# Biofuel Impacts on Aftertreatment Devices

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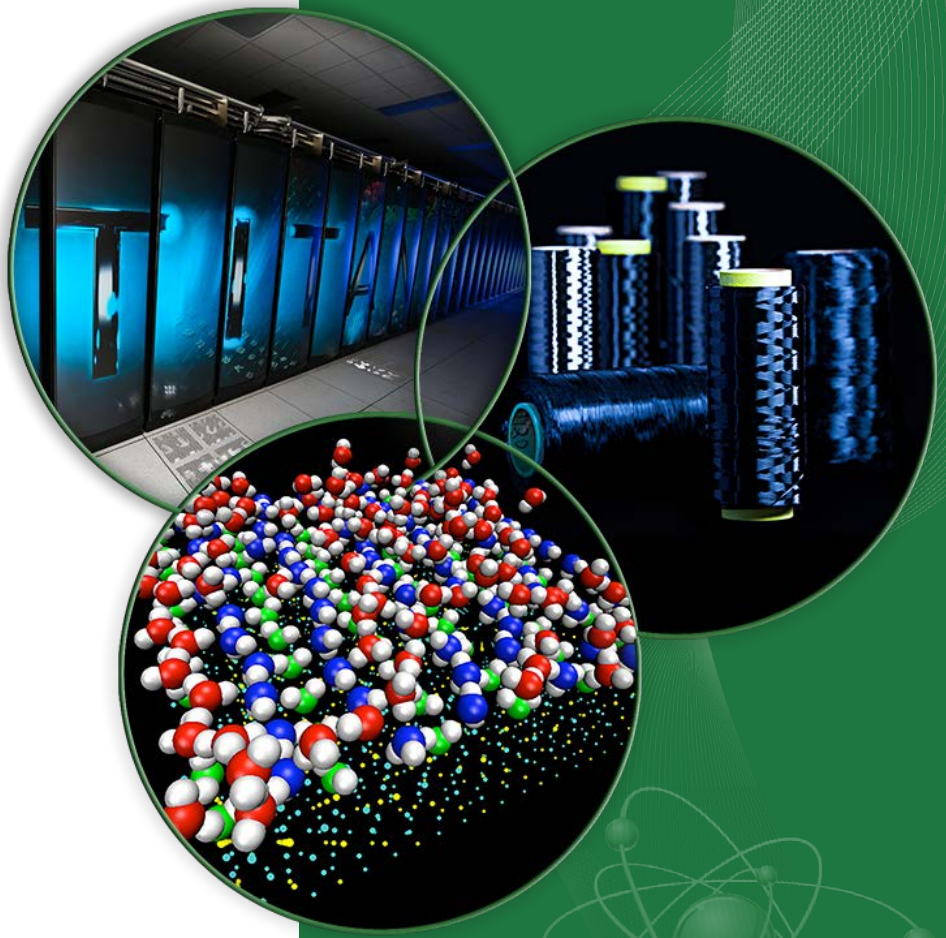
June 9th, 2016

Project ID # PM055



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# Overview

## Timeline

- Start: August 2013
- End: September 2018
- 52% complete

## Budget

- Total Project Funding
  - DOE: $400K
- Funding Received:
  - FY15: $130K
  - FY16: $165K

## Barriers

- Multi-Year Program Plan: Evaluate the impact of at least one renewable fuel blend on at least one heavy-duty emission after-treatment device.
- 2013 LD Materials Workshop Report: "Reduce petroleum dependence by developing propulsion materials that are compatible with advanced fuels."

## Partners

- Cummins
- Ford
- National Renewable Energy Laboratory (NREL)
- Manufacturers of Emission Controls Association (MECA)
- Truck and Engine Manufacturers Association (EMA)
- National Biodiesel Board (NBB)
- MIT-Sloan Automotive Laboratory

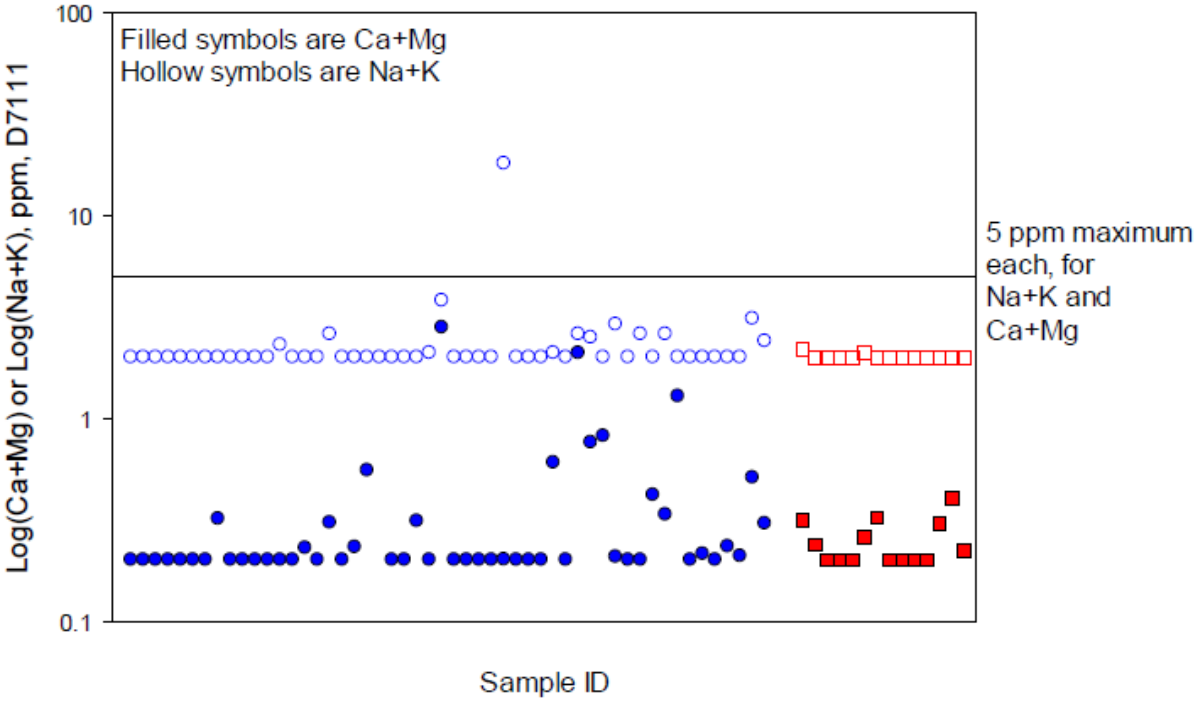
# Relevance

- US Renewable Fuel Standards call for increased biodiesel utilization
- Biodiesel contains Na & K metal impurities from production
- Impurities may impact catalyst system performance & durability
- Objective: investigate impact of Na on commercial catalyst system
  - Use full-useful-life rapid-aging protocol based on ASTM Standard Na limit
- Determine if ASTM-Standard limits are sufficient or need tightening

| **Relevant US Regulatory Standards** | |
|---|---|
| Renewable Fuel Standard | 1.9 billion gallons in 2017 |
| ASTM D6751 | 5 ppm Na + K in 100% Biodiesel (B100) |
| Catalyst end-of-life $NO_x$ Limit | 0.33 g/bhp-hr |
| Catalyst end-of-life mileage | 435,000 miles |
| Drive cycle | FTP: Federal Test Procedure |

# NREL Biodiesel Fuel Quality Survey – (Na + K)

- 2011 B100 survey results
- Over 90% of samples below detection limit for both metals
  - Lower limit of detection was 1 ppm for Na and K, so much of the data was reported as <1 ppm.
  - Each result was assigned a value of 1 ppm for purposes of illustration, resulting in a combined value of 2 ppm.




