Biofuel Impacts on Aftertreatment Devices

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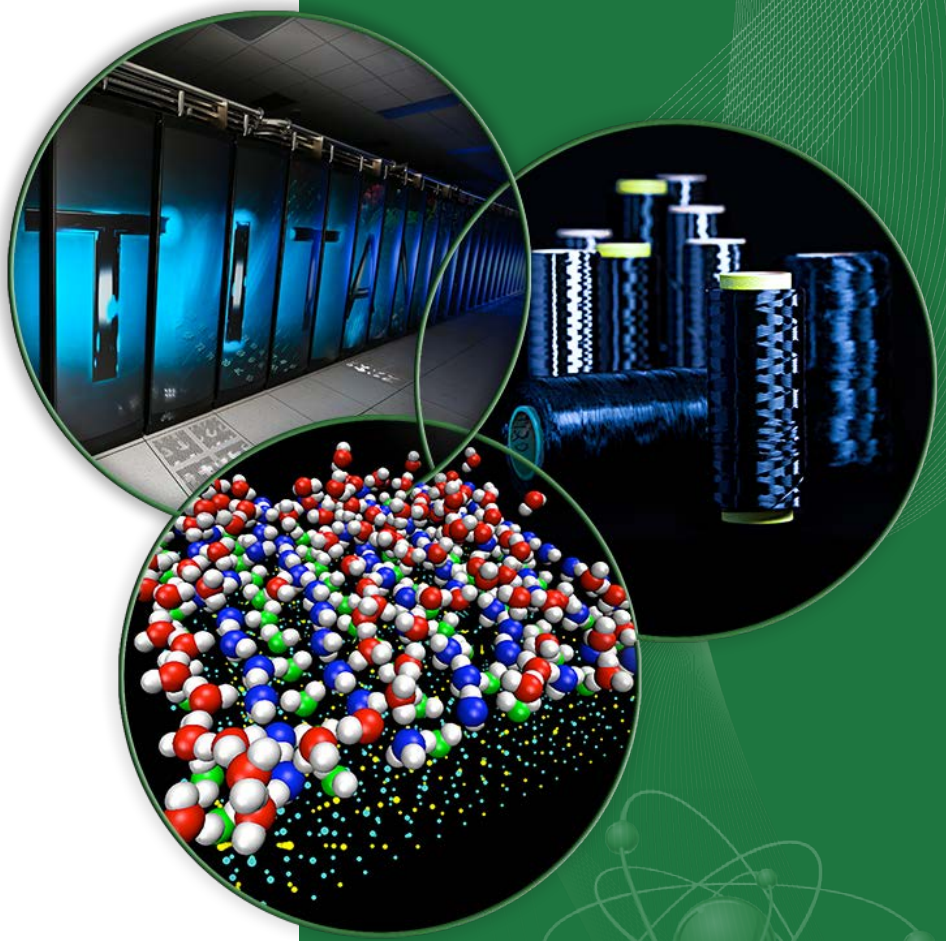

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Overview

Timeline

- Start: August 2013
- End: September 2017
- 48% complete

Budget

- Total Project Funding
  - DOE-$200K
- Funding Received:
  - FY13: $50K
  - FY14: $150K
  - FY15: $0K ($130K expected)

Barrier

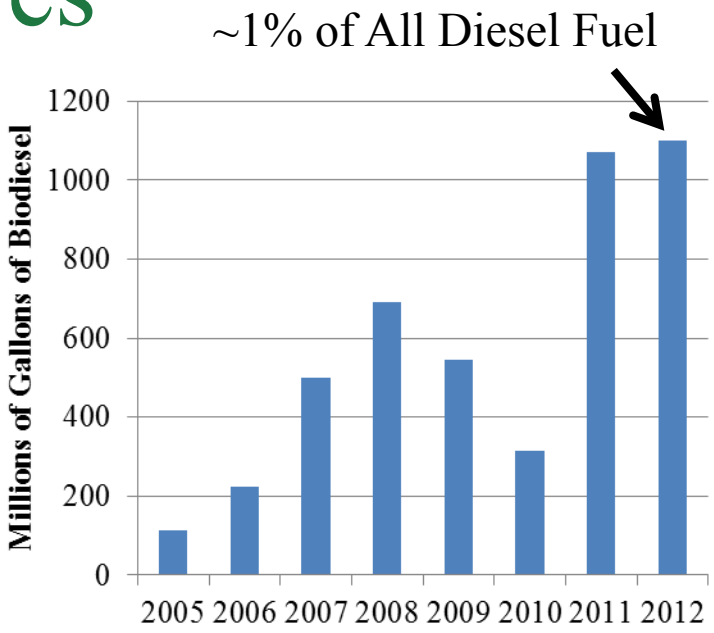
- Multi-Year Program Plan: By 2015, evaluate the impact of at least one renewable fuel blend on at least one heavy-duty emission after-treatment device.
- 2013 LD Materials Workshop Report: “Reduce petroleum dependence by developing propulsion materials that are compatible with advanced fuels.”

Partners

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

Relevance and Objectives

- What is the impact of metal impurities present in biodiesel on the performance and durability of diesel oxidation catalysts (DOC), selective catalytic reduction (SCR) catalysts and diesel particulate filters (DPF)?



- Expose aftertreatment devices to metal impurities in 20% biodiesel (B20) as specified by the current ASTM standard (1 ppm Na + K).
  - ✓ Total Na Exposure from B20 at 435,000 miles = 670 grams
- Conduct accelerated aging tests to simulate full-useful-life operation.
- Provide technical data to help determine if the ASTM standard needs to be tightened or if the current standard is acceptable.
  - ✓ Biodiesel has specs for Na/K, Ca/Mg; Petrodiesel does not.

Milestones

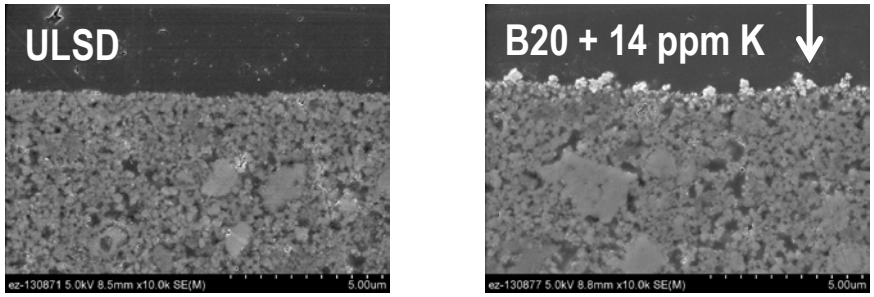
Milestones (FY15)
Q1: Conduct elemental maps on cross-sectioned samples to identify the location of Na, P, Ca, Zn and S elements in both SCR and DOC cores following accelerated aging at NREL: COMPLETED
Q2: Identify deactivation mechanisms in heavy-duty SCR and DOC samples aged with Na-doped fuel provided by NREL: ON TRACK
Q3: Mimic conditions and dopant levels used at NREL using our Gen-set at ORNL: ON TRACK
Q4: Submit annual report.

