody>
</table>

* As of 04/10/2017
Selective parameter screening with ZSM-5 model system

- Focused on ZrO$_2$–based SCO phase, to evaluate the effect of …
  - SCO phase on Cu/ZSM-5 performance
  - Binary catalyst mass ratio (SCO to SCR)
  - Binary catalyst loading
  - Varying catalyst preparation procedures (i.e., different ‘lots’)
  - Catalyst loading symmetry
  - ZrO$_2$ source

- PACCAR
  - Sample acquisition/preparation

- PNNL
  - Performance & durability assessment

- Detailed interrogation of SCR and contributing reaction performance
  - Multi-step protocol testing

- Soot loading & passive soot oxidation study
TECHNICAL ACCOMPLISHMENTS
Impact of SCO-phase on NO₂ balance

Fast SCR NO₂ Balance

NO₂ balance
- total ppm
- NO₂/NOₓ
... IS impacted by SCO-phase contribution
TECHNICAL ACCOMPLISHMENTS
Impact of SCO phase on NRE

Variables involved in this data set include …
- SCO-phase chemistry
- Catalyst ratio
- Catalyst loading
- Cu loading
- SCO-phase particle size

No SCO phase
- 0.1-µm colloidal ZrO₂
- 1-µm ZrO₂ (600°C decomp.)
- 1-µm ZrO₂ surface modified w/ Nb₂O₅

We ARE seeing the expected impact of increased NO oxidation on SCR performance (standard & fast)

SCR reaction rate

\[ \frac{\text{NO}_2/\text{NO}_X}{0} \]
## TECHNICAL ACCOMPLISHMENTS

### SCO/SCR system optimization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22B</td>
<td>0.84</td>
</tr>
<tr>
<td>24</td>
<td>0.30</td>
</tr>
<tr>
<td>25</td>
<td>0.19</td>
</tr>
<tr>
<td>28</td>
<td>0.23</td>
</tr>
<tr>
<td>29</td>
<td>0.21</td>
</tr>
</tbody>
</table>

- NO oxidation also governed by SCR catalyst (e.g., Cu exchange level)
- Thus, optimization **WILL** necessarily consider both SCO and SCR phases

### Effect of Different Catalyst Preparation Lots

![Graph showing the effect of different catalyst preparation lots on NO oxidation and NH\textsubscript{3} Oxidation (by O\textsubscript{2})](image)

- Catalyst Inlet Temperature [°C]
- NO Oxidation
- NH\textsubscript{3} Oxidation (by O\textsubscript{2})

- Catalyst Preparation Lots:
  - 22B (66g/L)
  - 24 (64g/L)
  - 25 (67g/L)
  - 28 (65g/L)
  - 29 (67g/L)
TECHNICAL ACCOMPLISHMENTS
Multi-functional device engineering

- Symmetrical versus asymmetrical catalyst loading

![Graph showing NOx Reduction Efficiency vs Catalyst Inlet Temperature]

For multi-functional devices, device engineering (led by PACCAR) is a critical component to success.

- Improved activity with superior dispersion
- ... at lower pressure drop.

Clean ΔP @ GHSV ~35,000

Without soot

Clean

22A
22B
22C

Pressure Drop [kPa]

Temperature [°C]
TECHNICAL ACCOMPLISHMENTS
Impact(s) of soot/catalyst on each other

Soot ↔ SCR

SCR catalyst mainly impacts depth filtration of soot

Primary impact of soot on SCR function is on NO\textsubscript{x} make-up

Elucidating prior work
TECHNICAL ACCOMPLISHMENTS

SCO phase impacting soot oxidation

Passive soot oxidation (PSO)

<table>
<thead>
<tr>
<th>PSO metric</th>
<th>SCR</th>
<th>SCR + SCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>20ppm CO₂ production</td>
<td>395°C</td>
<td>365°C</td>
</tr>
<tr>
<td>Balance Point Temperature</td>
<td>515°C</td>
<td>490°C</td>
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</table>

SCO phase **IS** impacting passive soot oxidation light-off
First year of program, no comments to address.
Collaboration & Coordination

Pacific Northwest
NATIONAL LABORATORY

- Fundamental catalysis discovery
- Active site characterization & optimization
- Performance & durability
- Modeling

PACCAR Inc

- SCO phase discovery
- SCRF washcoat development
- SCR phase development
- DPF optimization

DPF Substrate Suppliers
- Cordierite
- SiC

SCR Catalyst Development
- Mesoporous Cu/SSZ-13

Catalyst Suppliers

Prototype Cannners
FY17/18

Identification of optimum SCO metal oxide phase, that when integrated with the SCR phase (Cu/SSZ-13), ...

