Impacts of Biodiesel on Emission Control Devices

Todd J. Toops and Bruce G. Bunting
Oak Ridge National Laboratory

D. William Brookshear and Ke Nguyen
University of Tennessee - Knoxville

DEER

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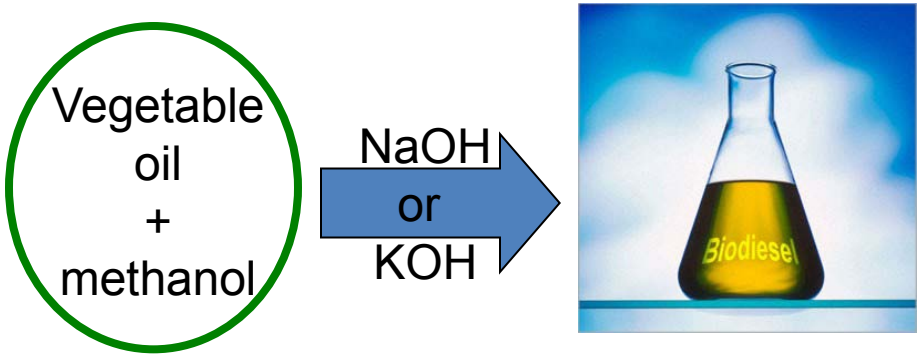
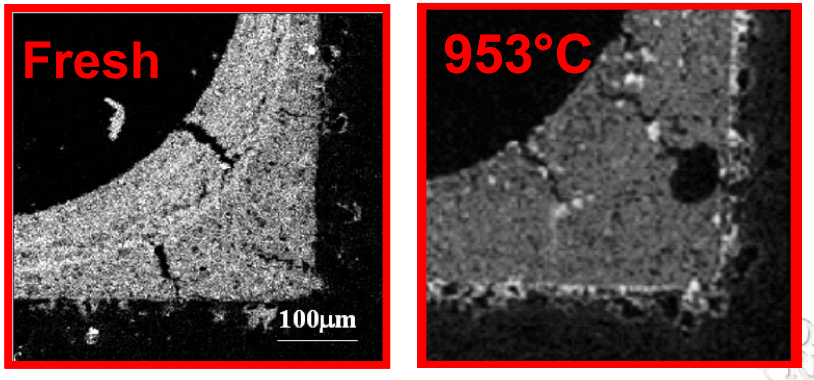
What impact could biodiesel have on emissions control devices?

- NaOH or KOH is a liquid-phase catalyst used in biodiesel synthesis
  - NaOH and KOH difficult to separate completely from products
  - Specification set at 5 ppm Na/K
- Anecdotal reports of accelerated ash accumulation with biodiesel use
  - Greater than 2 times faster ash accumulation observed at NREL
- Alkali absorption into monolith walls and possible weakening of monolith
  - K and Na would have similar impact
- Catalyst poisoning/fouling



Increased Ash Accumulation

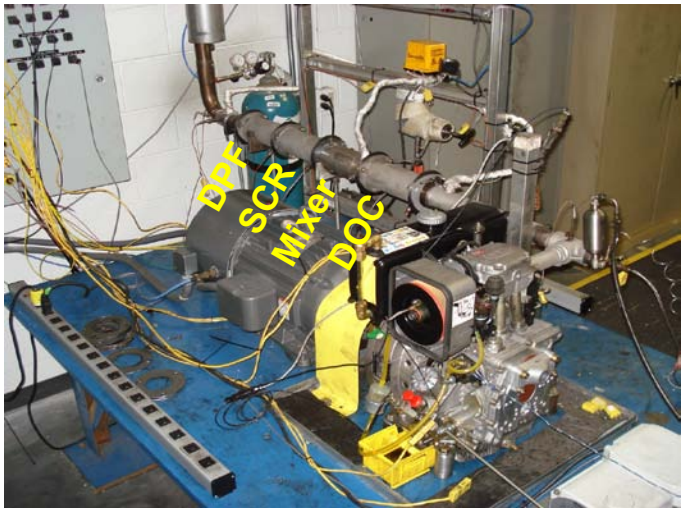
K migration into cordierite



Biodiesel Impact on Emissions Control Devices

- Focusing on Na impact
  - Analyzing effects on all fronts
- Long term engine- and field-aged samples
  - Industry cooperation (GM samples)
  - NREL-aged samples

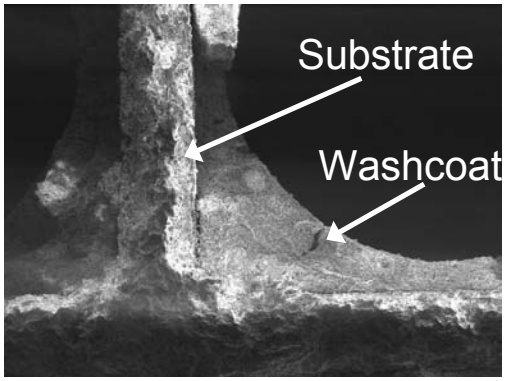
    SAE 2008-01-0080, SAE 2009-01-0281 & SAE 2009-01-1790
- Accelerated study using systems approach
  - Single cylinder engine; cycling to 650C
  - Artificially elevate levels of Na in B20
    - Accelerate aging
    - Levels elevated to achieve 435,000 mile Na exposure
- Characterization
  - Materials
  - Performance and kinetics
    - Bench reactor scale

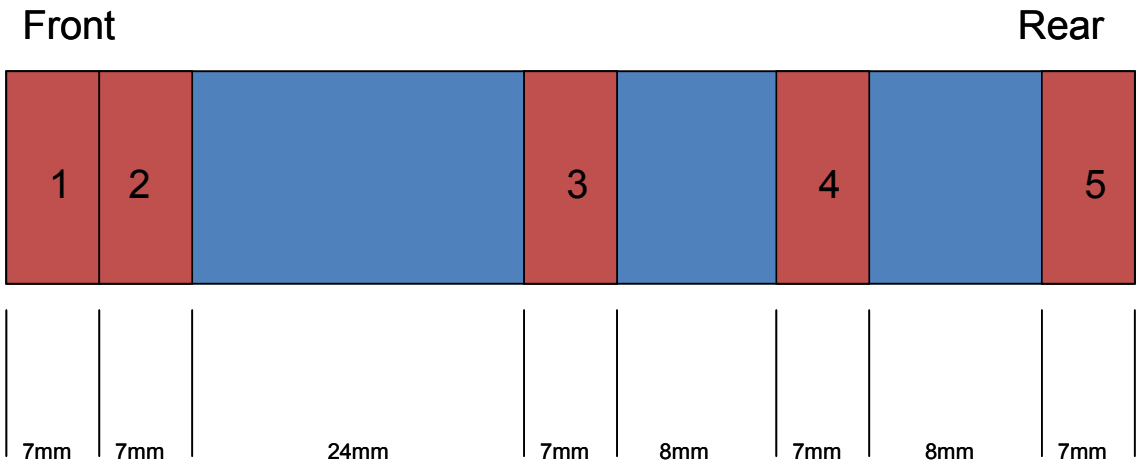


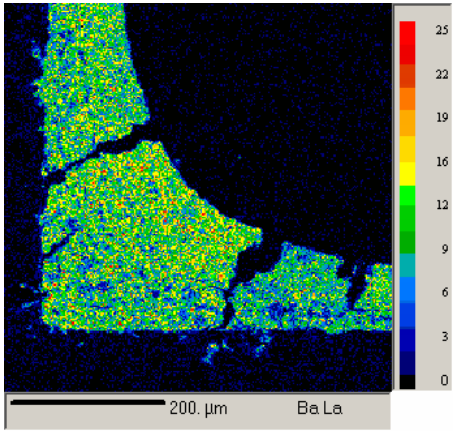
LNT

Electron Probe Microanalysis (EPMA)