Previous Technical Accomplishments: How much acceleration is appropriate?

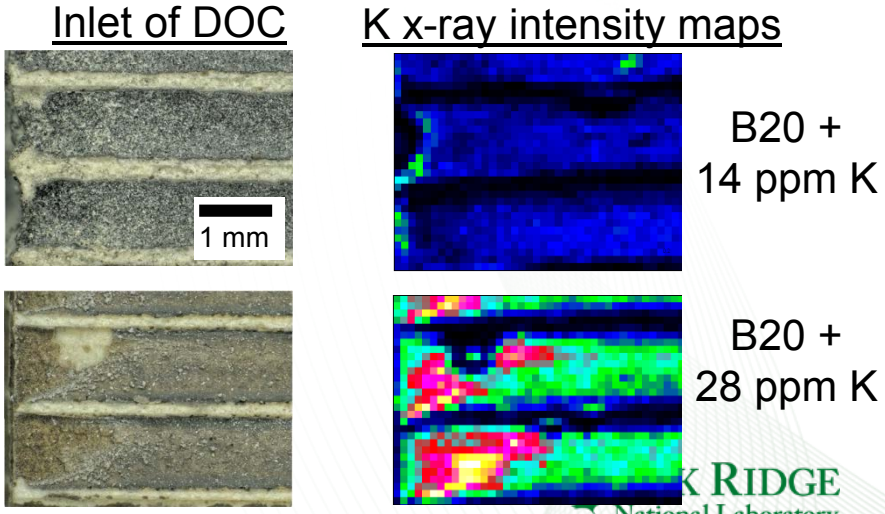
- Catalyst system from light-duty Ford F250 aged to equivalent of 150k miles exposure using three rates of accelerated aging (at NREL):
  - 200 hour test with B20 + 7ppm K
  - 100 hour test with B20 + 14ppm K
  - 50 hour test with B20 + 28ppm K
  - 100 hour test with ULSD + 0ppm K

  } Equal Total Doses of K
- Showed deactivation of SCR by displacement of Cu with K.
- Established acceptable dopant level of 14 ppm K or Na for accelerated aging.

Deactivation of SCR was due to displacement of Cu with K resulting in Cu_xO particles on the SCR surface

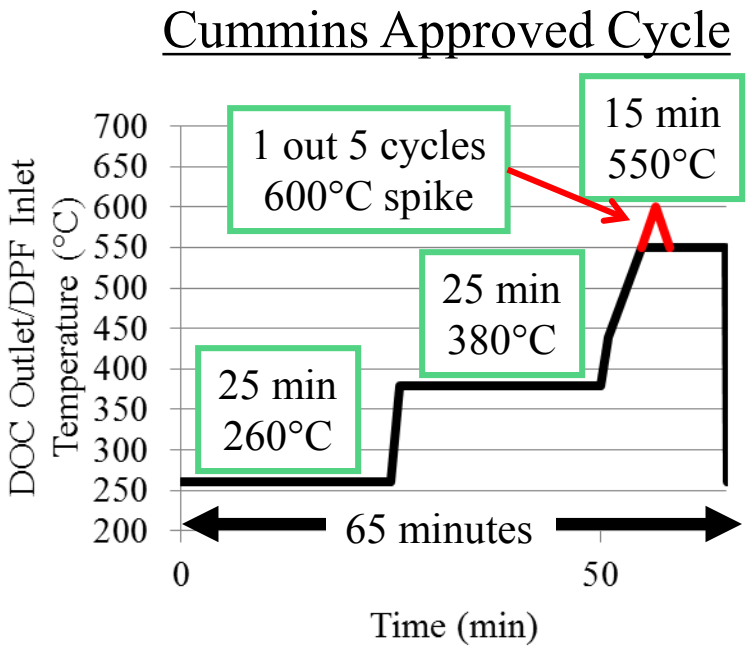


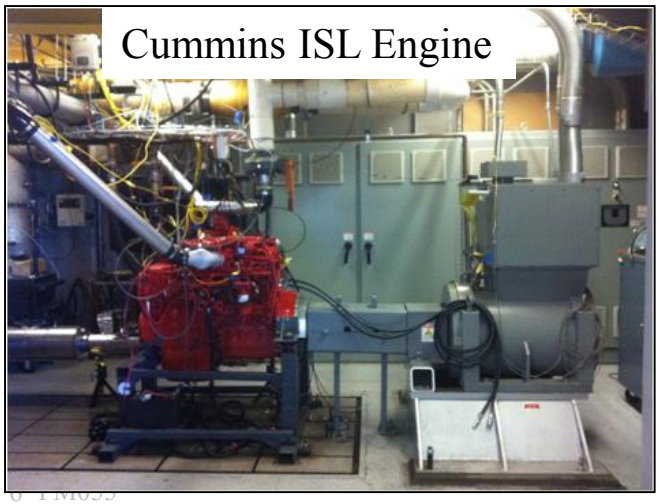
28 ppm K falsely accelerates aging

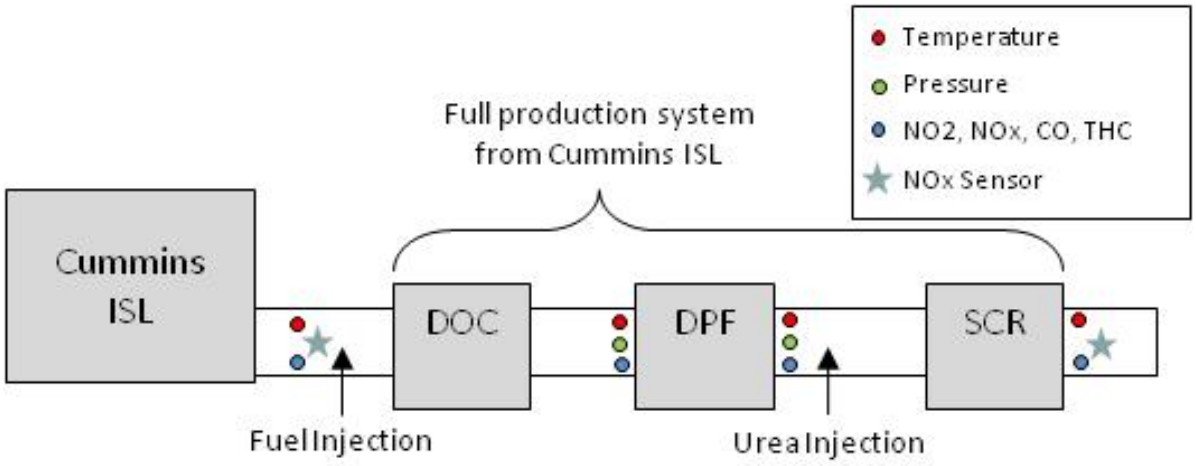


Approach

- Aged a full production exhaust system from a heavy-duty Cummins ISL engine (at NREL) using exhaust generated by a Cat C9 engine.
- 435,000 miles/14,000 hrs were simulated in 1000 hrs using a 65 minute, three-mode, aging cycle repeated 923 times.
- Thermal aging: 179 hours at or above 550°C.
- Na impurity aging: B20 + 14 ppm Na (14x).