- ... enables passive soot oxidation capacity for HD diesel ...
  - Identification of optimum SCO-phase metal oxide chemistry (e.g., ZrO₂, Zr-based solid solutions) to generate NO₂ at the SCR catalyst surface
  - Methods of efficiently screening SCO candidates (i.e., catalyst discovery) that accurately predict/determine passive soot oxidation impact

- ... while exhibiting necessary SCR performance.
  - Identification of SCO-phase metal-oxide chemistry that balances activity for NO₂-make with subsequent effect on (i) SCR durability, and (ii) parasitic NH₃ oxidation at elevated temperature
  - Optimizing method of integration of the SCO-phase with the SCR catalyst that achieves the necessary activity (NO₂) and durability (SCR)
  - Understanding the impact of the SCO-phase on performance & aging-behavior of active Cu-centers
Future Work

FY17/18 Any proposed future work is subject to change based on funding levels

- Complete ZSM-5 model system study for metal oxide screening
  - Needs to be quick!
  - High-level screening for candidate identification

- Clearly show feasibility on Cu/SSZ-13
  - Surface nitrate formation (transmission IR, TPD)
  - SCR reaction performance

- Directly correlate to soot oxidation impact, and use correlation to guide SCO-phase evolution
  - Iterate surface science and active-phase (i.e., powder) study to core for evaluating passive soot oxidation impact

- Develop strategy for understanding SCO-phase impact on SCR behavior & durability
  - Active Cu centers (TPR, EPR), understanding impact of aging and Cu transition: Cu(OH)$^{1+}$ to Cu$^{2+}$ to Cu$_x$O$_y$
  - SSZ-13: NMR
**SUMMARY**

Aftertreatment **effectiveness, durability, cost**

**SCO-SCR binary catalyst development**

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**PSO metric**

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<td>490°C</td>
</tr>
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**Catalyst Inlet Temperature [°C]**

- Fast SCR
- Std SCR
- No SCO phase
  - 0.1-µm colloidal ZrO₂
  - 1-µm ZrO₂ (600°C decom.)
  - 1-µm ZrO₂ surface modified w/ Nb₂O₅

**NOₓ/NOₓ Out [200°C]**

- SCR
- SCO1
- SCO2
- SCO3
- SCO4

**NO Reduction Efficiency**

- SCR
- Fast SCR
- Std SCR

22A asymmetrical

22B

22C symmetrical

Soot SCR
Technical Back-Up Slides
The SCRF washcoat

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**SCRF – findings from prior CRADA**

**Flow**

**Cu/Z slurry**

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**Graphs**

- **Pressure Drop, kPa**
- **Accumulated Soot, g/L**

**Upstream**

- 90 g/L SCR catalyst
  - ∆P after initial loading phase: ~11.5 kPa @ ~0.5 g/L soot

**Downstream**

- 150 g/L SCR catalyst
  - ∆P after initial loading phase: ~20.5 kPa @ ~0.52 g/L soot

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**Incremental Pore Volume (mL/g)**

**Pore Diameter (μm)**

- ~150 g/L Catalyst: ~54% porosity
- ~90 g/L Catalyst: ~53% porosity
- ~60 g/L Catalyst: ~60% porosity
- No Catalyst: ~68% porosity
Technical Back-Up Slides
SCR reaction network (simplified)

4NH₃ + 3O₂ → 2N₂ + 6H₂O
4NH₃ + 5O₂ → 4NO + 6H₂O
NO + ½ O₂ ⇌ NO₂

2NH₃ + 2NO + ½O₂ → 2N₂ + 3H₂O
2NH₃ + 2NO + 2NO₂ → 2N₂ + 3H₂O
8NH₃ + 6NO₂ → 7N₂ + 12H₂O

2NO₂ + 2NH₃ → N₂ + H₂O + NH₄NO₃
NH₄NO₃ ⇌ NH₃ + HNO₃
2NO₂ + H₂O ⇌ HONO + HNO₃

NH₃ + HNO₃ → N₂O + 2H₂O

► Standard SCR reaction (NO₂/NOₓ = 0)
► Fast SCR reaction (NO₂/NOₓ = 0.5)
► NO₂-only SCR reaction (NO₂/NOₓ = 1)
10% O$_2$, 8% CO$_2$, 7% H$_2$O, 300 ppm NO$_x$, 300 ppm NH$_3$