- Micrographs taken on each sample, with two micrographs being performed at separate locations on section 1
- Na, S, Ba, and S EPMA micrographs were obtained from each sample
- Elemental analysis achieved through line scans of image

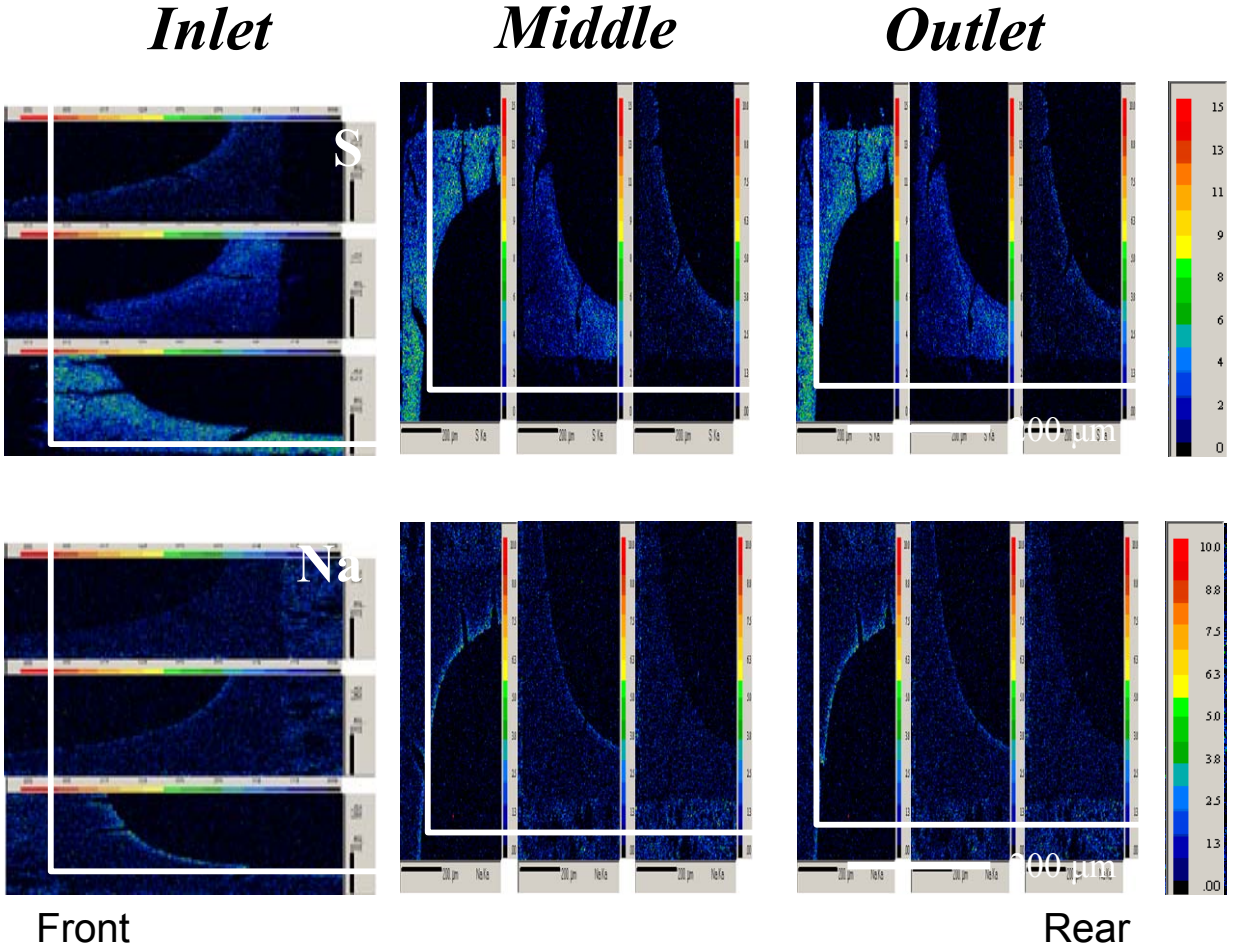






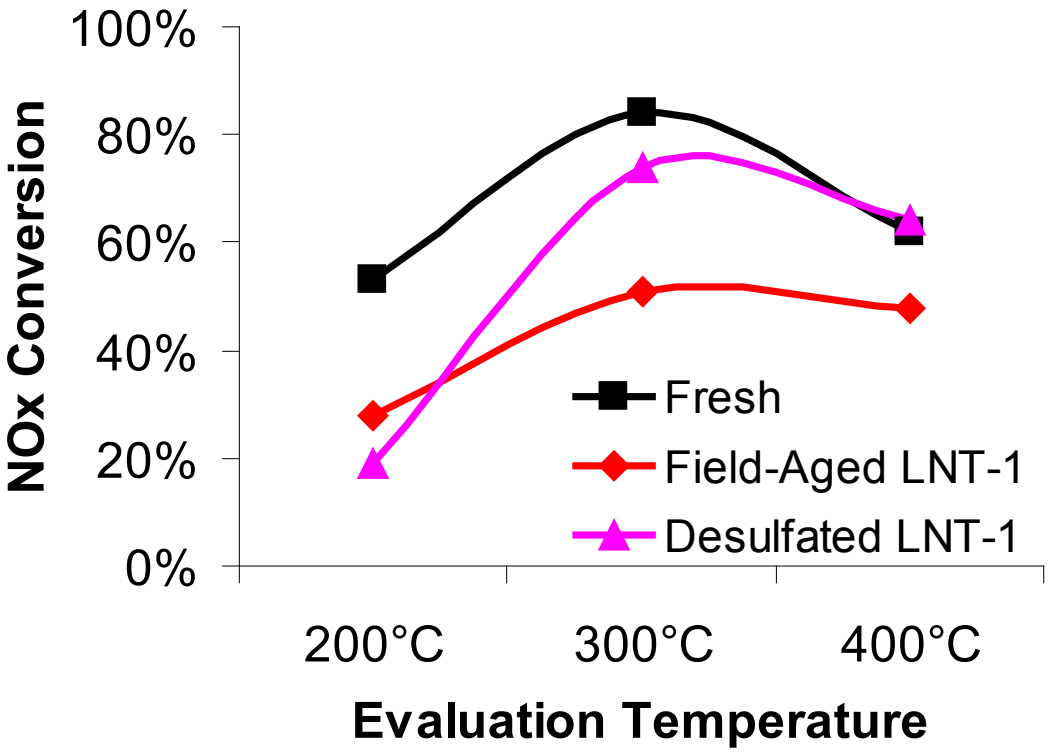
Cross-Sectional EPMA of LNT-1

- Five samples obtained from front NREL-aged LNT
  - Dual LNT system
  - Rear LNT not analyzed
- Na, S, Ba, and K EPMA micrographs were obtained from each sample
- Sulfur content is highest in first 10mm of front section
- Na layer on washcoat surface diminishes front to rear
  - Top 30 microns has up to 0.5%wt



