

Biofuel Impacts on Aftertreatment Devices

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PM055

Overview

Timeline

- Start: August 2013
- End: September 2016
- 17% complete

Budget

- Total Project Funding
 - DOE-\$75K
- Funding Received:
 - FY13: \$50K
 - FY14: \$25K (\$140K expected)

Barrier

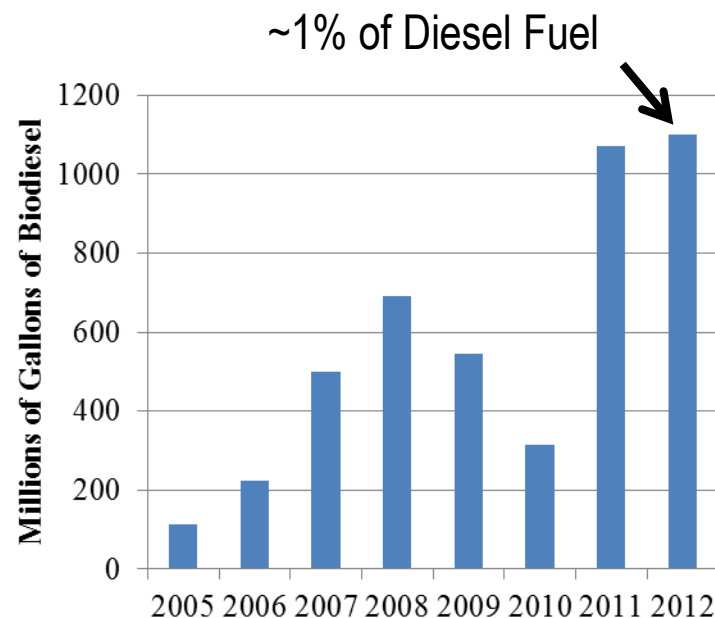
- Multi-Year Program Plan: By 2015, evaluate the impact of at least one renewable fuel blend on at least one heavy-duty emission after-treatment device.
- 2013 LD Materials Workshop Report: “Reduce petroleum dependence by developing propulsion materials that are compatible with advanced fuels.”

Partners

- Ford, Cummins, National Renewable Energy Laboratory (NREL), Manufacturers of Emission Controls Association (MECA), National Biodiesel Board (NBB).

Objectives/Relevance

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



- Conduct accelerated aging tests to simulate full-useful-life operation.
- Ash Exposure – Match ash exposure from B20 metal impurities at the current ASTM standard 14538.
 - ✓ Determine if the standard needs to be tightened or if the current standard is acceptable.

B20 Metal Impurities vs Aftertreatment Full Useful Life

B20 Alkali and Alkaline Earth Metal ASTM limits

Property	ASTM Method	Limits
Ca + Mg	EN 14538	1 ppm
Na + K	EN 14538	1 ppm

**Total Ash Exposure
from B20 at 435k miles
~ 670 grams**

- Versus -

Aftertreatment Full Useful Life Requirements

Weight Class (lbs. GVW)	OEM Full Useful Life (miles/yrs)
Light-duty (<8500)	120,000/10
Light heavy-duty (8500-19,500)	110,000/10
Medium heavy-duty (19,500-33,000)	185,000/10
Heavy heavy-duty (>33,000)	435,000/10

Milestones

Milestones (FY14)

Q1: Complete analysis of potassium aged samples: COMPLETED

Q2: Identify deactivation mechanism in DOC and SCR devices caused by alkali metal impurities: COMPLETED

Q3: Reproduce accelerated aging done by NREL using ORNL stationary generator: ON TRACK

Q4: Use stationary generator to expose fresh emission control systems to targeted doping set-points guided by the results from the NREL full-scale aging samples.

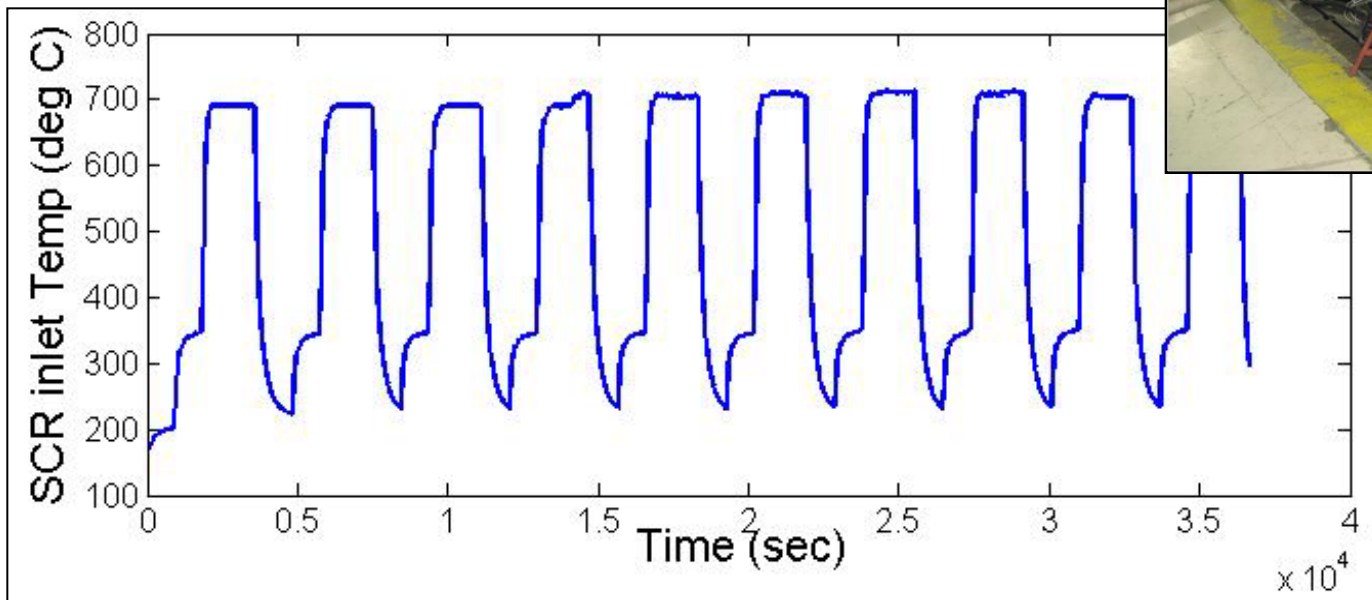
Approach

- Catalyst system from Ford F250 aged to equivalent of 150k miles exposure.
- Four rates of accelerated aging:
 - 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
- Vehicle emissions tests of aged systems to determine emissions compliance
- Post mortem analysis of aged catalysts to look at K location and for signs of localized catalyst deactivation
- Does rate of acceleration impact the location/penetration of K or magnitude of catalyst deactivation?