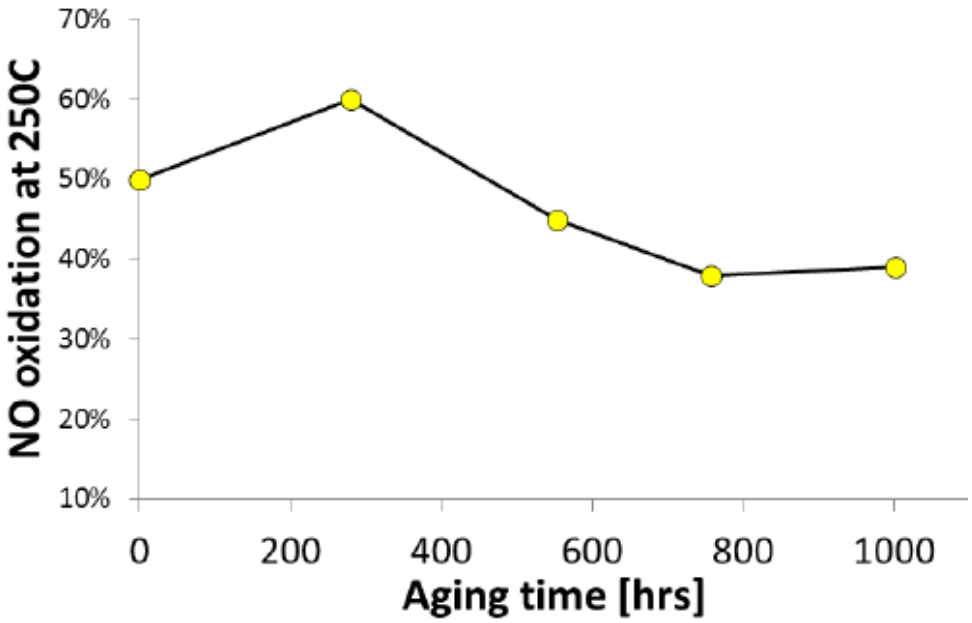




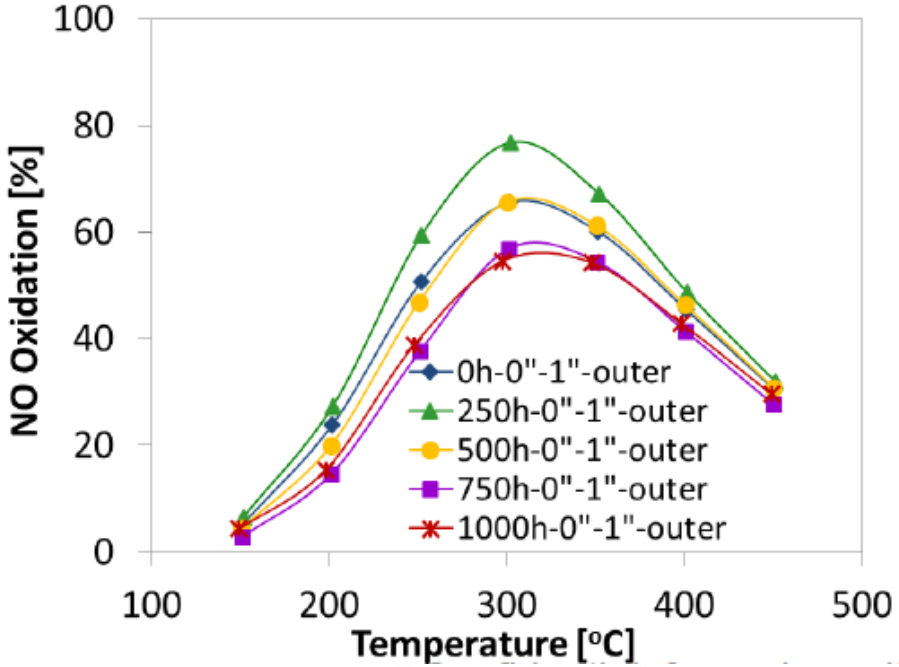


Technical Accomplishment: The DOC NO oxidation declined with aging (Cummins)