LNT performance primarily affected by S

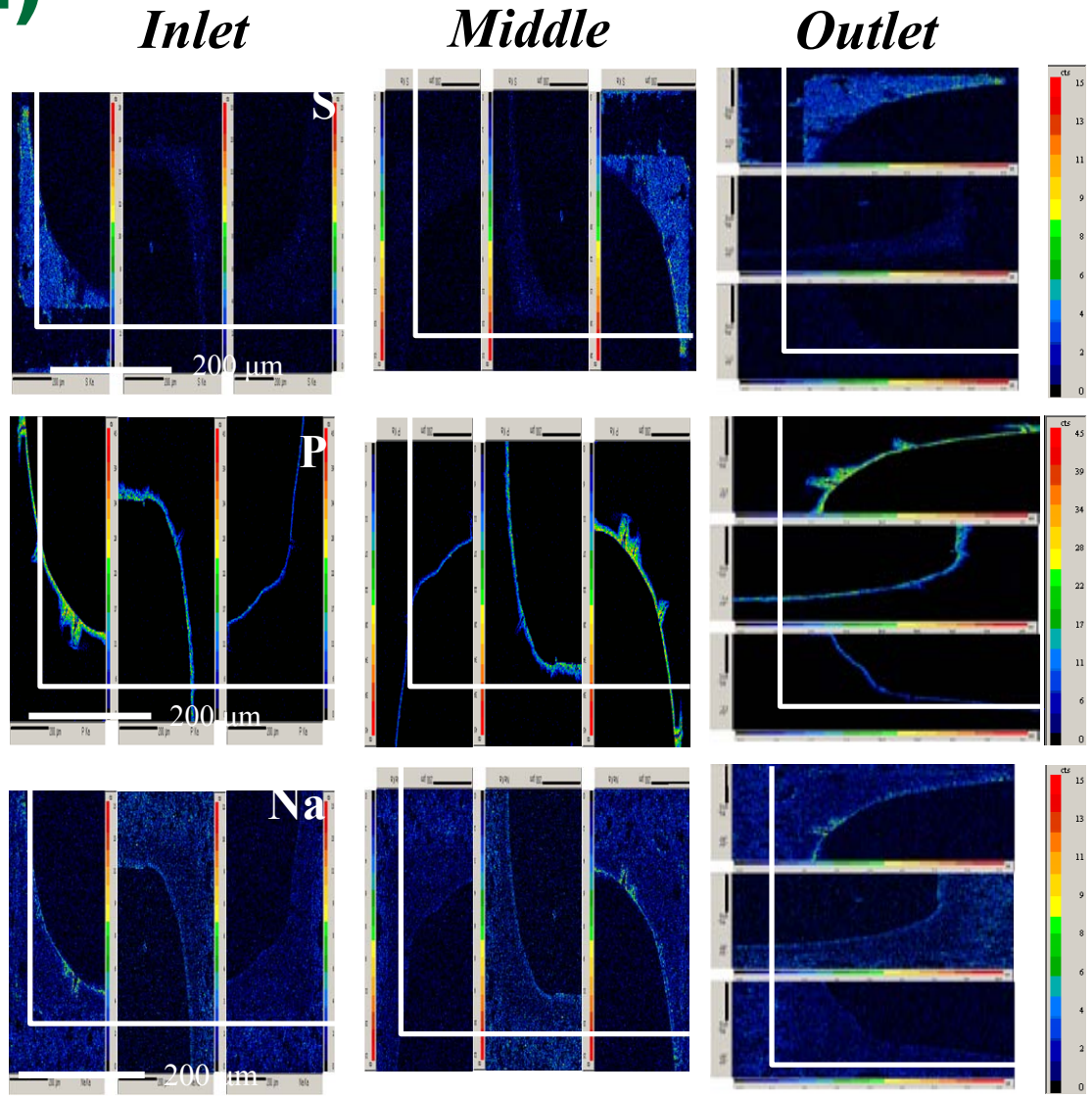
- Sulfur primary deactivation mechanism
- Performance recovered at 400 C after bench desulfation (at 700 C)
- Materials characterization suggests thermal effects impact performance at 200 and 300 C
  - i.e., B20 is not suspected to impact LNT
  - Not surprising, Na will adsorb NOx



DOC

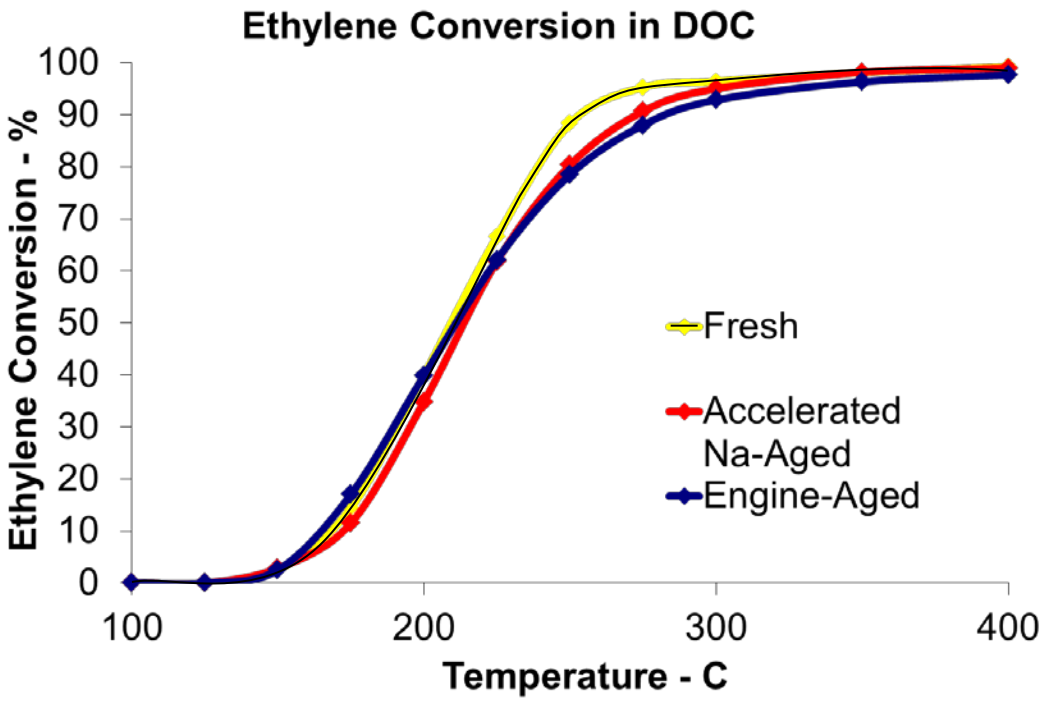
Biodiesel and lube oil components found in DOC (GM-aged)