Alleman, T.L., Fouts, L., Chupka, G. "Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011" Technical Report, NREL/TP-5400-57662, March 2013.

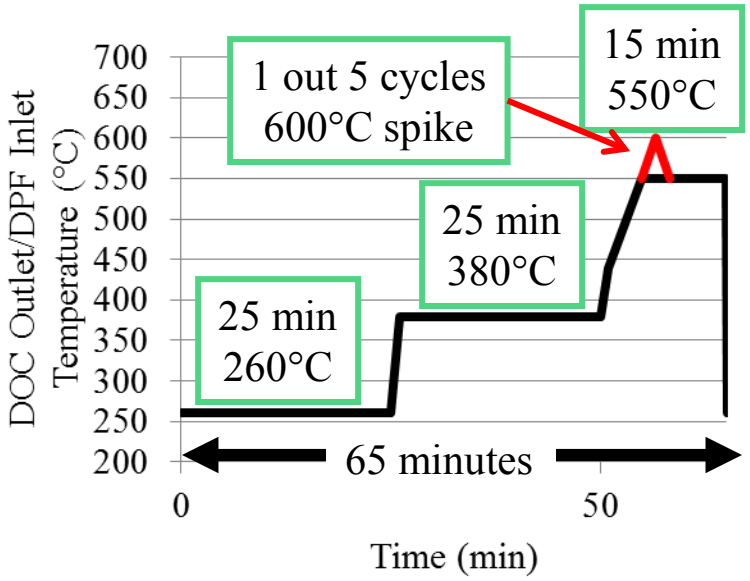
# Milestones

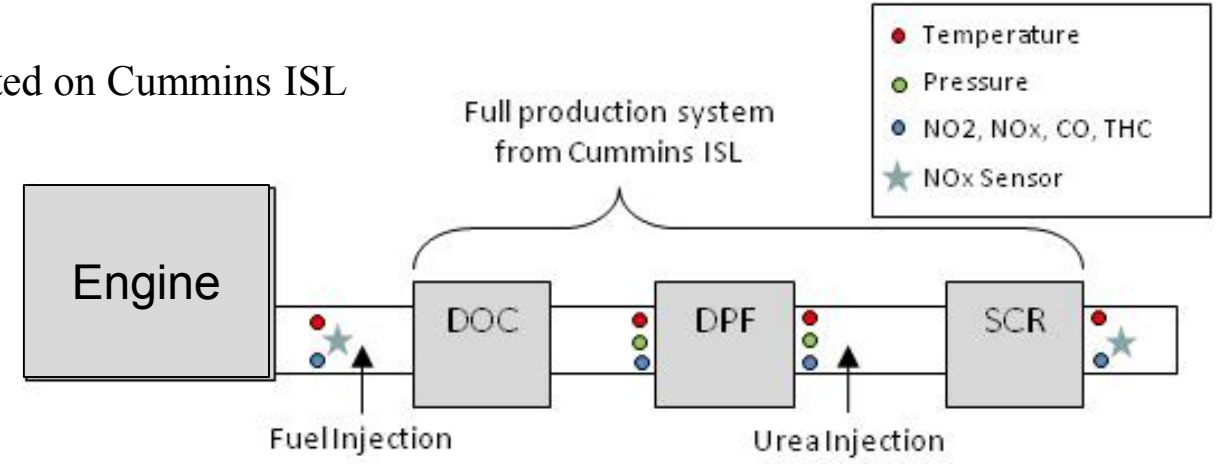
| Date | Milestones | Status |
|---|---|---|
| **June 2015** | **Identify deactivation mechanisms in heavy-duty SCR and DOC samples aged with Na-doped fuel provided by NREL.** | **Complete** |
| **September 2015** | **Submit annual report.** | **Complete.** |
| **March 2016** | **Replicate thermal conditions and dopant levels used for NREL engine tests using the Genset at ORNL, to enable lower cost accelerated testing of after treatment devices.** | **Complete.** |
| | | |
| | | |

# Approach/Strategy

- Aged a full production exhaust system from a heavy-duty Cummins ISL engine (via NREL) using exhaust generated by a Cat C9 engine.
- 1000-hour rapid-aging protocol
  - 435,000 miles/14,000 hrs equivalent
  - 65 minute, three-mode, aging cycle with 923 cycles.
- Na impurity aging: B20 + 14 ppm Na.
  - 14x ASTM Standard per SAE 2014-01-1500.
- Thermal aging: 179 hrs ≥ 550 °C.
- Performance Assessment
  - Emissions evaluation conducted on Cummins ISL
  - Bench reactor
  - Microscopy, electron probe microanalysis (EPMA), mechanical properties.
- Accelerated aging with diesel genset.

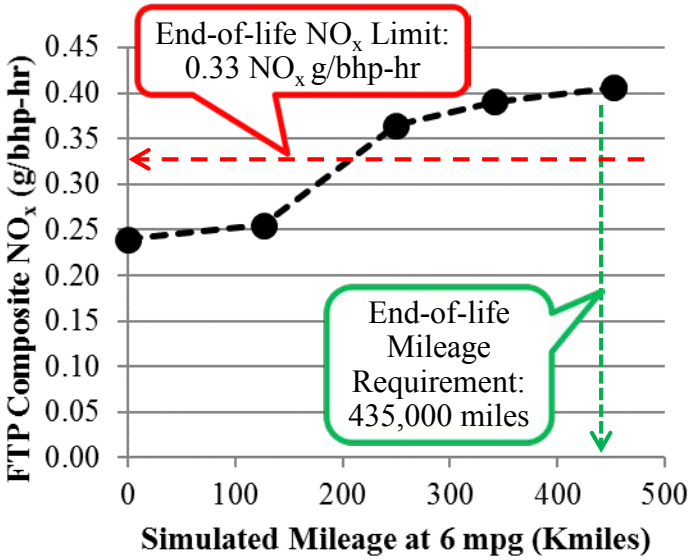
Cummins-Approved Rapid-Aging Cycle



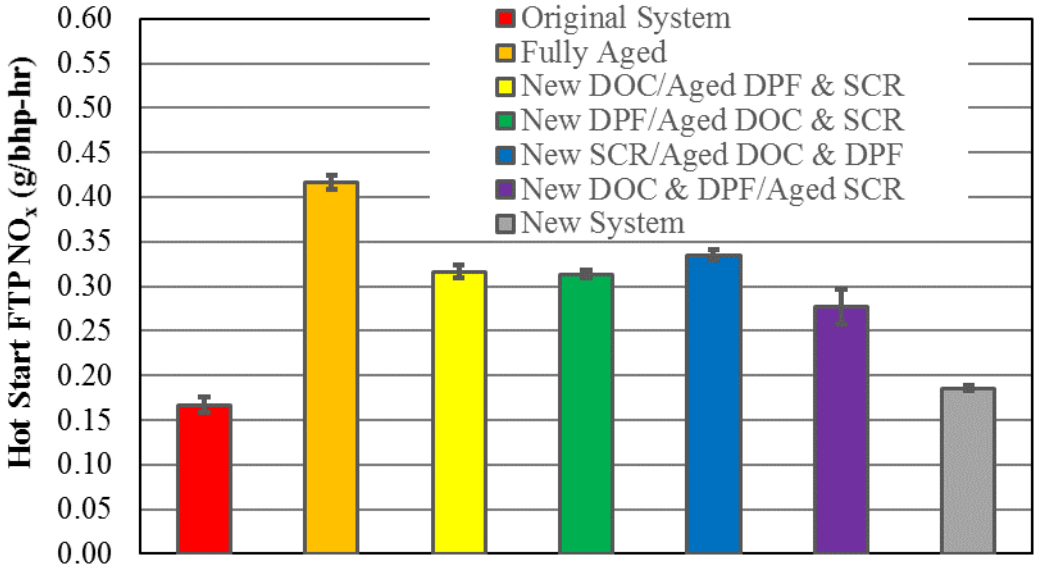



# Technical Accomplishment: Cummins ISL tailpipe NOx emissions increased from 0.25 to 0.40 g/bhp-hr over the course of the test