Accelerated aging cycle (at NREL)

- A three-mode, one-hour test cycle was developed for catalyst aging
- Space velocity and catalyst temps were selected from data of the F250 operating the FTP and US06 cycles
- Emissions evaluation conducted on an F250 truck over the FTP on a chassis dynamometer



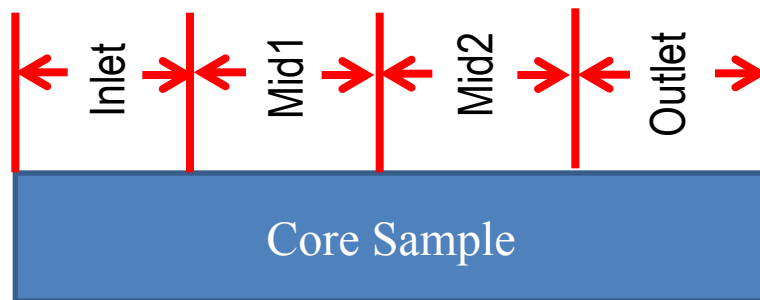
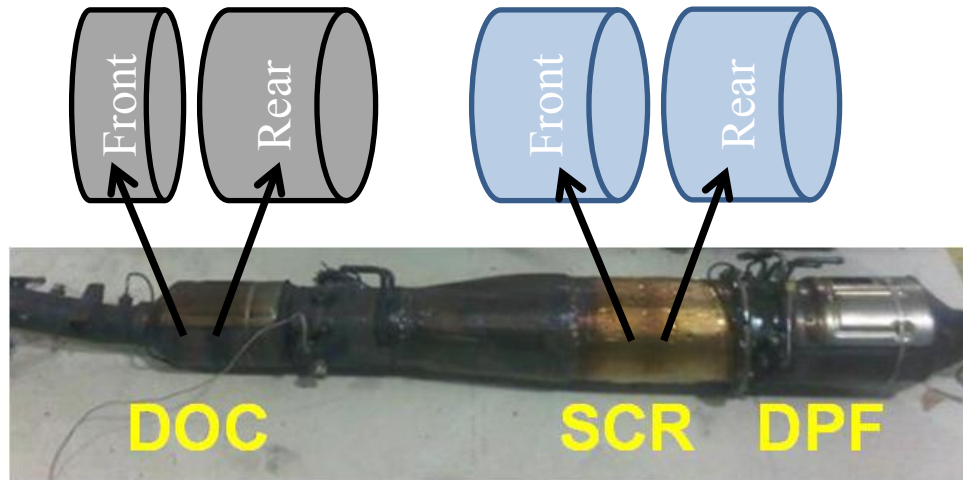
Technical Accomplishment: Engine/Vehicle Results

Test	B20 + 28 ppm K	B20 + 14 ppm K	B20 + 7 ppm K
Test Time (h)	50	100	200
Time >600 °C (h)	45.0	45.1	45.0
NO _x after test (g/mi)	0.30*	0.12	0.20

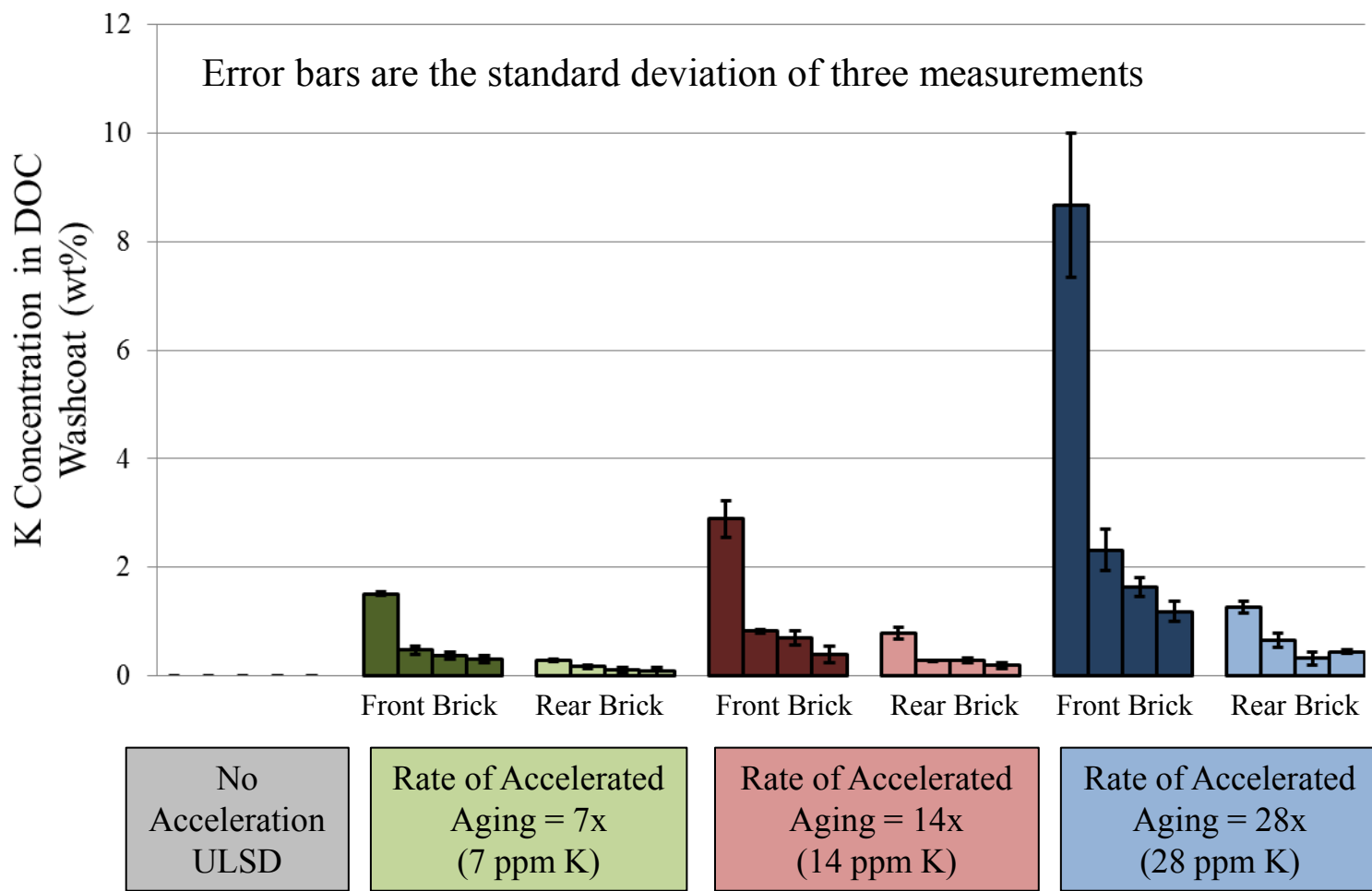
***System exceeded the 0.20 g/mile NO_x standard**