NO Oxidation to NO_2 at 250°C

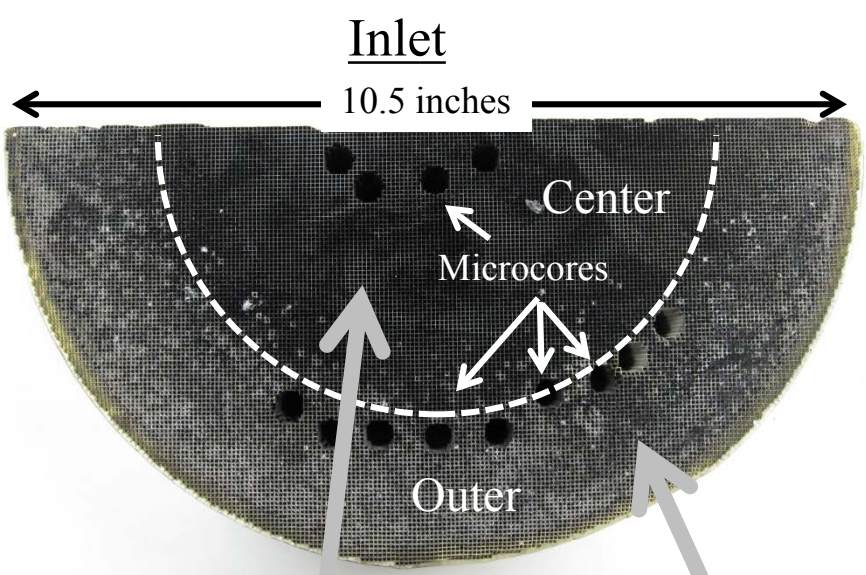


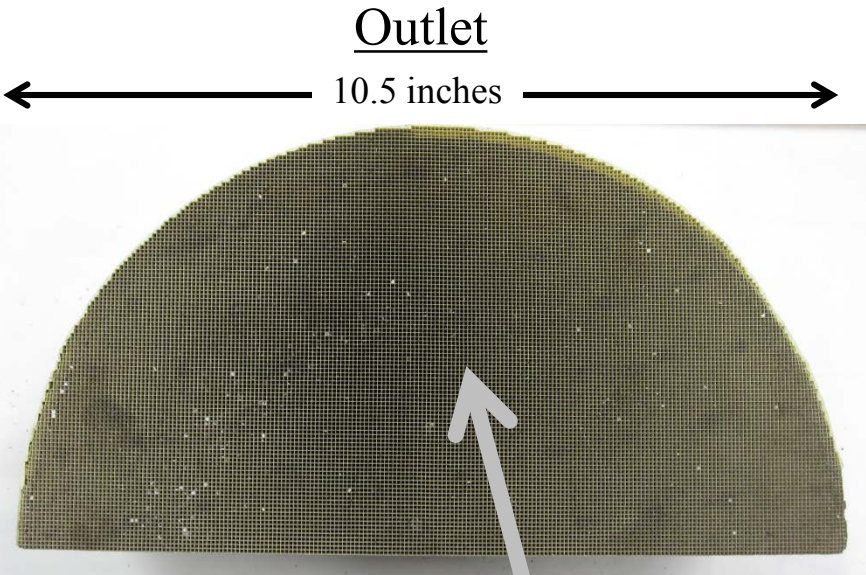
NO Oxidation vs. Exposure time

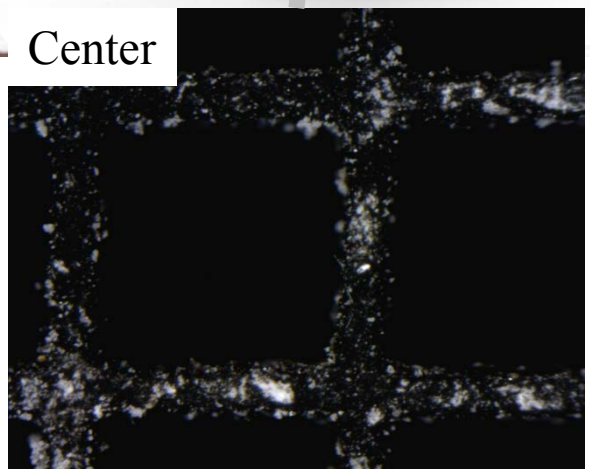


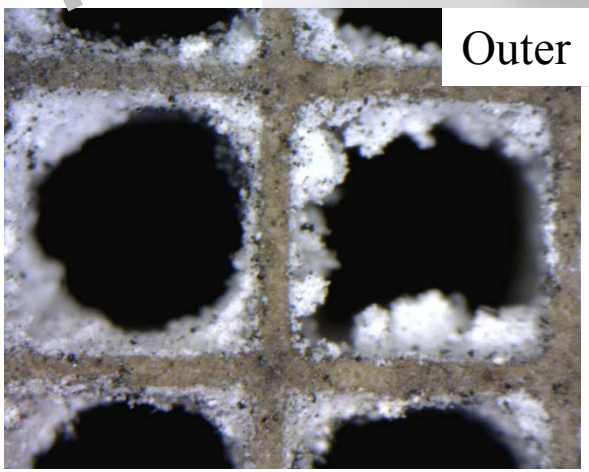
- Decline in NO_x oxidation is most likely related to the accumulation and stabilization of chemical contamination.
- Could be from Na or lube oil metals.

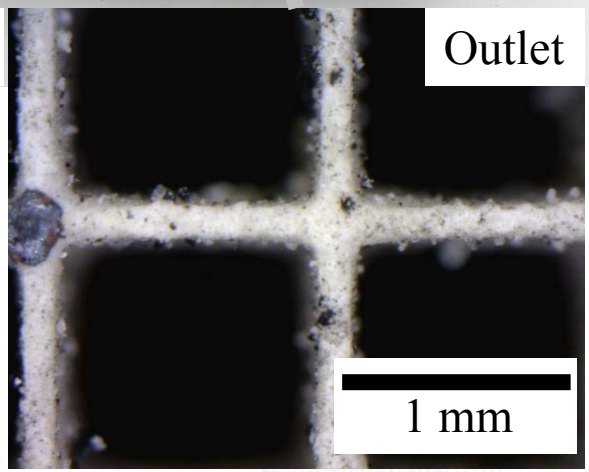
Technical Accomplishment: A white powder was present within an annulus ~2 inches wide on the front face of the DOC







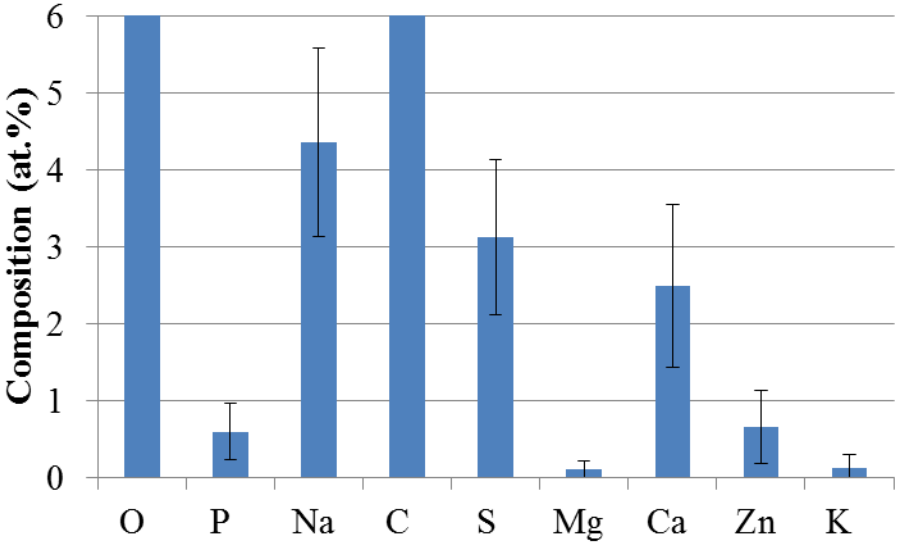




- Microcores were extracted at 0, 280, 553, 756 and 1000 hours.