FTP Emissions Testing



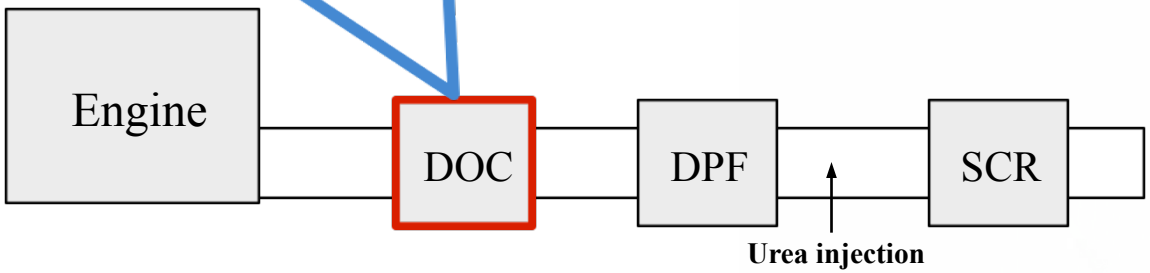

Hot Start FTP Emissions Testing




- End-of-life $NO_x$ limit (0.33 g/bhp-hr) was reached before the 435,000 mile end-of-life requirement.
- Hot-start FTP was used to assess component contributions by systematically swapping aged for degreened components.

**DOC, DPF & SCR all contribute to aging degradation**

# Diesel Oxidation Catalyst



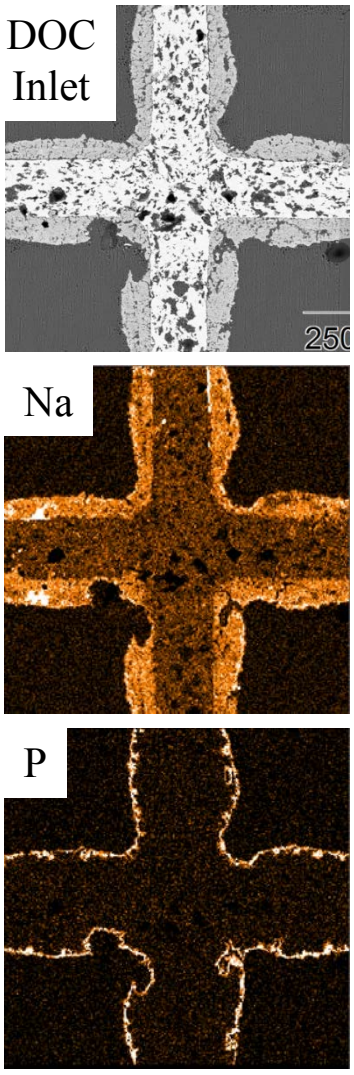

**DOC:**

Washcoat: Pt:$Al_2O_3$

Monolith support: Cordierite

# Cummins-Developed Protocols Applied to Identify Individual Contaminant Impacts

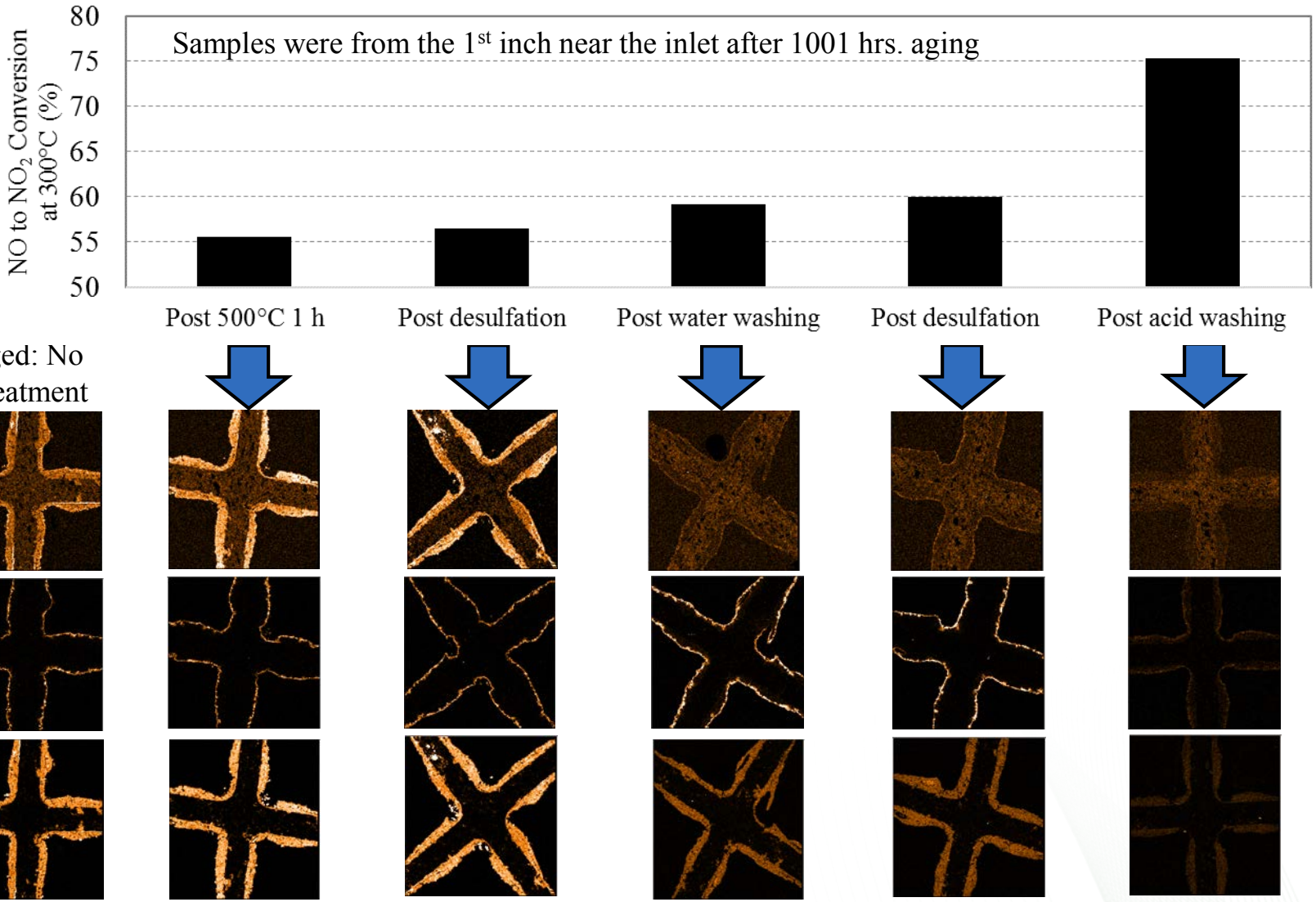
Fully Aged




| Purpose | Protocol Conditions |
|---|---|
| **Remove HC, $H_2O$, etc.** | **High-temperature oxidation**<br>500°C, 1h, 60k/h, 10%$O_2$+7%$H_2O$+Ar |
| **Remove S** | **DeSulfation** (2 cycles)<br>600°C; 5min:5min rich:lean cycling<br>Lean: 10%$O_2$+7%$H_2O$+Ar<br>Rich: 1% $H_2$+7%$H_2O$-Ar |
| **Remove Na** | **DI water washing** (4 cycles)<br>Ultrasound, 70°C 15min each cycle |
| **Remove P** | **Acid washing** (1 cycle)<br>organic acid mixture, ultrasound, 70°C 1h.<br>(SAE 2012-01-1094) |
| **Performance evaluation** | **NO Oxidation**<br>200ppm NO+ 10%$O_2$+7%$H_2O$+Ar, 60k/h SV; 150°C→450°C; 50°C steps |