- All systems experienced the same thermal aging.
- 28x acceleration factor failed the NO_x standard.

Schematic of catalyst cores

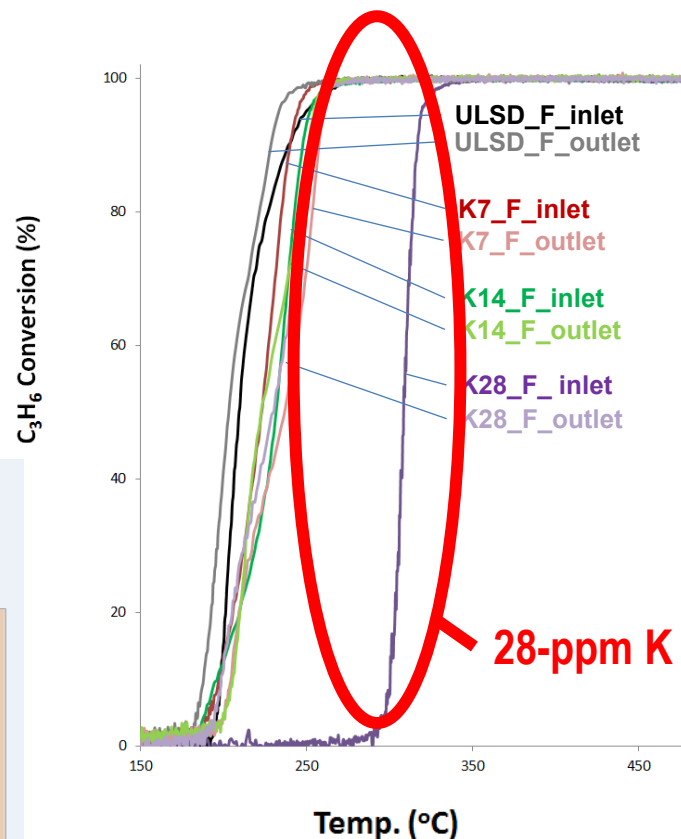
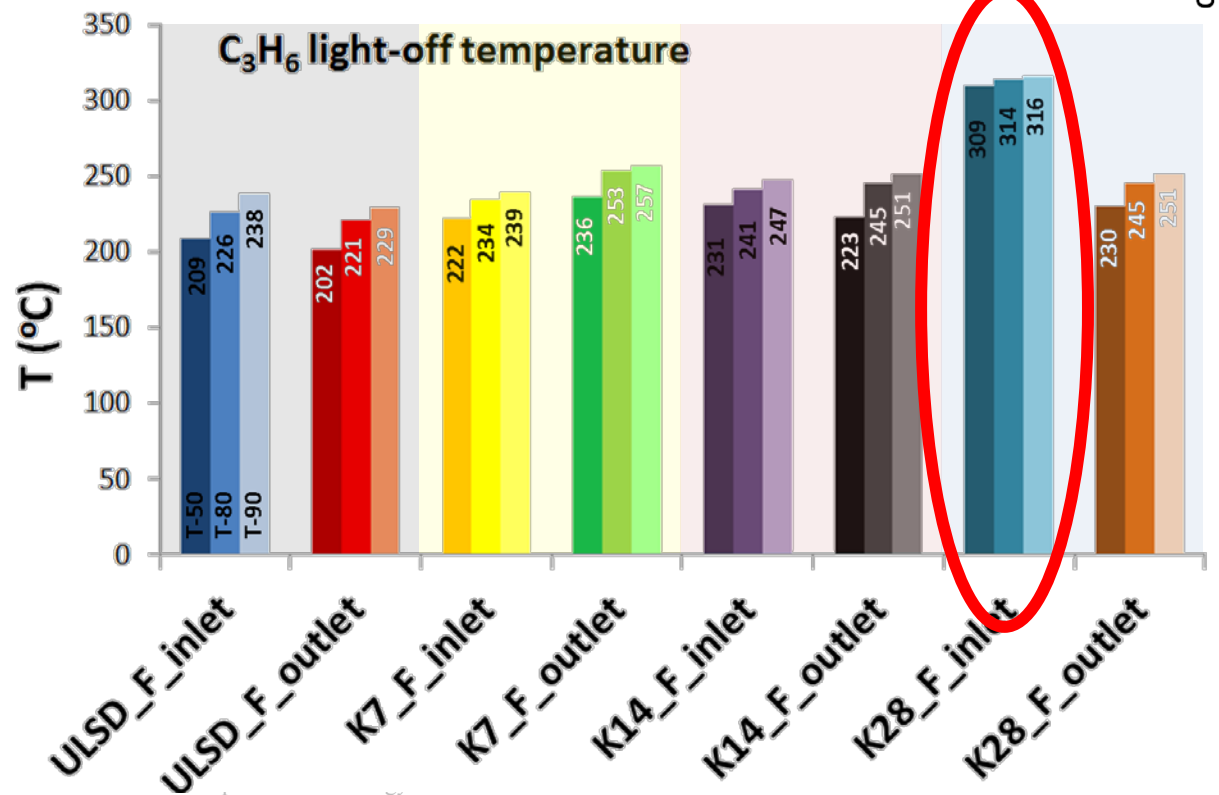