Technical Accomplishment: Electron probe microanalysis (EPMA) and X-ray diffraction (XRD) collected from the front face of the DOC revealed mostly Na-Ca sulfate

Composition Measured with EPMA



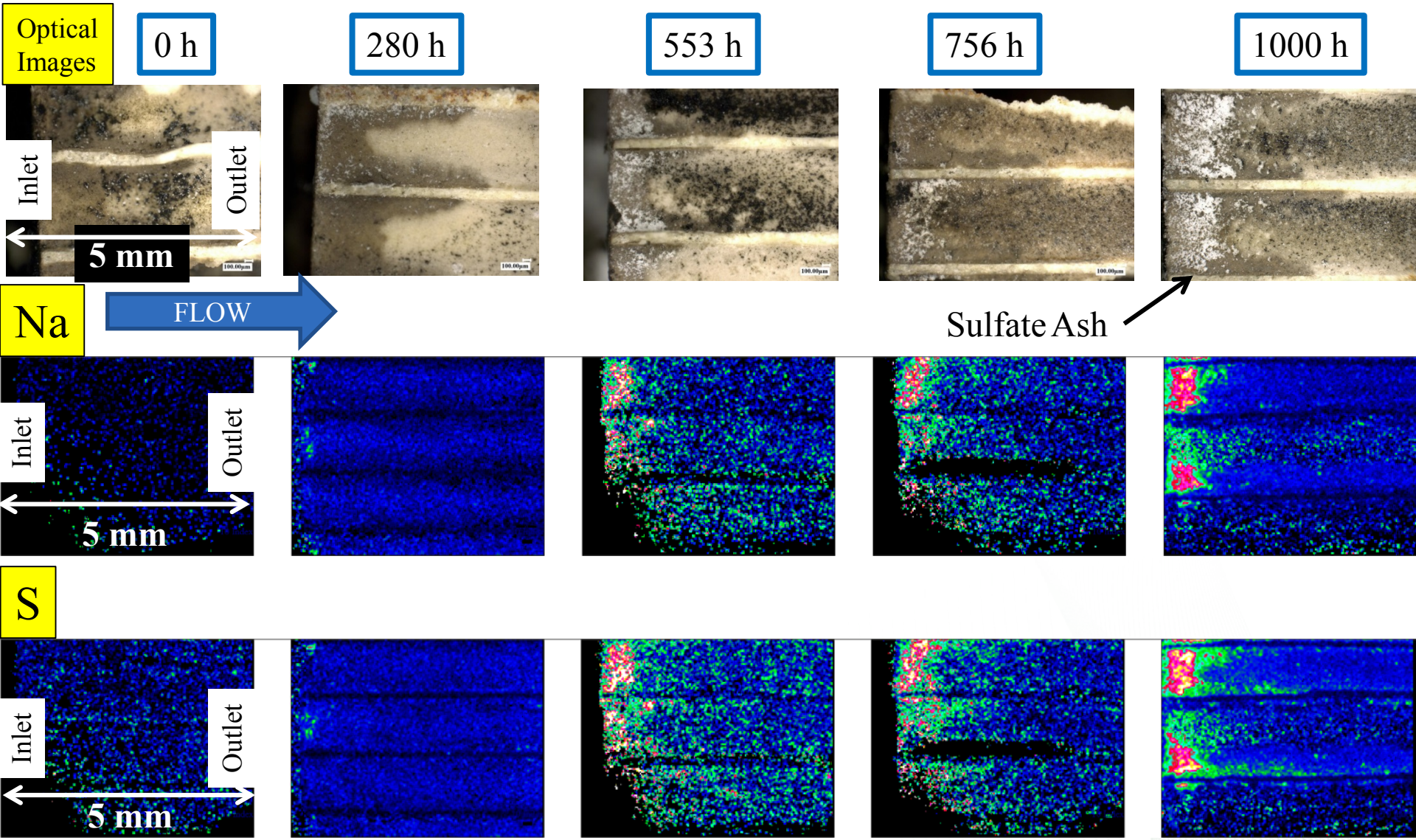
Composition measured with XRD

Compound	Weight Percentage (%)
Na_2SO_4	23
$CaSO_4$	16
$Na_2Ca(SO_4)_2$	32
$Na_2C_2O_4$	21
$Ca_3(PO_4)_2$	8

71% Sulfate

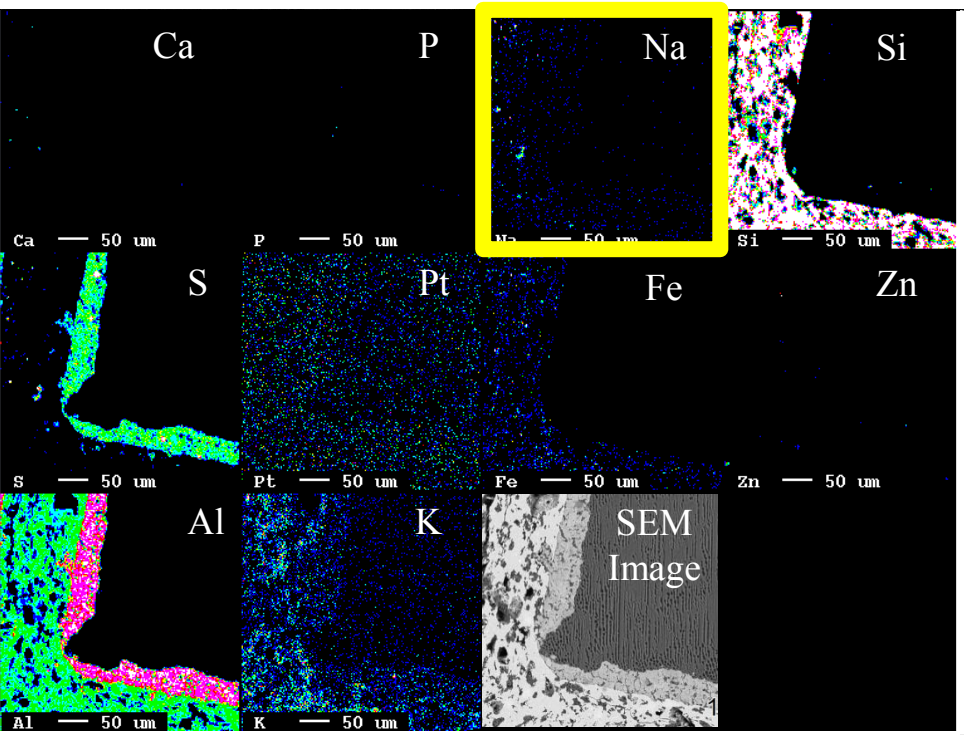
- Na is the largest constituent of the powder.
- P, S, Ca, and Zn are present in engine lube oil. (S is also in the fuel dopant)

Technical Accomplishment: Na and S at the DOC inlet increase with exposure time. Ash penetrates only 1-2 mm out of 102 mm.