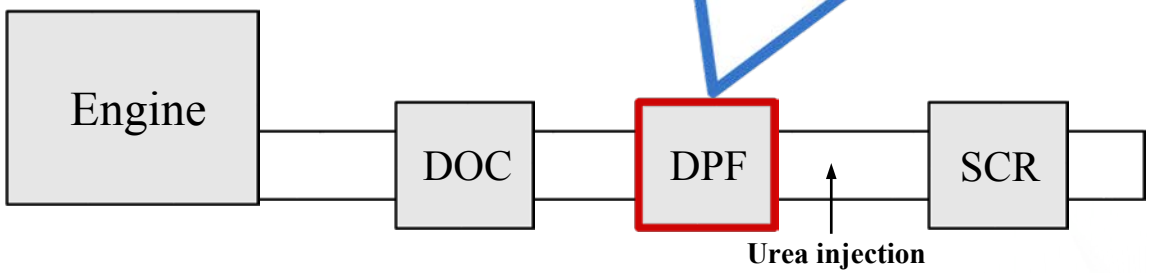
- Na and P both deposit on the DOC.
- Performance evaluation after each cleaning step.

# Effect of Treatments on NO to $NO_2$ Conversion Efficiency




- Acid washing removed significant amounts of P and led to significant recovery of NO oxidation. This indicates that engine oil P was the primary source of deactivation, not Na.

# Diesel Particulate Filter




**DPF:**

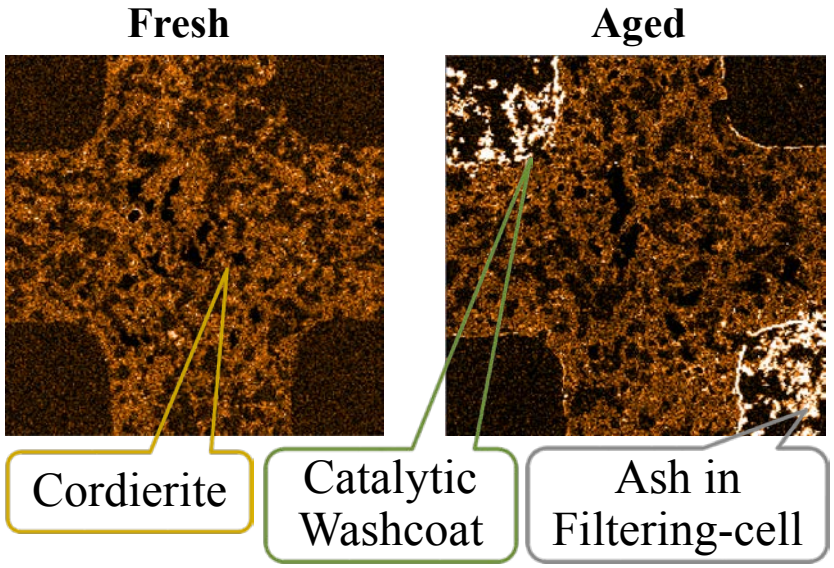
Filter: Cordierite

Washcoat: Pt/Pd:$Al_2O_3$

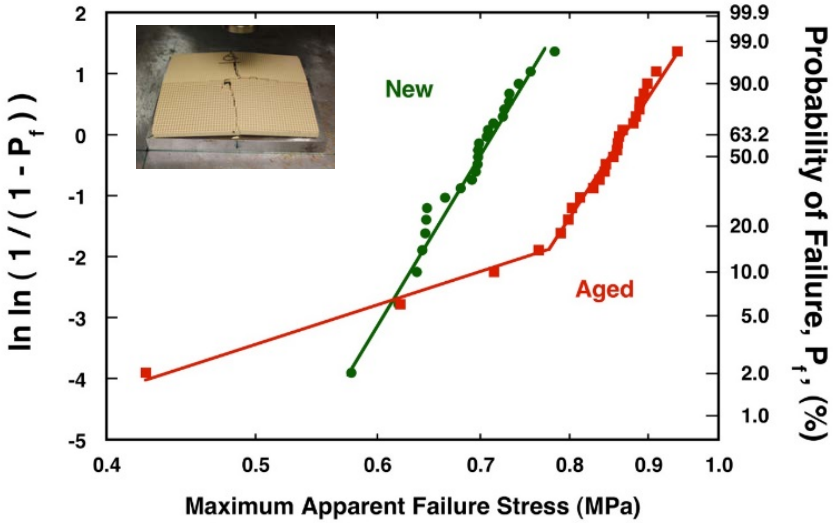
- ~5 µm layer on inlet & outlet channels

# Technical Accomplishment: Little to No Aging Impact on Mechanical Properties of the DPF

Na Map of DPF

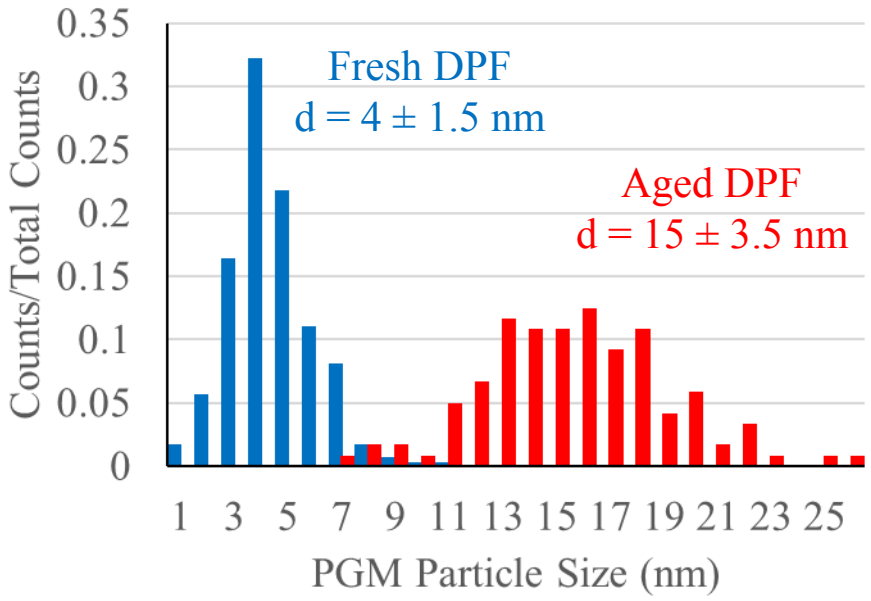



Weibull Distribution

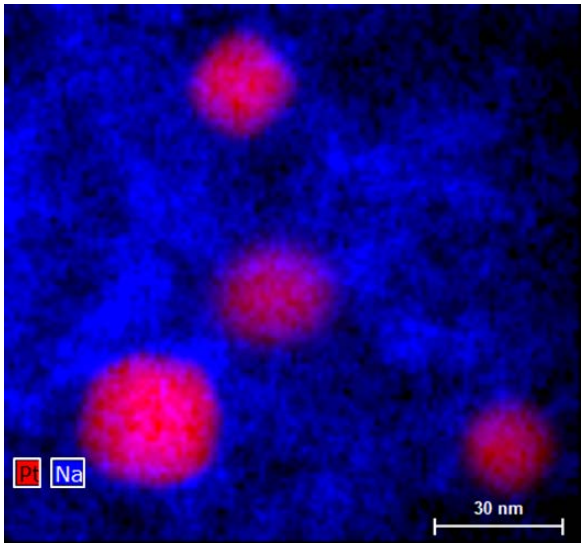



- During Phase 1, Na diffusion into cordierite occurred and degraded the DPF thermal shock resistance.
  - Regeneration temperature was 850 °C in previous study compared to 550 °C here.
- Aging increases the DPF strength possibly due to ash present in the cordierite pores.
  - A second flaw type may be present following aging.
- No change in thermal expansion coefficient with aging.