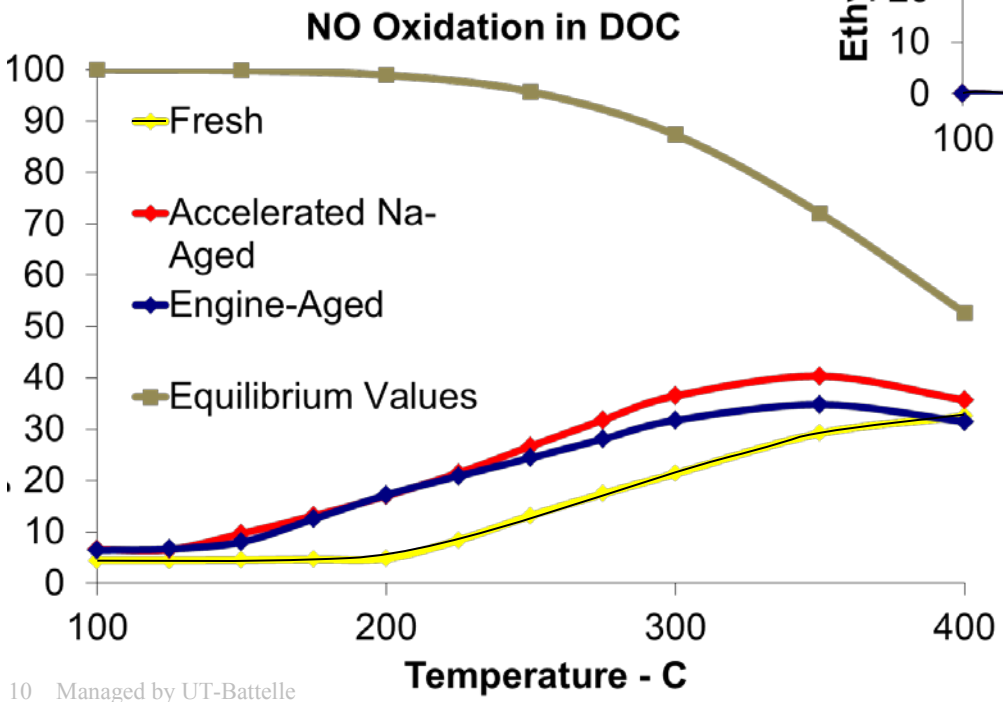
- S and P observed in DOC
  - S throughout washcoat at inlet of DOC
    - Average concentration
      - Inlet: 0.7%wt
      - Middle: 0.1%wt
      - Outlet: 0.03%wt
  - P at surface of washcoat
    - EPMA line scans
      - Maximum: 8%wt
      - Penetration: 30 µm
- Na observed at low levels
  - primarily in front section at washcoat surface
  - EPMA line scans
    - Maximum: 0.4%wt
    - Penetration: 30 µm



DOC minimally affected by aging

- Analysis of fresh, GM engine-aged and accelerated Na-aged DOCs
- Ethylene conversion minimally affected by aging
  - 88% → 80% at 250C



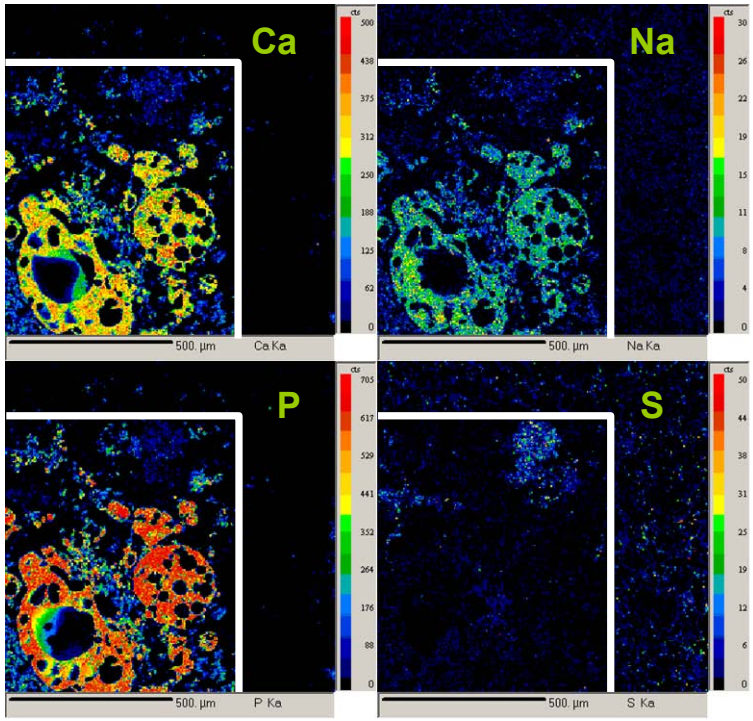


- Oxidation of NO to NO_2 is slightly higher in aged DOC samples compared to fresh
  - May be due to small increase in PGM size