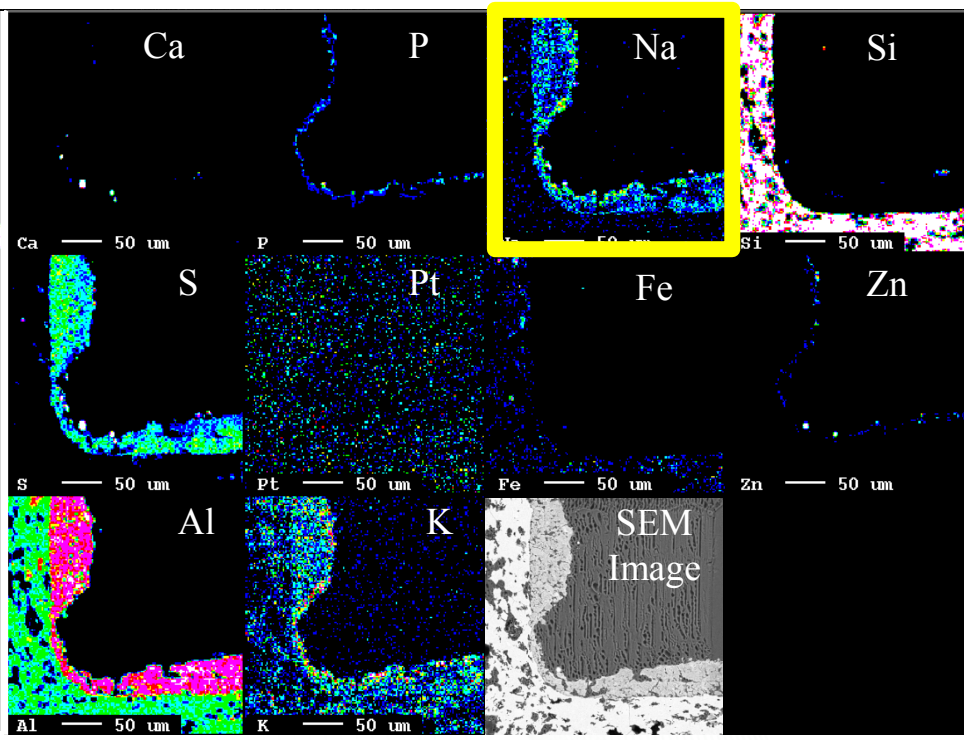


Technical Accomplishment: EPMA of DOC showed Na throughout the washcoat following aging

Not Aged, 0 Hours, 5 mm from Inlet

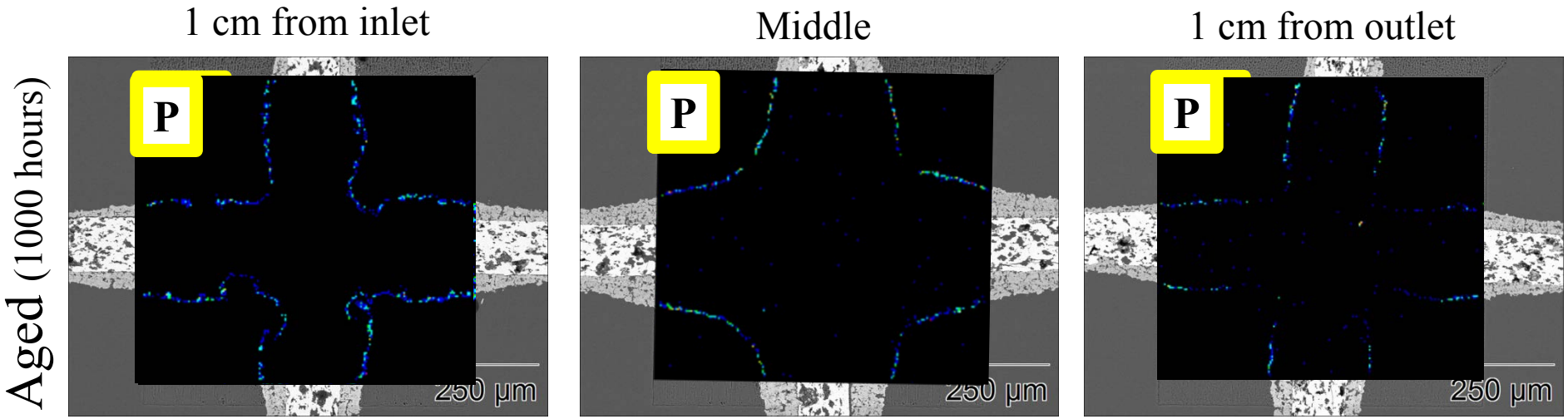


Aged, 1000 Hours, 5 mm from Inlet



- P, Zn and Ca on the aged washcoat surface are from the engine oil.