# Pt/Pd Coarsening & Ash Buildup Observed in Aged DPF Washcoat




Elemental Maps in Aged DPF Washcoat

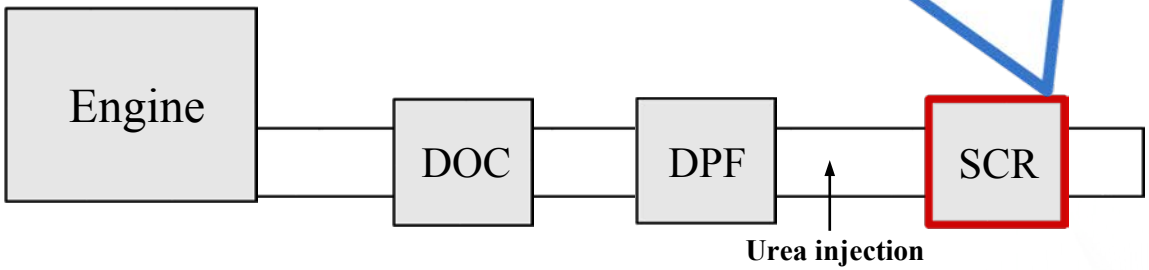



Collected with FEI Talos F200X S/TEM

- Pt particles in the DPF washcoat coarsened following aging which is indicative of thermal aging.
- Na is evenly distributed throughout the wash coat and not coating the Pt/Pd particles.
- 857 g (45g/L) of ash during full aging with ~79% coming from the biodiesel.
  - For this particular system test, it is estimated that B20 fuel at the Na spec limit would have resulted in 25% more ash into the DPF

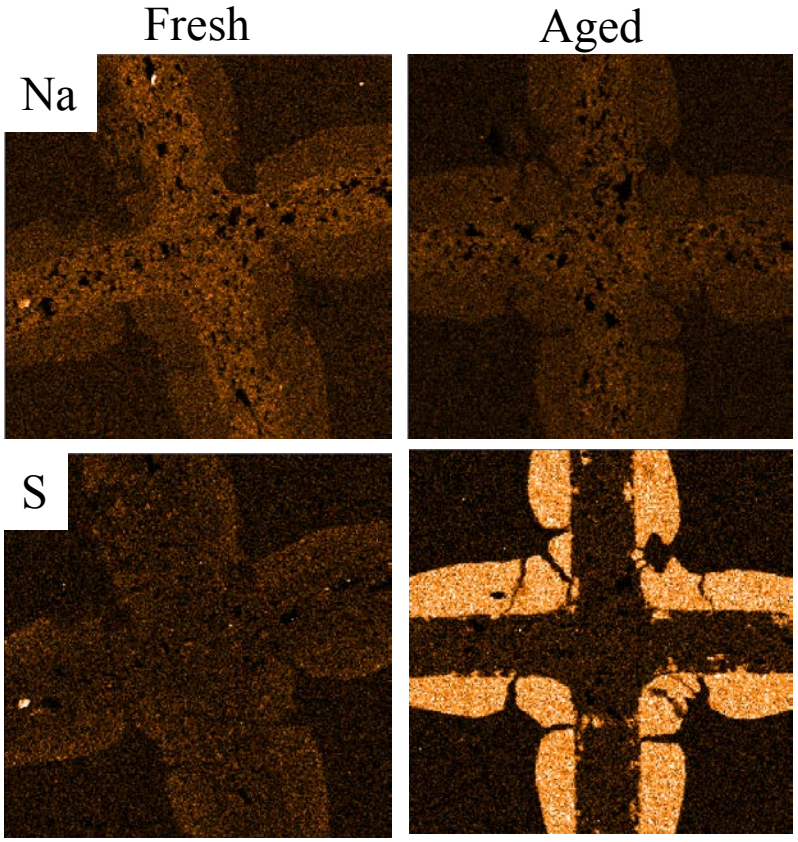
This research was performed, in part, using instrumentation provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program, and the Nuclear Science User Facilities

# Selective Catalytic Reduction




**SCR:**
Catalyst: Cu/SAPO-34
Monolith support: Cordierite

# Technical Accomplishment: Na Does Not Cause Aged-SCR Performance Loss



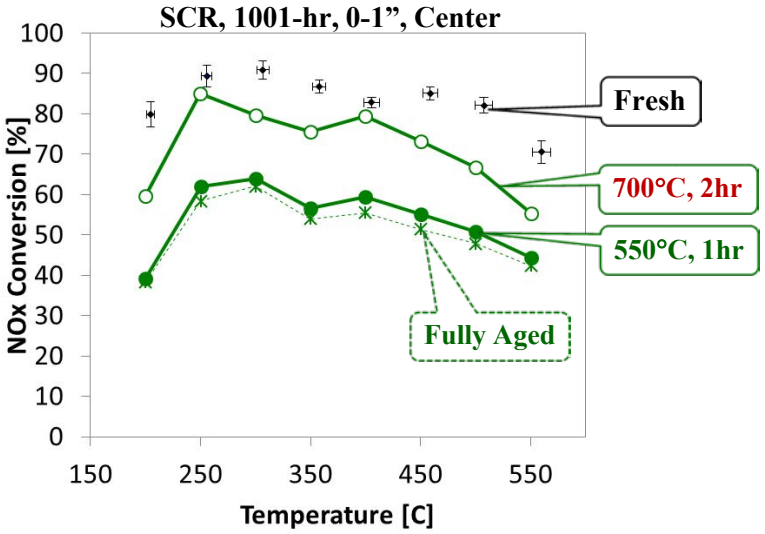

ICP-MS

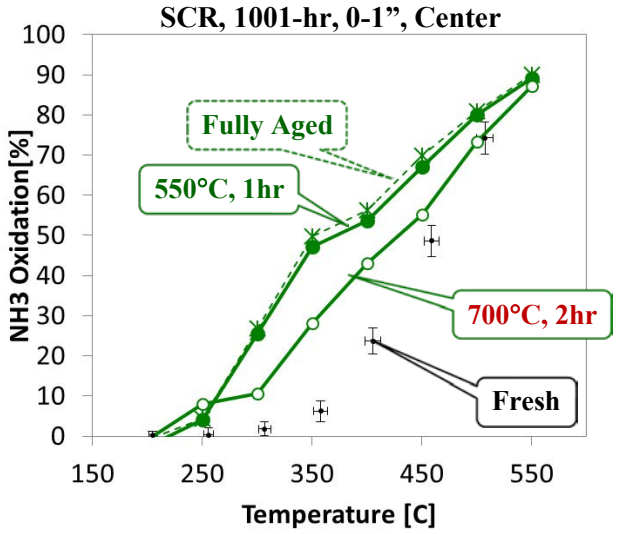
| Sample | Na (µg/g) |
|---|---|
| Fresh SCR Washcoat (Inlet) | 309 |
| Aged SCR Washcoat (Inlet) | 486 |
| Aged SCR Washcoat (Outlet) | 640 |

- The DPF shields the SCR from Na. Only S increased after aging
- Inductively coupled plasma mass spectrometry (ICP-MS) of SCR showed little increase in Na following aging.
- Measurements at Cummins revealed a slight decrease in surface area but not enough to account for the reduced performance.