DPF

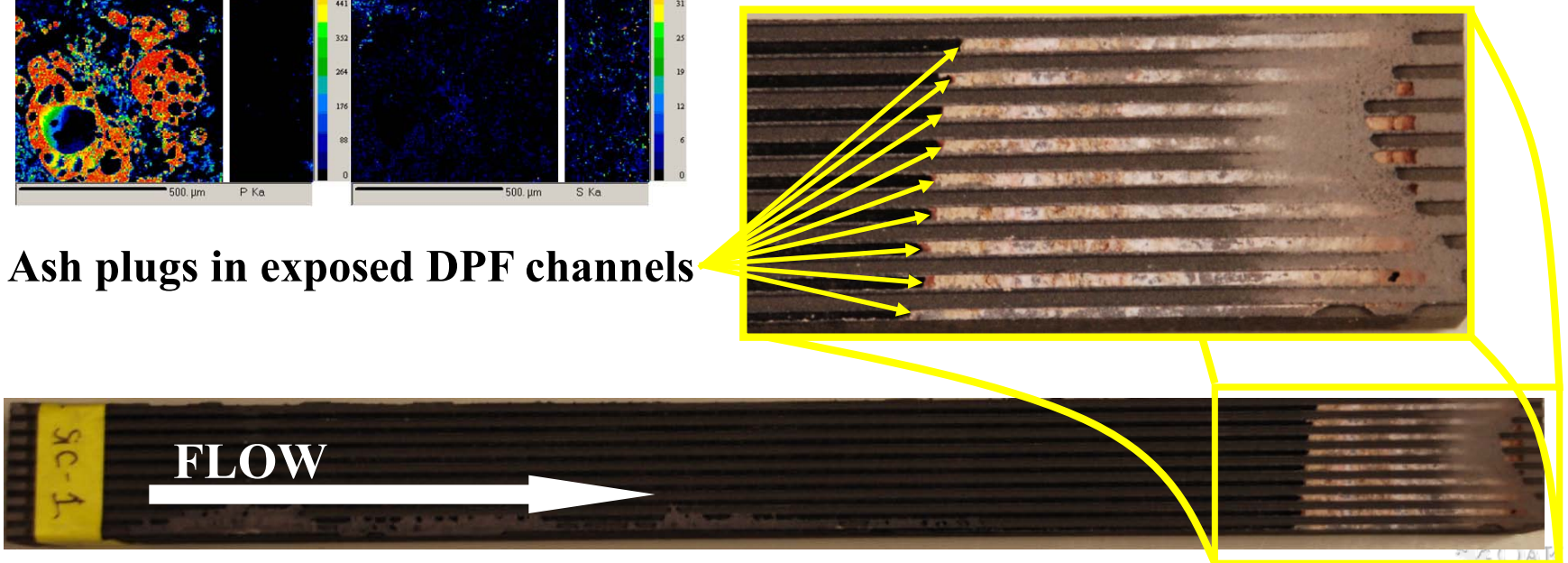
Ash in GM-aged DPFs – 20:1 for Ca:Na

EPMA of ash plugs in DPF



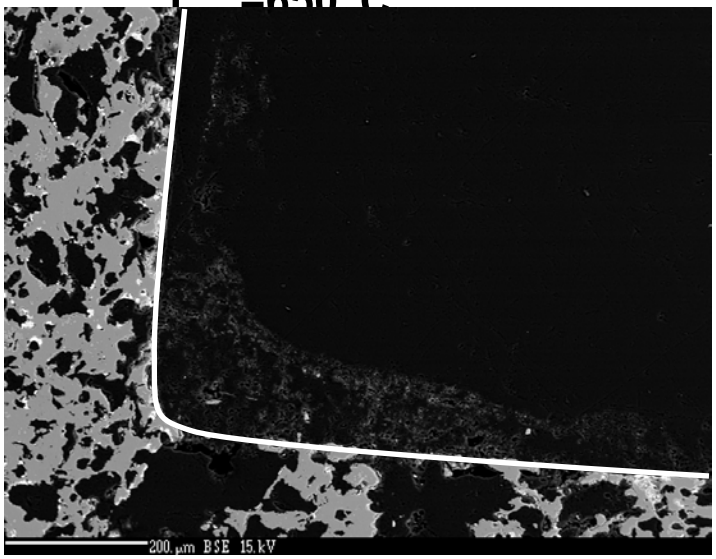
- Ash plugs apparent in rear of DPF
- 20x more Ca than Na detected in ash
  - Ca associated with standard lube oil
- Reported increase in ash accumulation may be due to:
  - Out of spec biodiesel, or
  - Increased oil consumption
- Little Na detected in wall of SiC DPF

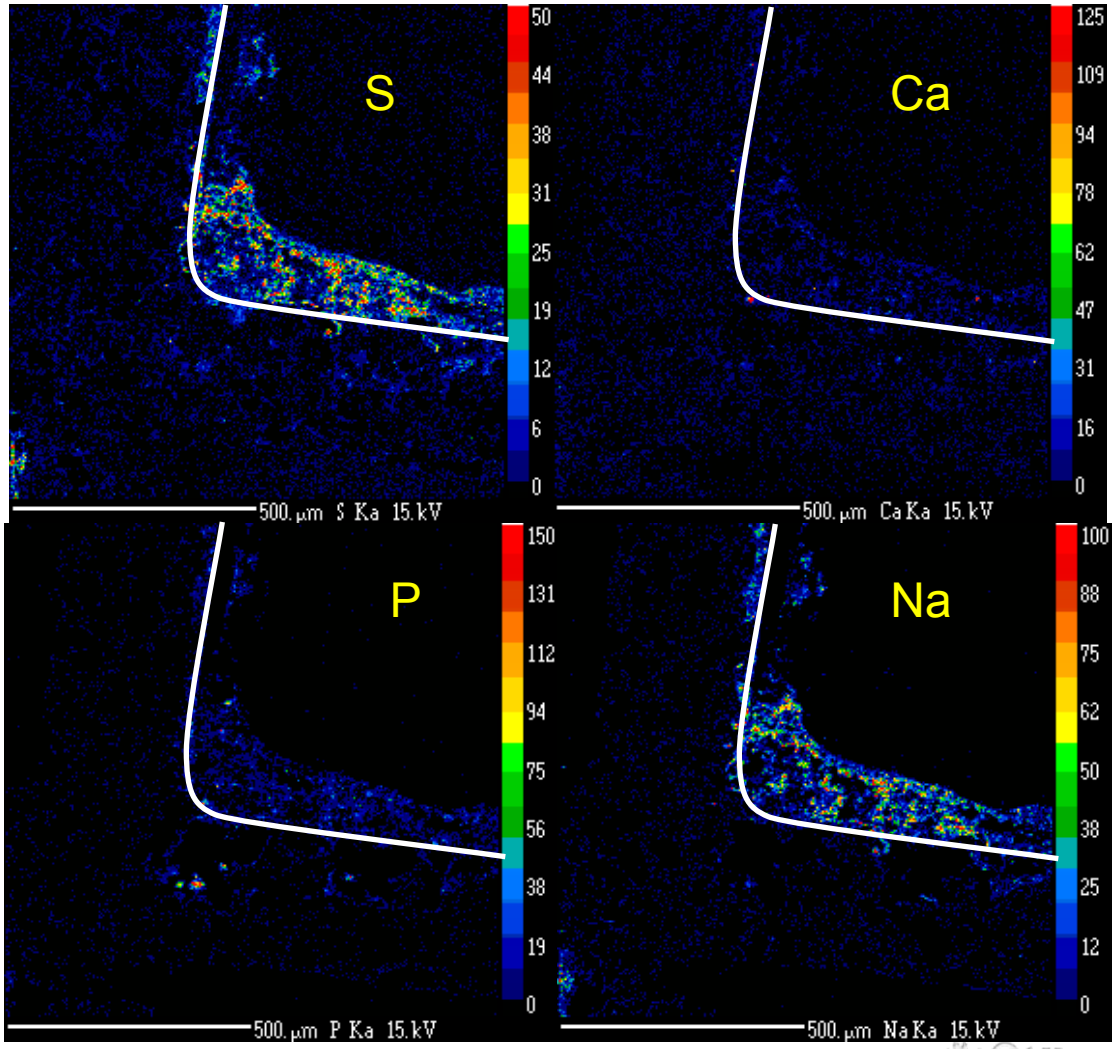
Ash plugs in exposed DPF channels



EPMA micrographs at mid-section of accelerated Na-aged DPF (ORNL)

- High levels of S and Na present at mid-section of DPF
- Ash layer begins in middle and continues to outlet
- No significant Na penetration into cordierite DPF wall
  - DPF periodically regenerated at T = 650 C