Technical Accomplishment: K Concentration measured in DOC Washcoat (SEM-EDX)



Technical Accomplishment: HC light-off at DOC-inlet affected at the highest K concentration

- Of the DOCs where K was introduced, the 28 ppm K exposure had the largest impact
 - Inlet of DOC significantly impacted
 - All other K-samples show similar behavior
- ULSD-exposed samples have slightly lower light-off temperatures

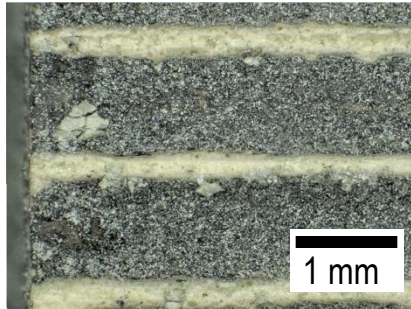


Combined with EDAX data, suggests 28 ppm K may falsely accelerate

aging

Technical Accomplishment: New micro x-ray fluorescence (μ -XRF) instrument revealed a K_2SO_4 coating at the inlet of the 28 ppm K DOC

Ultra-Low Sulfur Diesel



B20 + 7 ppm K



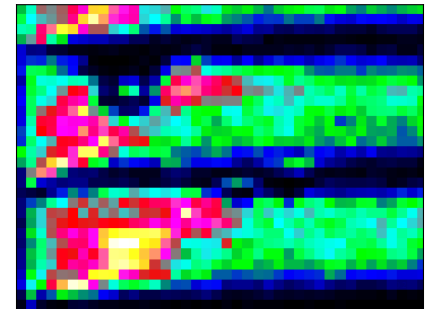
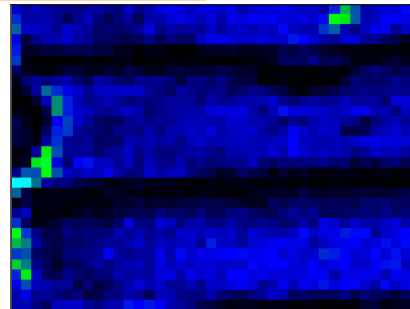
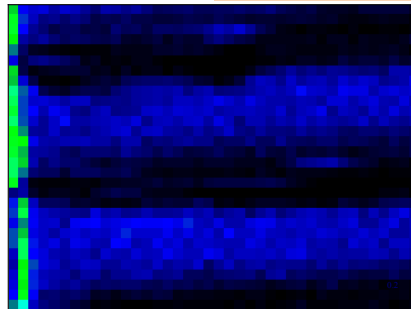
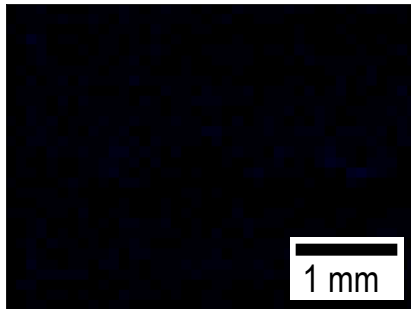
B20 + 14 ppm K