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

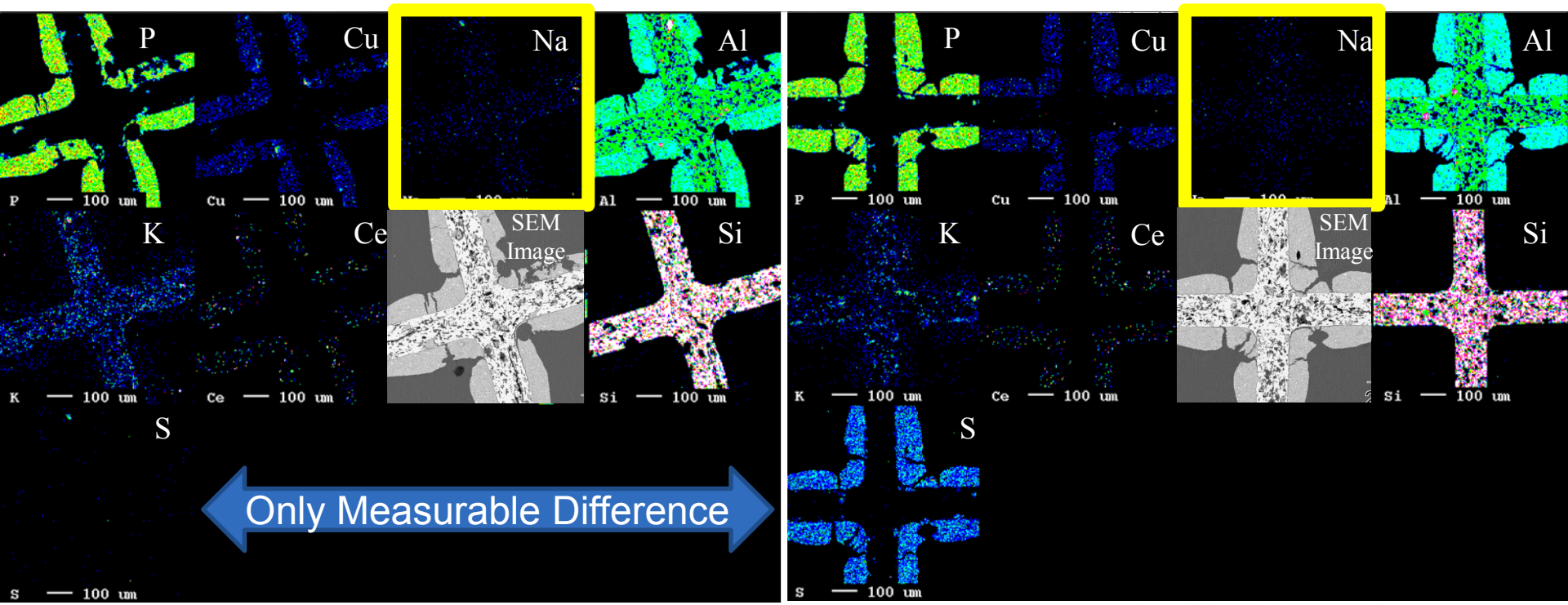


- Phosphorous from the lube oil is also present on the surface.
- Aged samples treated at Cummins through desulfation, water washing and acid washing will be used to separate the effect of Na and P on the DOC.

Technical Accomplishment: Sulfur in the SCR increases slightly following aging. Na was not detected after aging.

0 Hours, 5 mm from Inlet

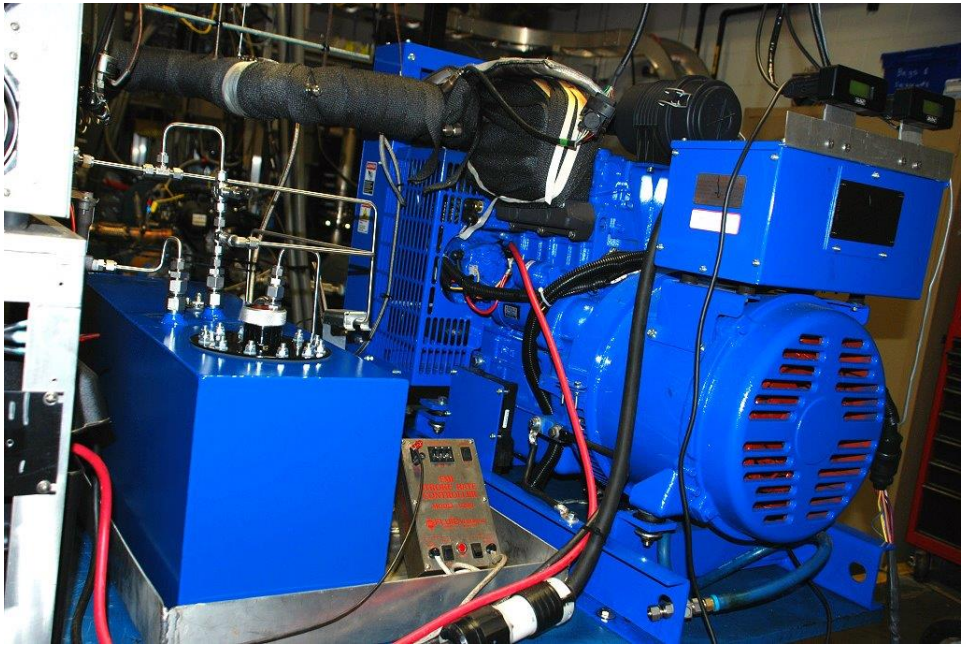
1000 Hours, 5 mm from Inlet



- The DPF shields the SCR from Na.
- BET measurements at Cummins revealed a slight decrease in surface area but not enough to account for the reduced performance.

Technical Accomplishment: Installed new, higher quality stationary diesel generator for unattended 24/7 operation

9 kW Northern Lights Generator



- A first run with B20 doped with Na on the same Ford aftertreatment devices previously studied has been completed.
- Aging with a gen-set has the potential to greatly reduce the expense of accelerated engine testing.

Responses to Previous Year Reviewers' Comments

Comment: "The reviewer expressed some concern that the focus was only on potassium and not on other elements or a combination of elements. The reviewer questioned if the other elements would be included later in the project."

Response: The current phase is focusing on Na which is the most common contaminant in biodiesel fuel and Ca and K have previously been studied.

Comment: "The reviewer opined that this project may not be focused on the correct catalyst poisons related to current biodiesel fuel production. Potassium and sodium fuel contaminants are associated with homogeneous fuel production. The industry is moving toward heterogeneous processes in order to more efficiently produce increased quantities of biodiesel fuel. The fuel-borne contaminants or poisons associated with those fuel production processes would not be the same."

Response: The contaminants studied were recommended by the National Biodiesel Board, a trade association that pools insights across the entire U.S. biodiesel industry from producers to consumers and are specified in ASTM 14538. We will investigate other poisons as they become a concern for our collaborators.

Comment: "The reviewer mentioned that there is good future research being proposed for Cummins, but indicated a concern that element and element combinations were not being addressed, including calcium, magnesium (Mg), and sodium, and questioned if there was certainty that none of these elements were of concern based on potassium."

Response: Calcium and sodium have been studied in an earlier phase of this research and based on those results it was decided to focus on Na in the current phase as it resulted in catalyst degradation and is the most common contaminant in biodiesel fuel.

Collaborations

- Cummins
  - Conducted a variety of testing on aged samples, offered advice on subsequent testing and devised the catalyst testing protocol.
- Ford Motor Company
  - Provided in kind work on aftertreatment device characterization.
- National Renewable Energy Laboratory (NREL)
  - Performed accelerated engine tests.
- Manufacturers of Emission Controls Association (MECA)
  - Advised project.
- Truck and Engine Manufacturers Association (EMA)
  - Advised Project.
- National Biodiesel Board (NBB)
  - Funded engine testing and advised the project.

Remaining Challenges and Barriers

- The reduction in emissions performance upon accelerated aging might not be due to Na but to other elements from the lube oil or to thermal aging of the DOC.
- The gen-set may not simulate the full scale engine test.

Future Work

- Collaboration with Cummins, NREL, MECA, EMA, and NBB will continue with analysis of accelerated biodiesel-aged specimens.
  - Na-aged samples treated at Cummins through desulfation, water washing and acid washing to quantify the effect of Na on the DOC.
  - Analysis of DPF catalyst washcoat.
  - Mechanical properties of the DPF will be measured to understand if Na degrades the thermal shock resistance.
- Ford samples aged with Na using the gen-set will be compared to previous Ford samples aged on a full scale engine.