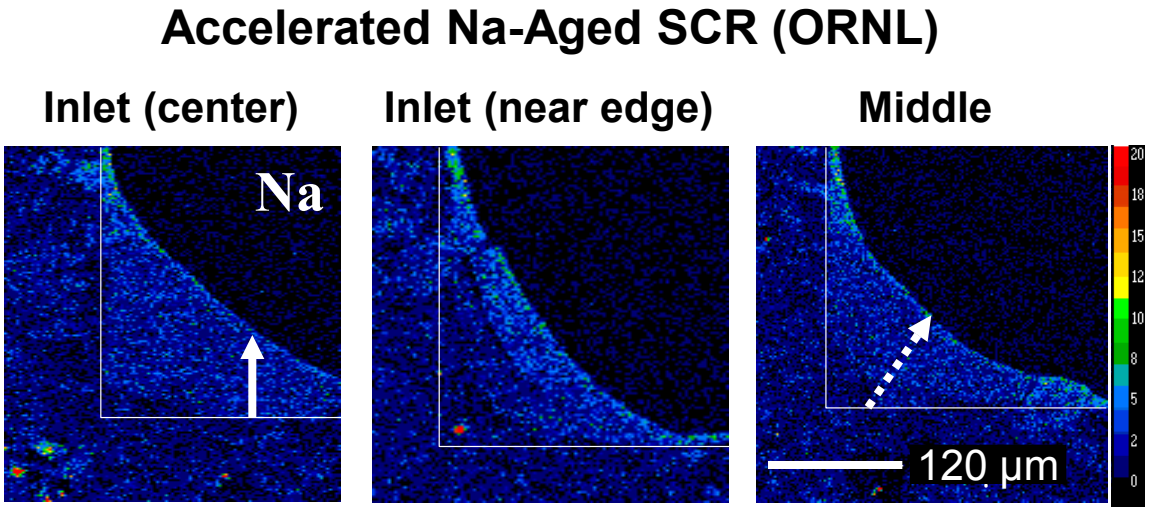


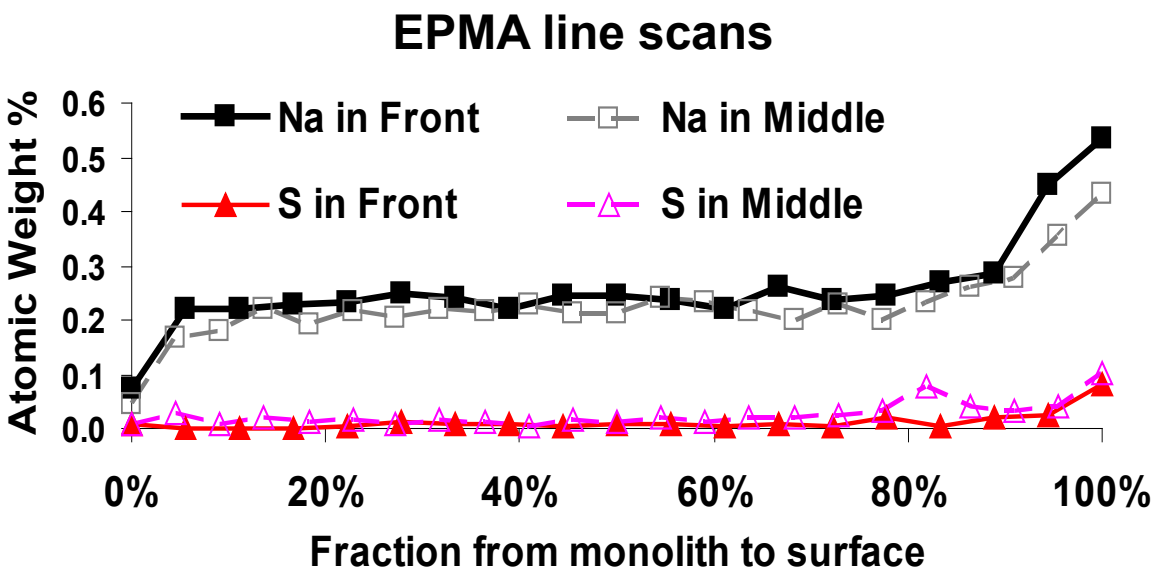


SCR

Na observed after accelerated aging in SCR, but not a surface-only effect

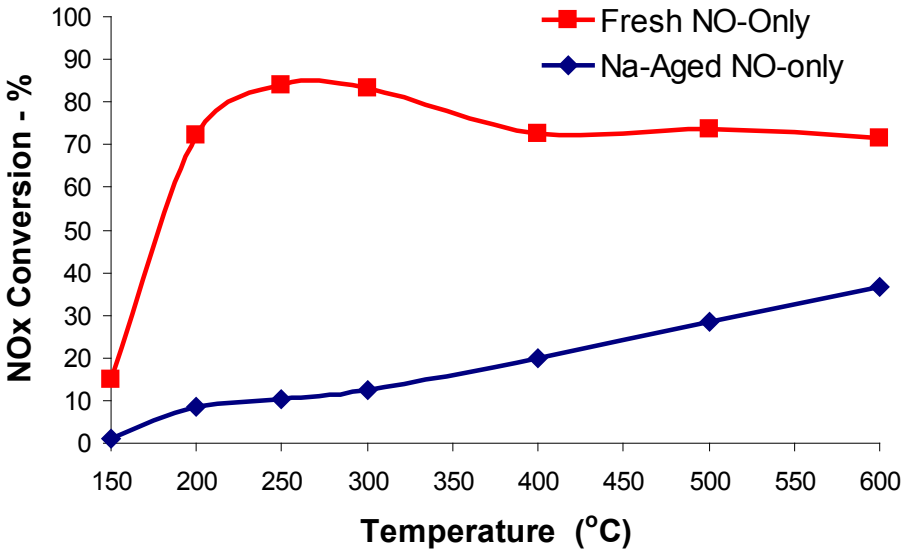
- Na throughout washcoat
  - In bulk ~0.2%wt
- Elevated Na levels also observed at surface
  - 0.3-0.6%wt
- Concentration of Na does not decrease significantly in the axial direction
- Low sulfur levels detected in SCR washcoat
  - Near detection limit
  - Increased level at surface ~0.1%wt



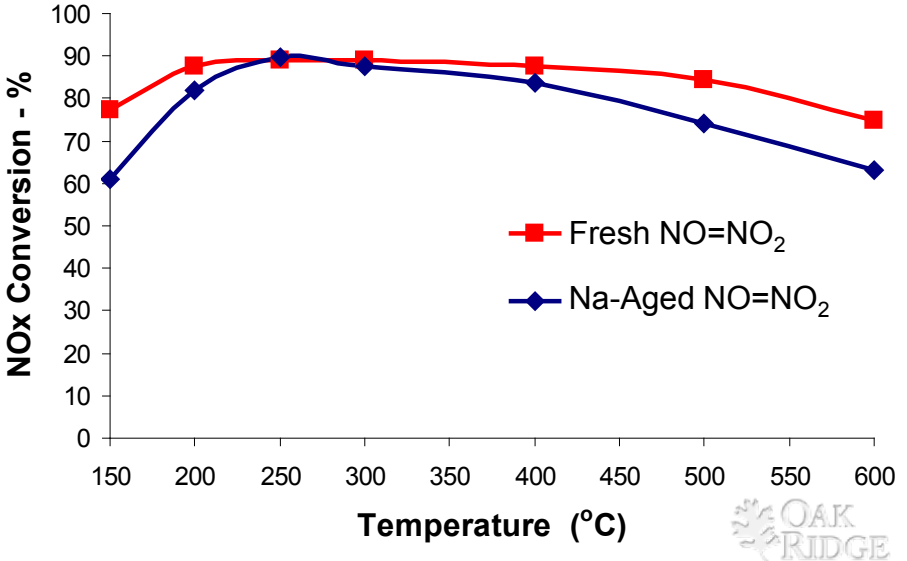


DOC→SCR→DPF system reveals impact in SCR performance with Na addition

- Single cylinder engine at constant load with high Na content
  - Periodic soot regeneration; T_{avg}=650 C
- Highly elevated Na-levels to achieve 435,000k mile equivalent Na (5 ppm basis)
  - 5000+ ppm Na and S in B20