B20 + 28 ppm K

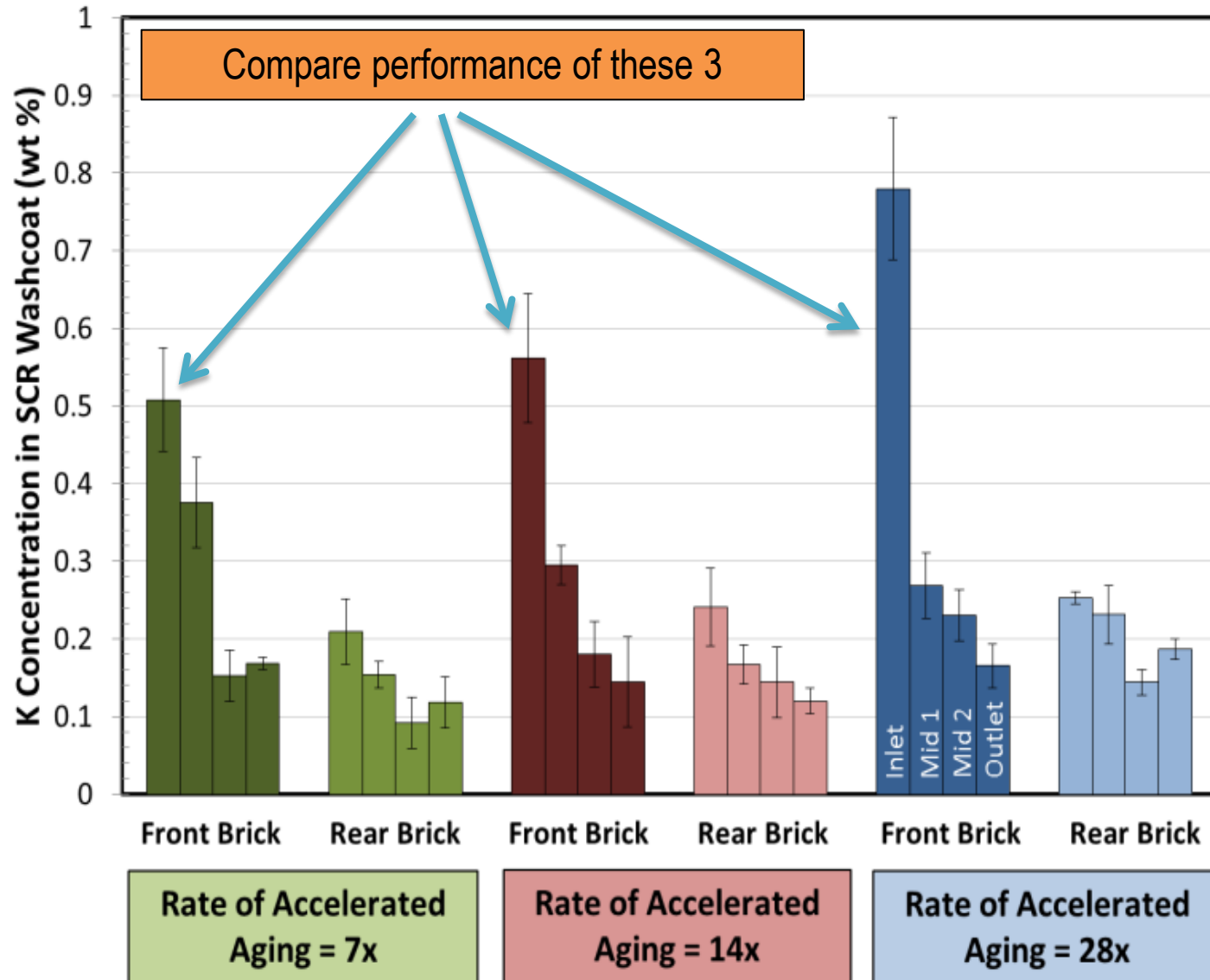


K x-ray intensity maps

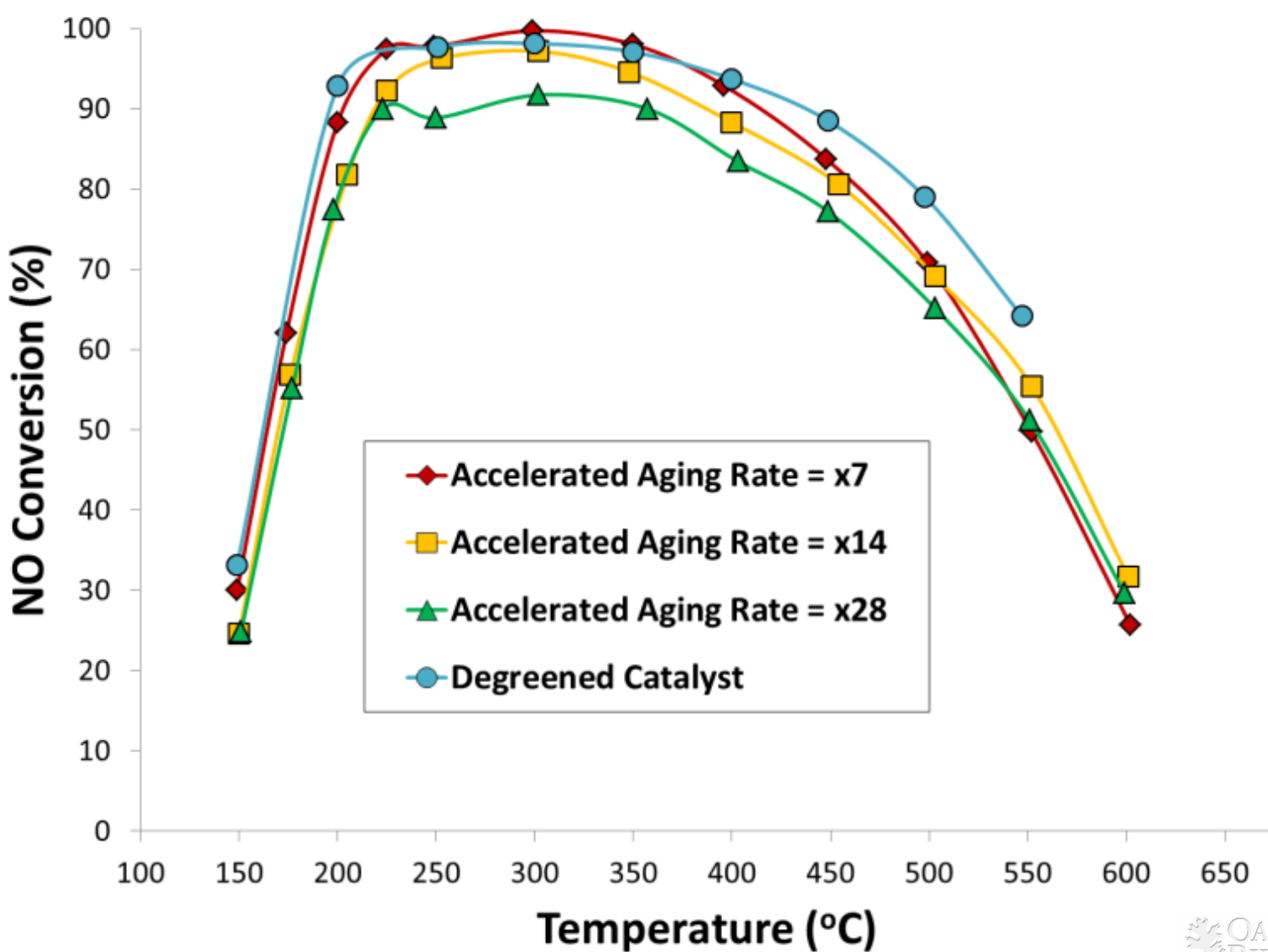


- The large amount of ash on the 28 ppm K DOC shows that this level of acceleration is too high.