# Technical Accomplishment: The signatures of performance evaluations on the aged sample are consistent with Pt contamination of the SCR

Cummins Data




Aged inlet core showed below features compared with lab reference:

- Increase in $NH_3$ oxidation activity
- Decrease in $NO_x$ conversion across the temperature range, especially at high temperature
- All above effects can be suppressed by high temperature treatment (700°C or so)

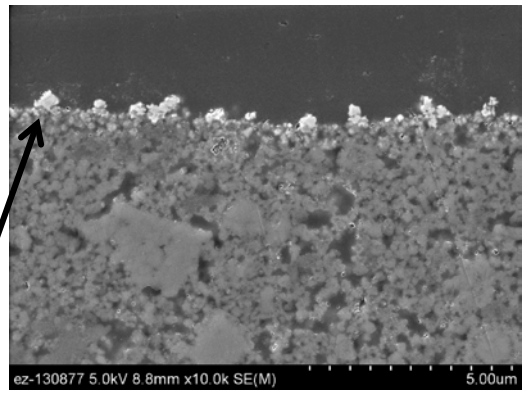
**It is speculated that vapor migration from the DPF during an atypical thermal event caused the Pt contamination**

# New stationary generator was operated with Na-doped B20 and the same SCR degradation mechanism observed on the LD Phase 2 full-scale test occurred

Aged

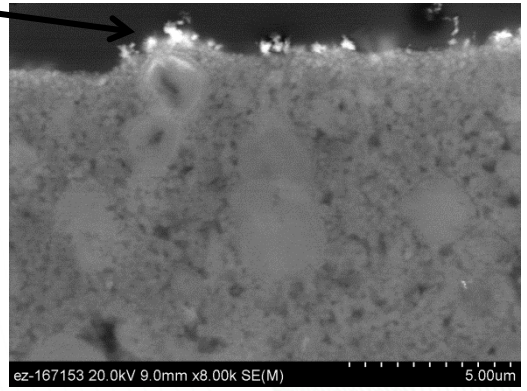
Fresh

Full-scale test on Dyno




$CuO_x$ Particles

Genset Test




- Discoloration from $CuO_x$ particles is observed following aging with the genset.
- Testing with a genset will greatly reduce the expense of accelerated engine testing.
- Targeted testing will be performed to isolate the effects of different elements and heat treatments on emission controls.

# Responses to Previous Year Reviewers' Comments

Comment: One reviewer expressed concerns regarding the lack of replicate tests. Another said that various engine duty cycles that better represent real operation would be of interest.

Response: The genset will allow us to test under different conditions at much lower costs.

Comment: One reviewer wondered about the solubility of sodium sulfate and the possibility of its migrating through the filter and causing downstream impacts.

Response: As shown above, we observed no increase in Na in the SCR. The degradation of the SCR was probably associated with Pt migration.

Comment: Separating the impacts of Na and K, apart from the demonstrated impacts of P, also needs to be addressed. The well-known influence of P on aftertreatment devices seems to cloud the assessment of Na and K in this work.

Response: Using the Cummins cleaning protocols, we were able to separate the effect of Na from P and show that P is the primary source of degradation of the DOC.

# Collaborations and Coordination with Other Institutions

- Cummins: Richard Ancimer, Hongmei An and Leigh Rogoski
  - Conducted emissions testing on aged samples, conducted cleaning of aged samples to isolate the impact of contaminants and helped devise the testing protocol.
- Ford Motor Company
  - Provided in kind work on LD aftertreatment device characterization (FY14).
- National Renewable Energy Laboratory (NREL): Robert McCormick, Aaron Williams and Adam Ragatz
  - Performed accelerated engine tests.
- Manufacturers of Emission Controls Association (MECA)
  - Advised the project.
- Truck and Engine Manufacturers Association (EMA)
  - Advised the project.
- National Biodiesel Board (NBB)
  - Funded engine testing and helped devise testing protocol.
- MIT Sloan Automotive Laboratory: Justin Kamp
  - Conducted AFM and X-ray CT measurements on DPFs.

2015 Biodiesel Researcher of the Year

# Remaining Challenges and Barriers

- Due to cost, only the accelerated Na test was performed which limited our ability to separate Na effects from the thermal and lube-oil effects.
- The accelerated aging protocols do not accurately simulate changes that would occur in the real-world.

# Proposed Future Work

- Using the genset, we will test fresh sets of samples with and without fuel dopant in order to isolate the effect of Na.
- A used catalyst system from a truck that uses mainly B20 will be acquired and compared to our accelerated-aging samples.

# Summary

## Relevance

Will biodiesel negatively impact catalyst materials in aftertreatment systems?

## Approach/Strategy

- Accelerated aging with NREL/Cummins and materials characterization at ORNL.
- Low cost accelerated aging at ORNL using a genset.

## Technical Accomplishments and Progress

- The main effect of Na metal appears to be on the DPF through increased ash loading (with a secondary effect on NO oxidation in the DPF).
- The Na metal contamination is not a key factor in the degradation of NO oxidation of the DOC.
- When the SCR is downstream of a DPF, there is little or no Na contamination.

## Collaborations with Cummins, Ford, NREL, MECA, EMA, NBB, and MIT.

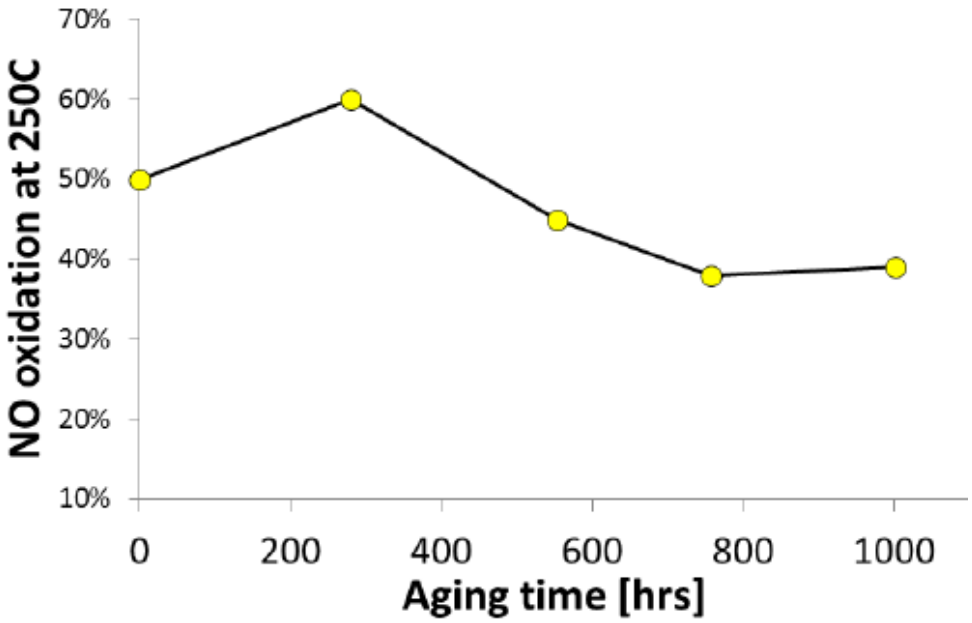
## Proposed Future Work

- Genset will be used to conduct accelerated biodiesel aging in order to determine the effect of metal additives on emissions control devices.
- Field-aged aftertreatment devices will be compared to our laboratory-tested samples.