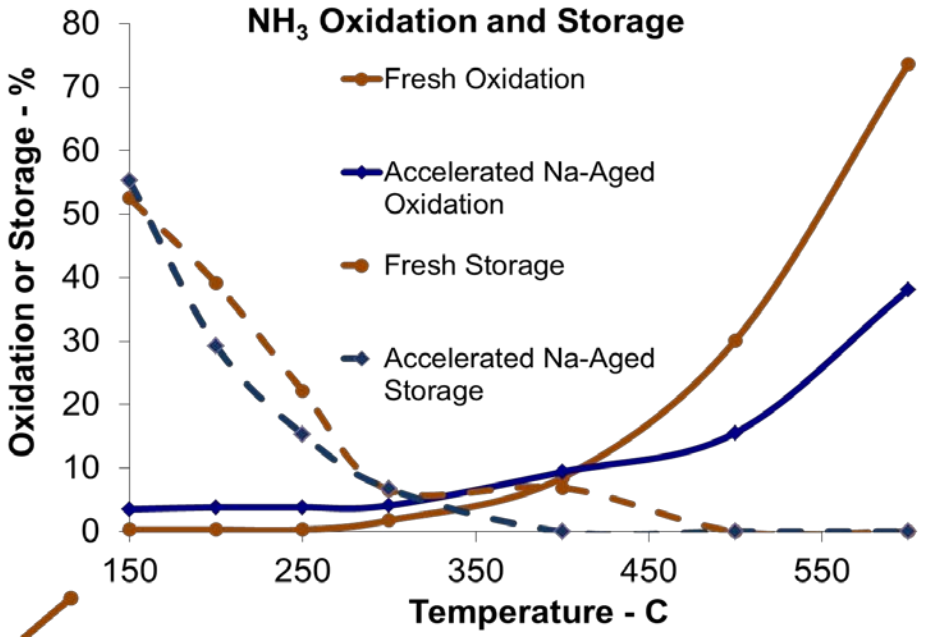


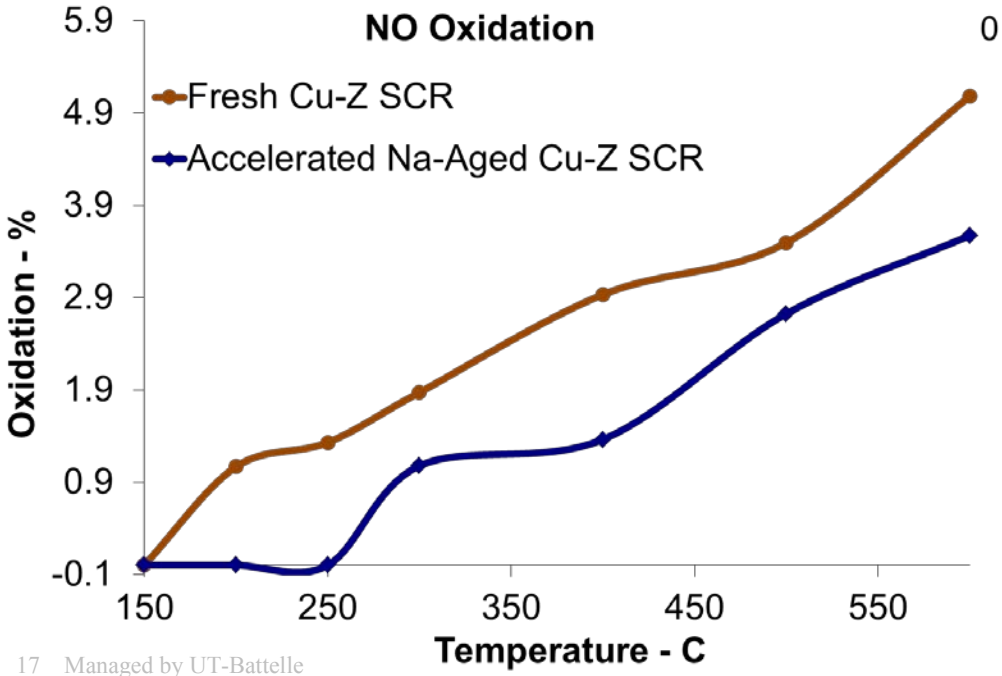
- SCR performance measured on bench reactor with aged core
- NO-only performance evaluation is greatly impacted
  - When NO=NO_2 impact is minimal
  - Points to site specific deactivation



NH_3 interactions minimally impacted, but NO focused sites show deactivation

- No significant impact on NH_3 storage for the Na-aged sample
- NH_3 oxidation is inhibited above 400 C in the accelerated Na-aged SCR…does not explain deactivation
- **NH_3 adsorption sites are not impacted by Na**

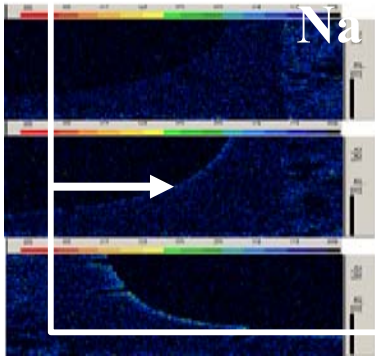


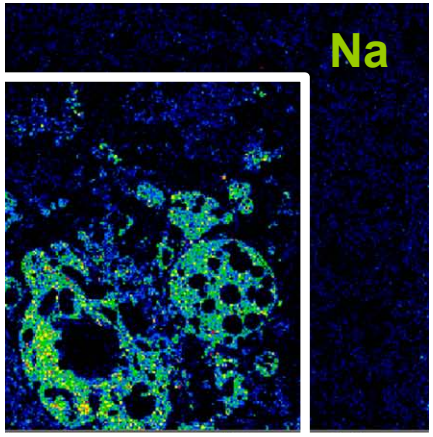


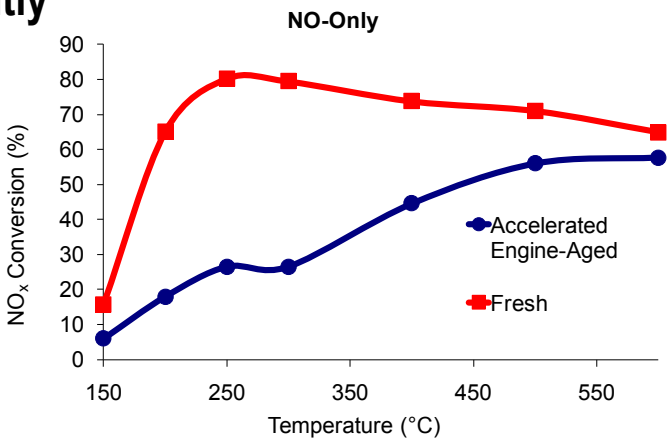
- **Na contamination reduces the ability of SCR to oxidize NO into NO_2 over entire temperature range**
- Combined with good conversions for $NO+NO_2$ feeds suggest:
  Na impacts Cu-exchanged sites