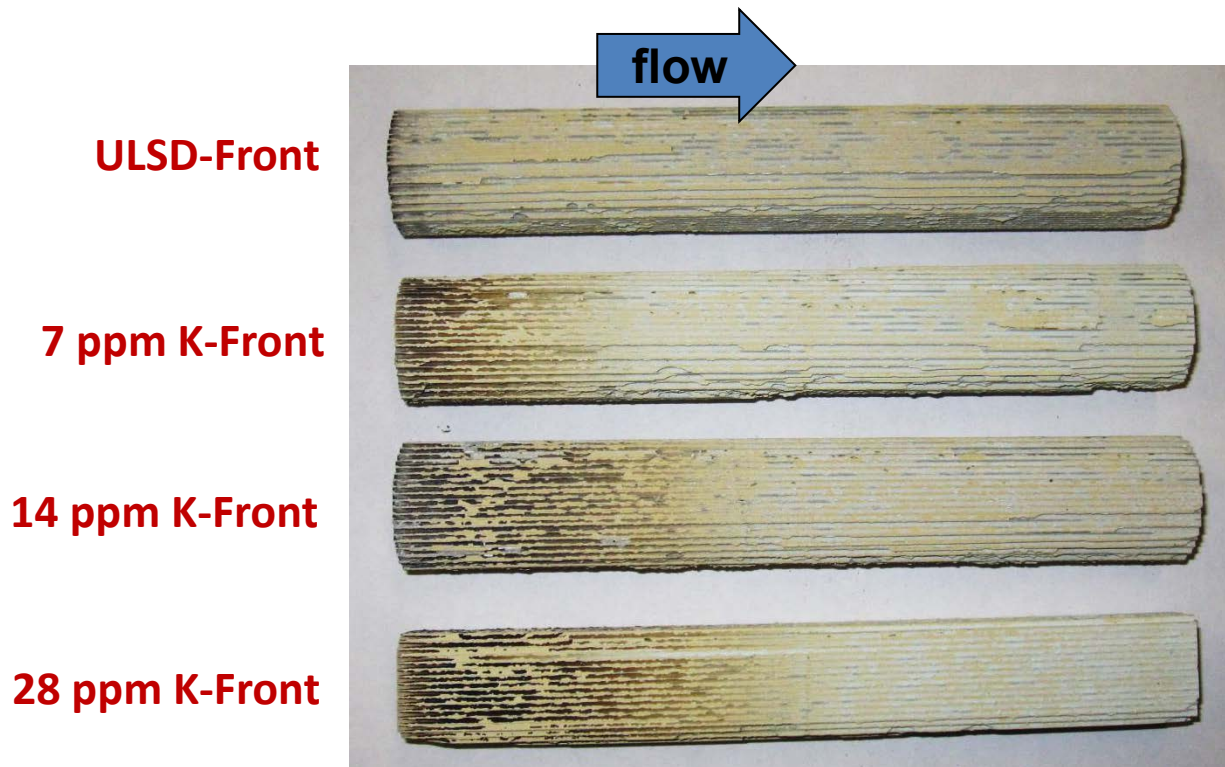
K Concentration in SCR Washcoat (SEM-EDX)



Some deactivation observed for front inlet of SCR aged by 7, 14, and 28 ppm K; Again 28x K concentration show biggest impact