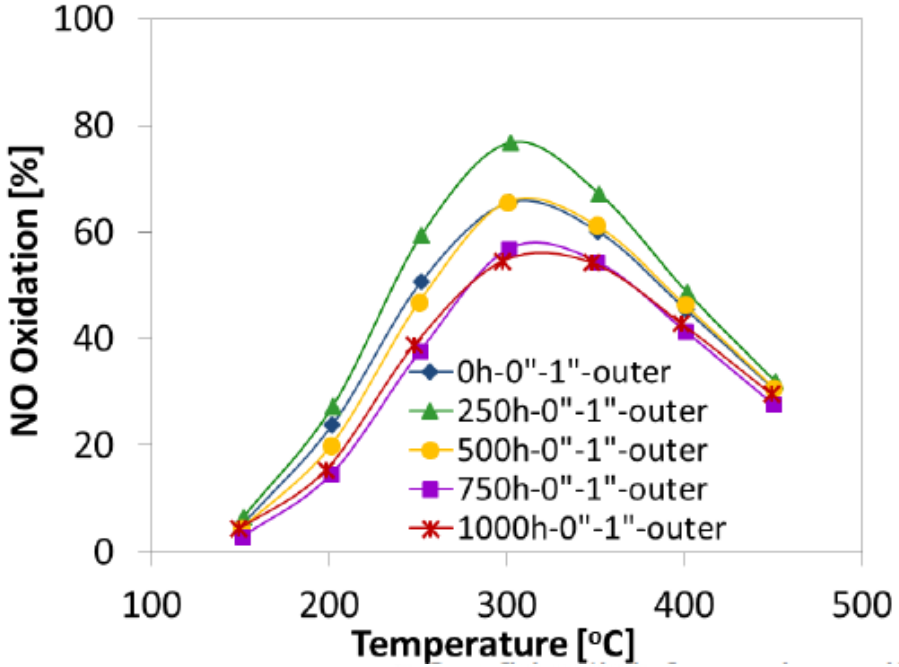
# Technical Back-Up Slides

# Technical Accomplishment: The DOC NO oxidation declined with aging (Cummins)

NO Oxidation to $NO_2$ at 250°C

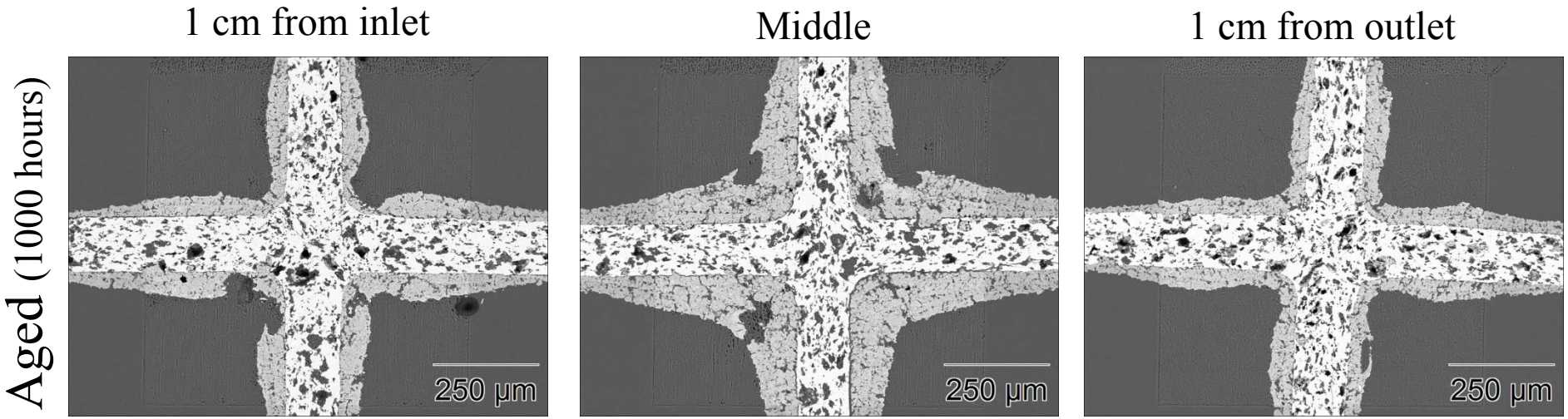



NO Oxidation vs. Exposure time




- Decline in $NO_x$ oxidation is most likely related to the accumulation and stabilization of chemical contamination.
- Could be from Na or lube oil metals.

# Technical Accomplishment: EPMA maps show Na present at the same concentration along the entire length of DOC following aging.



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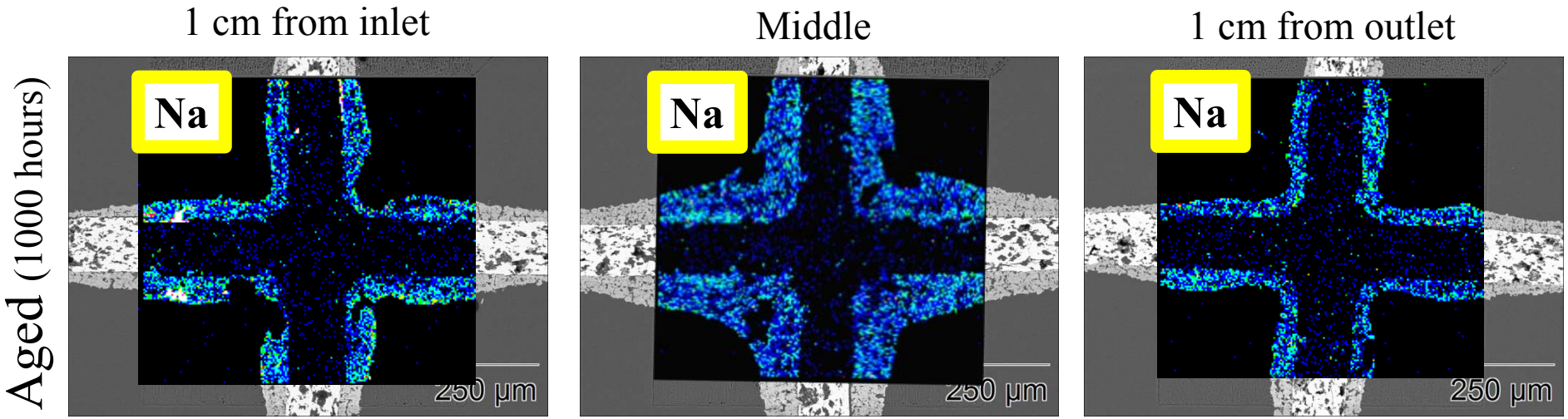