Summary

Relevance

Will biodiesel negatively impact emissions control devices?

Approach

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

Technical Accomplishments and Progress

- Characterized aged aftertreatment devices and showed that while Na did deposit on the DOC and DPF, it is pre-mature to say what were the major contributing factors in the reduction in emission performance observed. Additional work is in progress.
- Aged Ford aftertreatment system using a stationary gen-set for long-term low-cost testing of materials.

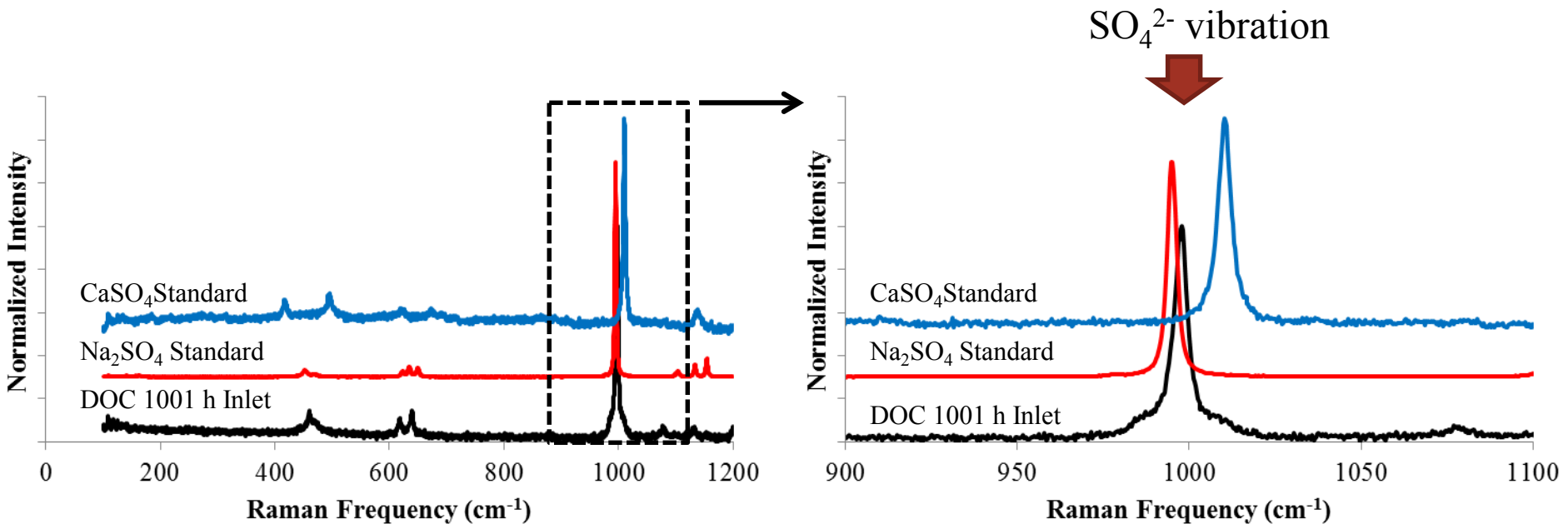
Collaboration with Cummins, Ford, NREL, MECA, EMA and NBB.

Proposed Future Work

- Continue analyses of aftertreatment devices aged with Na in conjunction with Cummins.
- Gen-set will be used to conduct accelerated biodiesel aging in order to determine the effect of metal additives on emissions control devices.

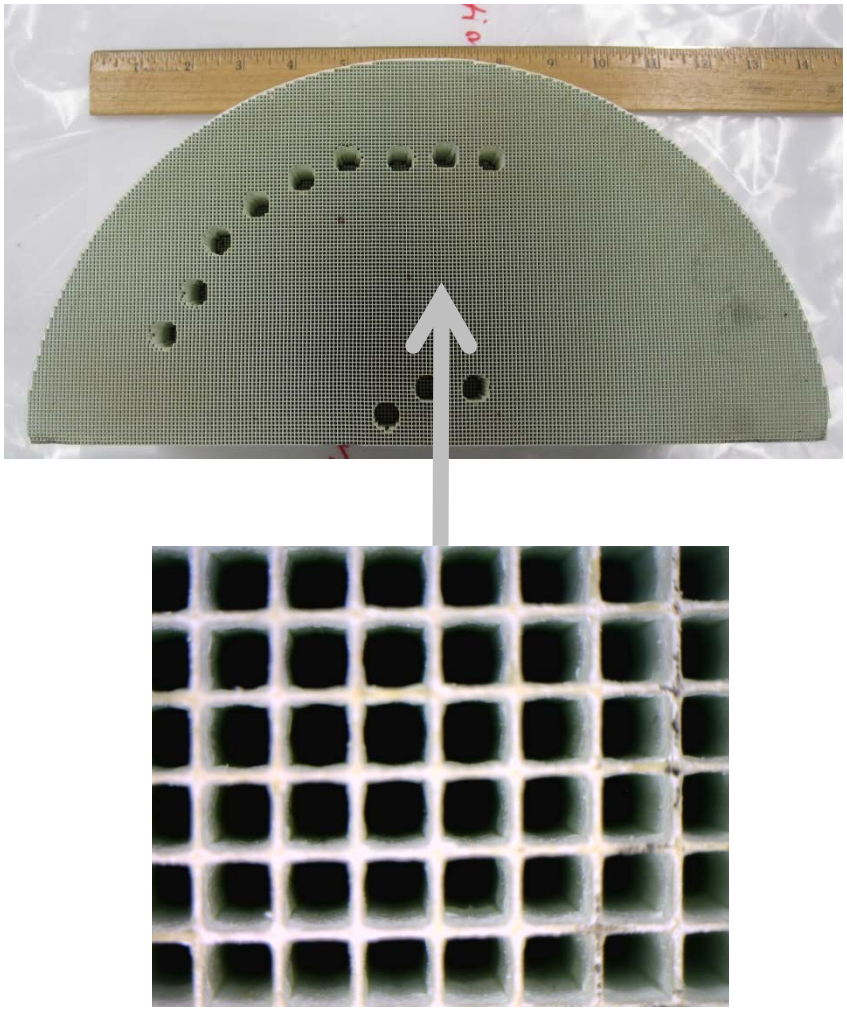
Technical Back-Up Slides

Technical Accomplishment: Raman spectra collected from the inlet DOC ash is consistent with the XRD result showing a $Na_2SO_4 – CaSO_4$ mixture



Technical Accomplishment: No noticeable degradation was present on the SCR.

Inlet



Outlet