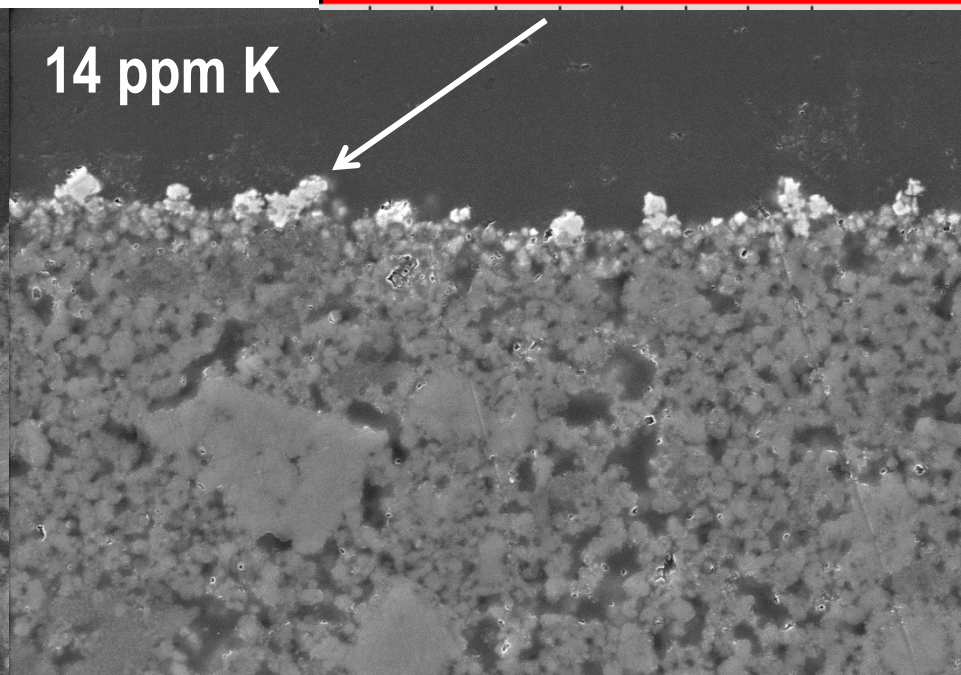
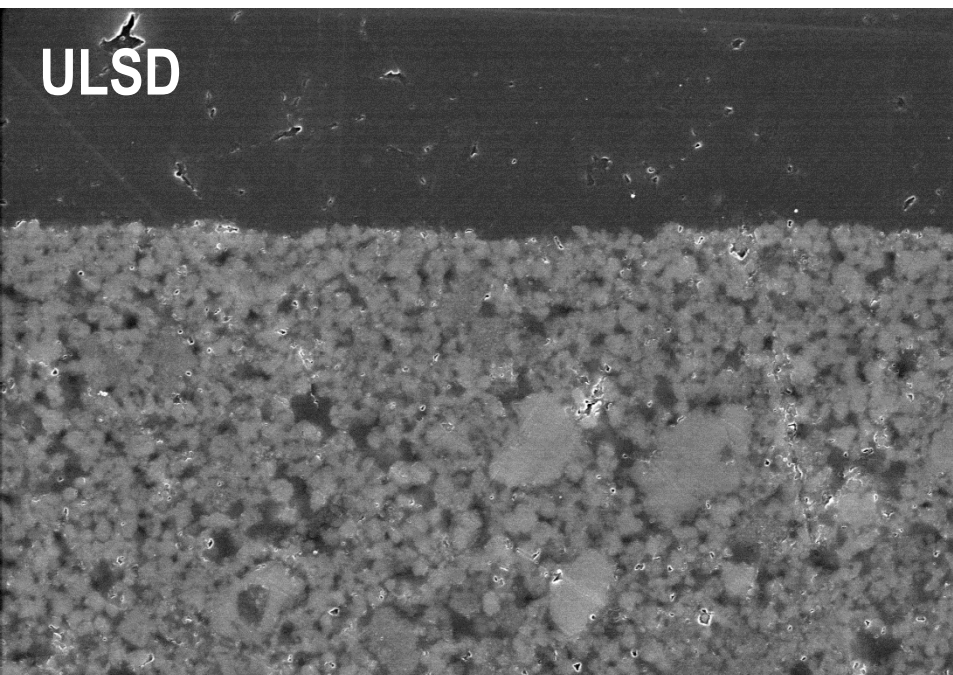
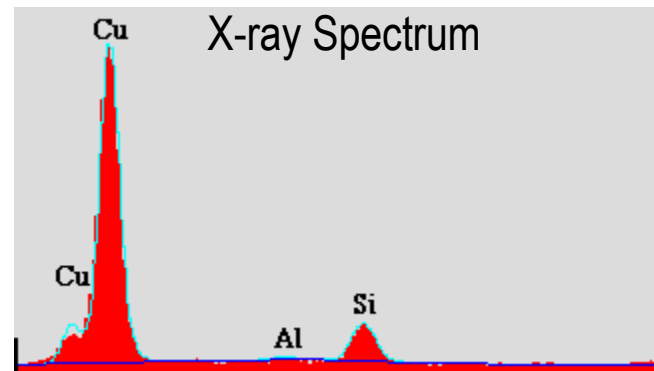


Effect of K evident with “unaided eye”



- Discoloration observed near the inlet of the front SCR bricks exposed to K.

Technical Accomplishment: Discoloration was due to Cu_xO particles on the SCR surface



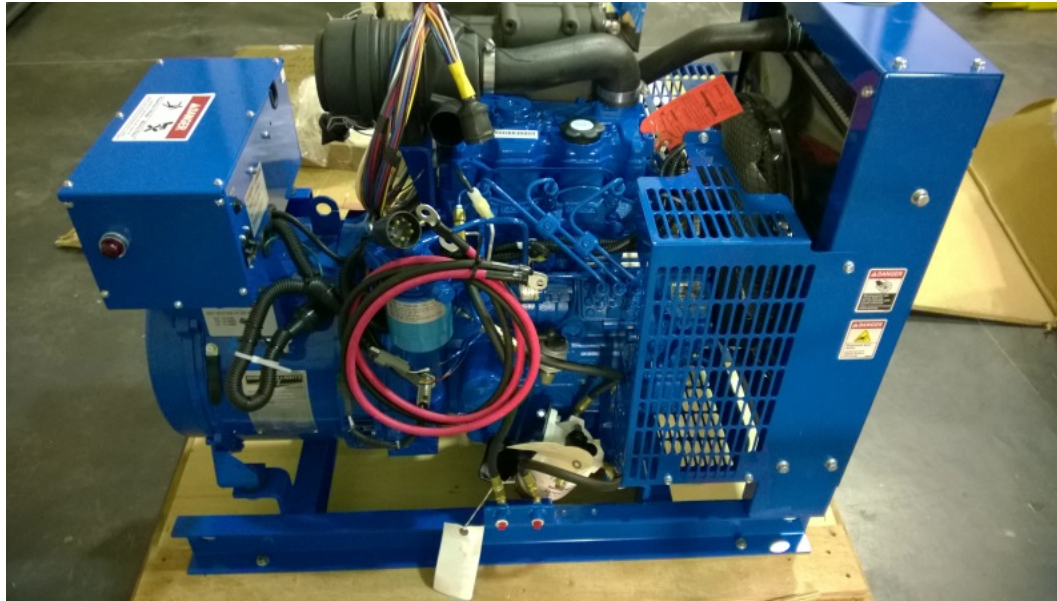
ez-130871 5.0kV 8.5mm x10.0k SE(M) 5.00um

ez-130877 5.0kV 8.8mm x10.0k SE(M) 5.00um

K-acceleration factor summary

- 28-ppm K is too high to use in acceleration studies
- Accelerating with 14-ppm K has minimal additional impact over 7-ppm K
 - *Appears to be a good balance between acceleration and reality*
- Impact of dosing concentration decreases along the length of the exhaust pipe
 - *...but affects are still apparent on sensitive systems*
- **Williams, A., McCormick, R., Lance, M., Xie, C. et al., "Effect of Accelerated Aging Rate on the Capture of Fuel-Borne Metal Impurities by Emissions Control Devices," SAE Int. J. Fuels Lubr. 7(2):2014.**

Technical Accomplishment: Diesel Gen-Set for 24/7 Operation



- Northern Lights diesel gen-set has been installed at the NTRC (National Transportation Research Center) building at ORNL. The engine is rated for 9 kW and is connected to an Avtron K490 load bank.
- Genset will be used for accelerated aging of emissions control devices at ORNL.