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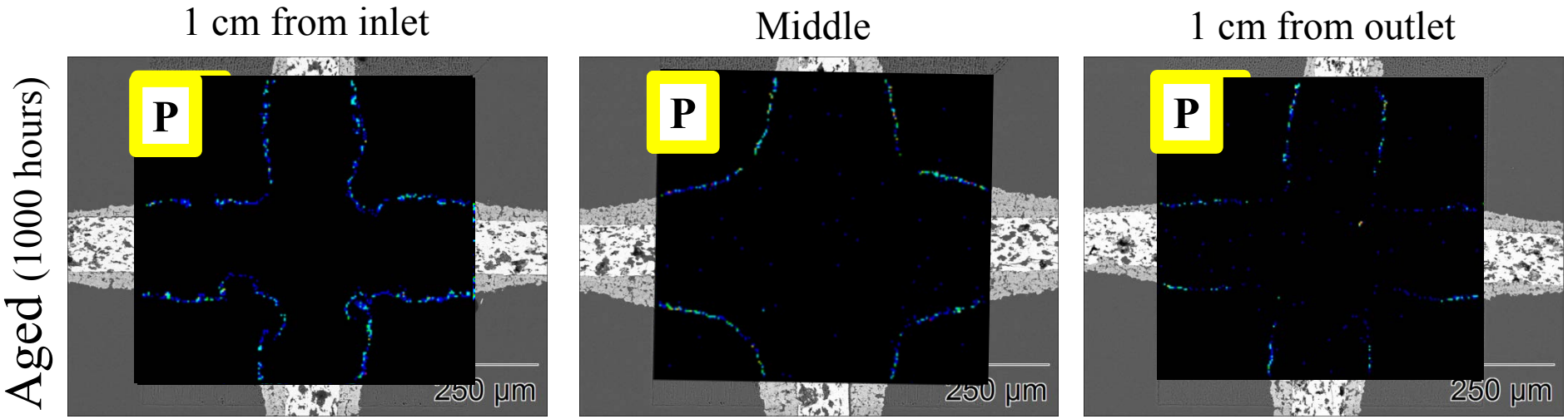
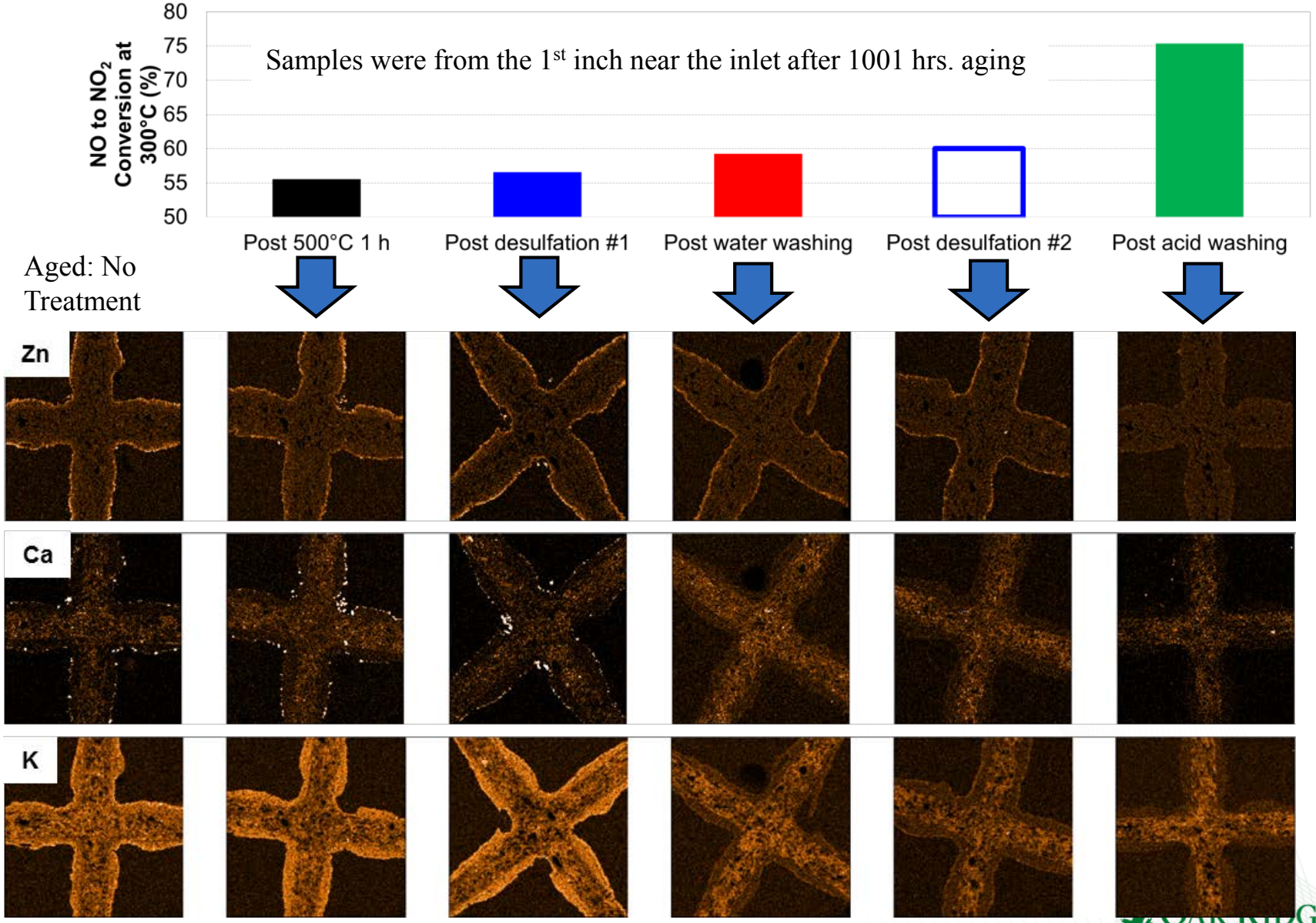
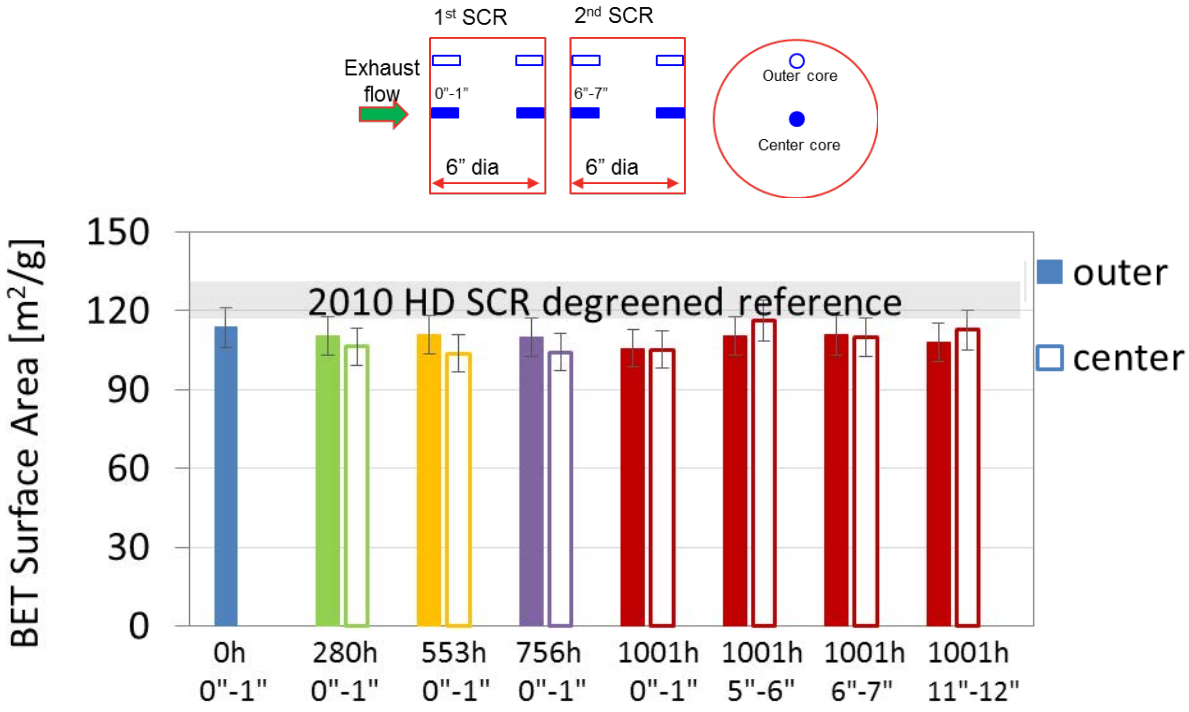



- Phosphorous from the lube oil is also present on the surface and may be contributing to the degradation.
- Aged samples treated at Cummins through desulfation, water washing and acid washing will be used to separate the effect of Na and P on the DOC.

# Effect of Treatments on NO to $NO_2$ Conversion Efficiency



# Technical Accomplishment: BET Surface Area Unchanged with Aging (from Cummins)




- BET surface area is spatially uniform and unchanged by aging.
- Other high-temperature impacts are possible.