Pre-treatment – 60 minutes @ 600°C

Protocol executed at 500°C, 450°C, 275°C, 200°C

### 8 Step SCR Protocol

<table>
<thead>
<tr>
<th>Step</th>
<th>NO</th>
<th>NO$_2$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
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<td>5</td>
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<tr>
<td>6</td>
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<td>150</td>
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</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>150</td>
<td>150</td>
<td>0</td>
</tr>
</tbody>
</table>
Steps 1 & 5
- NO oxidation (to NO₂)
- NOₓ storage

Steps 2 & 6
- SCR performance
- NH₃ slip
- Parasitic NH₃ oxidation
- N₂O selectivity
- NO₂/NOₓ in effluent
- NH₃ SCR storage

Steps 3 & 7
- NH₃ oxidation (by O₂)
- Vacant NH₃ storage

Steps 4 & 8
- Total NH₃ storage
**Technical Back-Up Slides**

**Example tabular data**

<table>
<thead>
<tr>
<th>Step</th>
<th>SS</th>
<th>D</th>
<th>SCR reaction</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Step 1</td>
<td>SS</td>
<td>D</td>
<td>NO oxidation</td>
<td>4.7%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NO\textsubscript{X} storage</td>
<td>19.5</td>
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<tr>
<td>Step 2</td>
<td>SS</td>
<td>D</td>
<td>NO\textsubscript{X} conversion</td>
<td>85.3%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NH\textsubscript{3} slip</td>
<td>10.4%</td>
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<tr>
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<td>Parasitic NH\textsubscript{3} oxidation</td>
<td>4.3%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>N\textsubscript{2}O selectivity</td>
<td>0.4%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NO\textsubscript{2}/NO\textsubscript{X} effluent</td>
<td>2.2%</td>
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<tr>
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<td>SS</td>
<td>D</td>
<td>NH\textsubscript{3} storage (SCR)</td>
<td>74.6</td>
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<td>Step 3</td>
<td>SS</td>
<td>D</td>
<td>NH\textsubscript{3} oxidation (by O\textsubscript{2})</td>
<td>18.5%</td>
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<td>NH\textsubscript{3} storage (vacant)</td>
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<td>Step 4</td>
<td>D</td>
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<td>NH\textsubscript{3} storage (total)</td>
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<tr>
<td>Step 5</td>
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<td>D</td>
<td>NO\textsubscript{X} oxidation</td>
<td>0%</td>
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<td>NO\textsubscript{X} storage</td>
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</tr>
<tr>
<td>Step 6</td>
<td>SS</td>
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<td></td>
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<td>NH\textsubscript{3} slip</td>
<td>1.8%</td>
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<tr>
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<td></td>
<td></td>
<td>Parasitic NH\textsubscript{3} oxidation</td>
<td>0.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N\textsubscript{2}O selectivity</td>
<td>0.6%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NO\textsubscript{2}/NO\textsubscript{X} effluent</td>
<td>13.2%</td>
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<td>NH\textsubscript{3} storage (SCR)</td>
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<tr>
<td>Step 7</td>
<td>SS</td>
<td>D</td>
<td>NH\textsubscript{3} oxidation (by O\textsubscript{2})</td>
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<td>Step 8</td>
<td>D</td>
<td></td>
<td>NH\textsubscript{3} storage (total)</td>
<td>193.8</td>
</tr>
</tbody>
</table>

**What are we looking for?**

- **SCR activity**
  - SCR activity **SHOULD** provide good indication if we are producing NO\textsubscript{2} insitu
  - Standard (NO only) SCR reaction conditions should yield superior results (with inclusion of fast SCR reaction)
  - Fast (equimolar NO, NO\textsubscript{2}) SCR reaction conditions should yield inferior results (with inclusion of NO\textsubscript{2}-only SCR reaction)