Response to Previous Year Reviewer Comments

This is a new project and was not reviewed last year.

Collaborations

- Ford Motor Company
- Cummins
- National Renewable Energy Laboratory (NREL)
- Manufacturers of Emission Controls Association (MECA)
- National Biodiesel Board (NBB)

Future Work: Investigation of HD Catalyst Durability

Cummins ISL

- Objective – Determine if lower metal limits are needed based on durability issues seen in previous tests
- Differences in this testing compared to previous study
 - Peak temperatures are lower (600°C vs 850°C)
 - Rate of accelerated aging is lower (14x vs 28x)
 - Dopant is 14 ppm Na + B20
 - SCR is downstream from the DPF



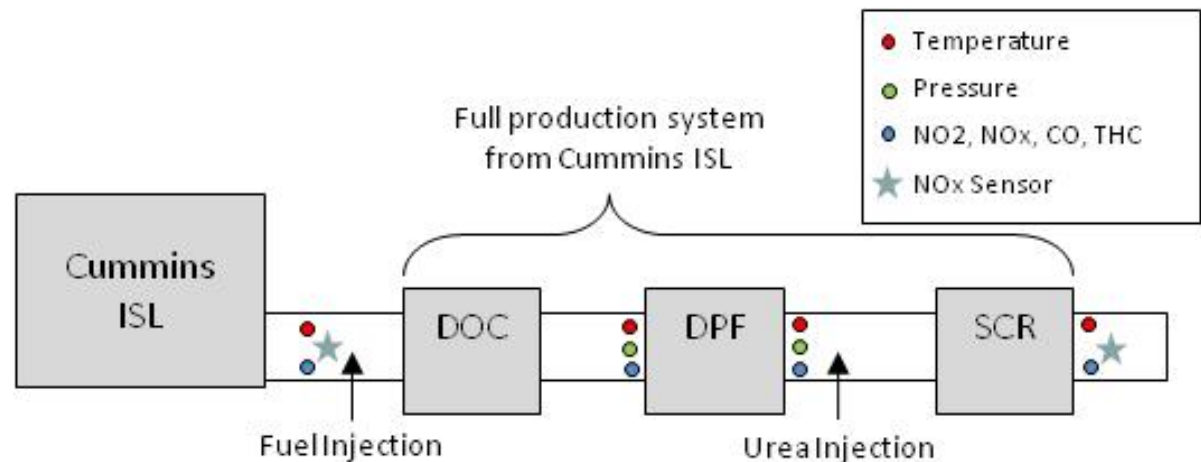
Future Work: Test Approach

- Aging a full production exhaust system from a Cummins ISL
- 435,000 miles simulated in 1000 hours
- Aging conducted on Cat[®] C9
- Emissions evaluation conducted on Cummins ISL

Cummins ISL



Cat[®] C9



Summary

Relevance

Will biodiesel negatively impact emissions control devices?

Approach

Accelerated aging with (1) NREL/Ford and (2) at ORNL.

Technical Accomplishments and Progress

- Showed that K had an impact on performance at the inlet of light-duty catalysts. However there is enough unaltered catalyst that the vehicle still meets emission standards.
- Showed that the rate of accelerated aging can impact performance. 28x acceleration is too rapid. 14x and 7x acceleration rates are similar.
- Long-term low-cost testing of materials in real diesel engine exhaust was established at ORNL.

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

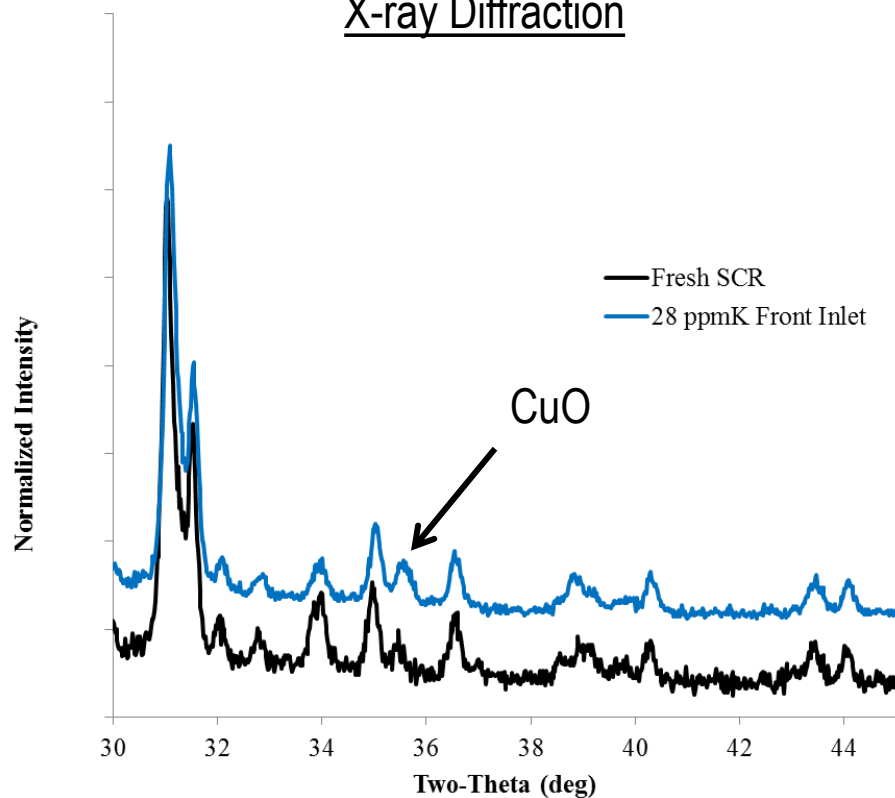
Proposed Future Work

- Phase 3 study on heavy-duty Cummins system.
- 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

X-ray diffraction and Raman spectroscopy were used to independently confirm the presence of oxides of copper

X-ray Diffraction



Raman Spectroscopy