Summary

- Na identified in varying levels of emissions control devices
  - DOC and LNT at washcoat surface; SCR throughout
  - In DPF, Na is concentrated in ash plug
- Minimal impact observed on DOC and LNT devices
- Increased ash accumulation from using B20 is most likely due to either
  - Increased oil consumption brought on by oil dilution
    - Follow-up study coming
- Na does not migrate into the cordierite monolith
  - Thus no weakening of the monolith is currently suspected
- Na impacts zeolite based SCR catalyst
  - NO-only activity greatly reduced
  - NO_2=NO activity decreases moderately







Acknowledgements

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  - Kevin Stork: Fuels & Lubricants – Non-Petroleum Based Fuels

- Long-term aged emissions control parts
  - DOC and DPF: Rahul Mital – General Motors
  - LNT: Ken Price – Umicore

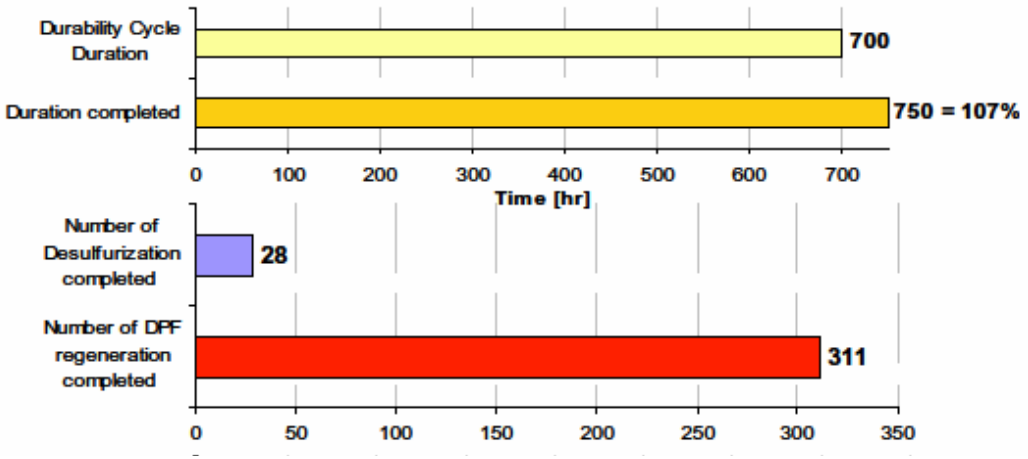
- Discussions and project development
  - Bob McCormick, Matt Thornton, Aaron Williams – NREL
  - Rasto Brezny – MECA

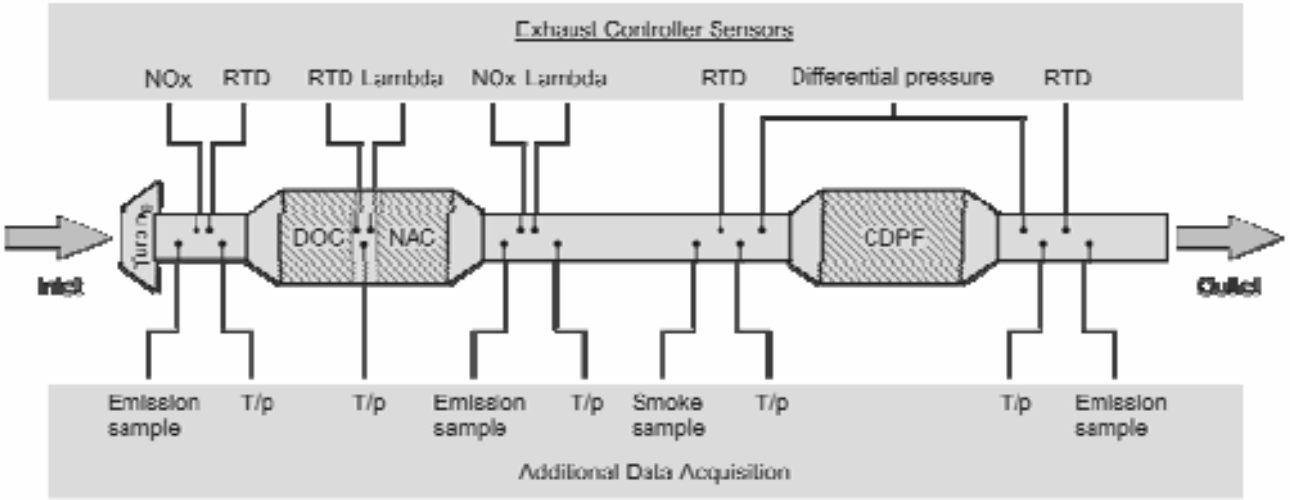
THANK YOU

Additional slides

System 1: Long-term NREL-aged LNT

- Part of long-term study at NREL to evaluate impact of B20
  - DOC → LNT-1 → LNT-2 → DPF
  - 120k miles aging equivalent (750h)
    - Operated at high loads to accelerate fuel consumption
  - < 0.5 ppm Na, K and 0.1 ppm Ca
- Only LNTs provided to ORNL for analysis
- Final state was before desulfation





NREL References: SAE 2008-01-0080, SAE 2009-01-0281 & SAE 2009-01-1790

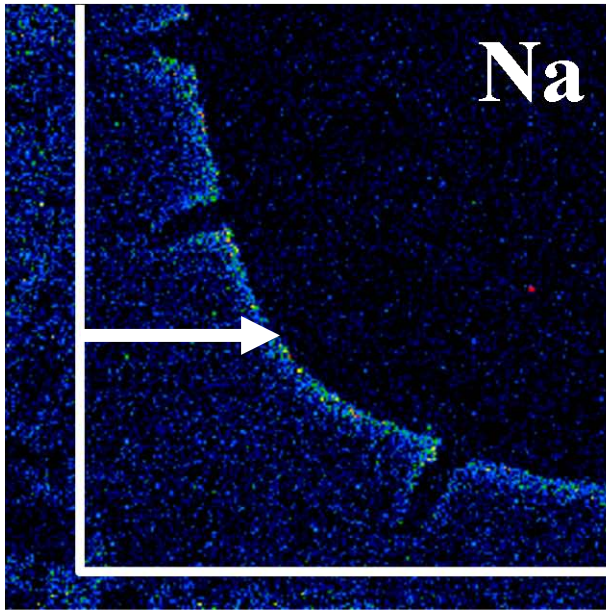
System 2: DOC and DPF from GM

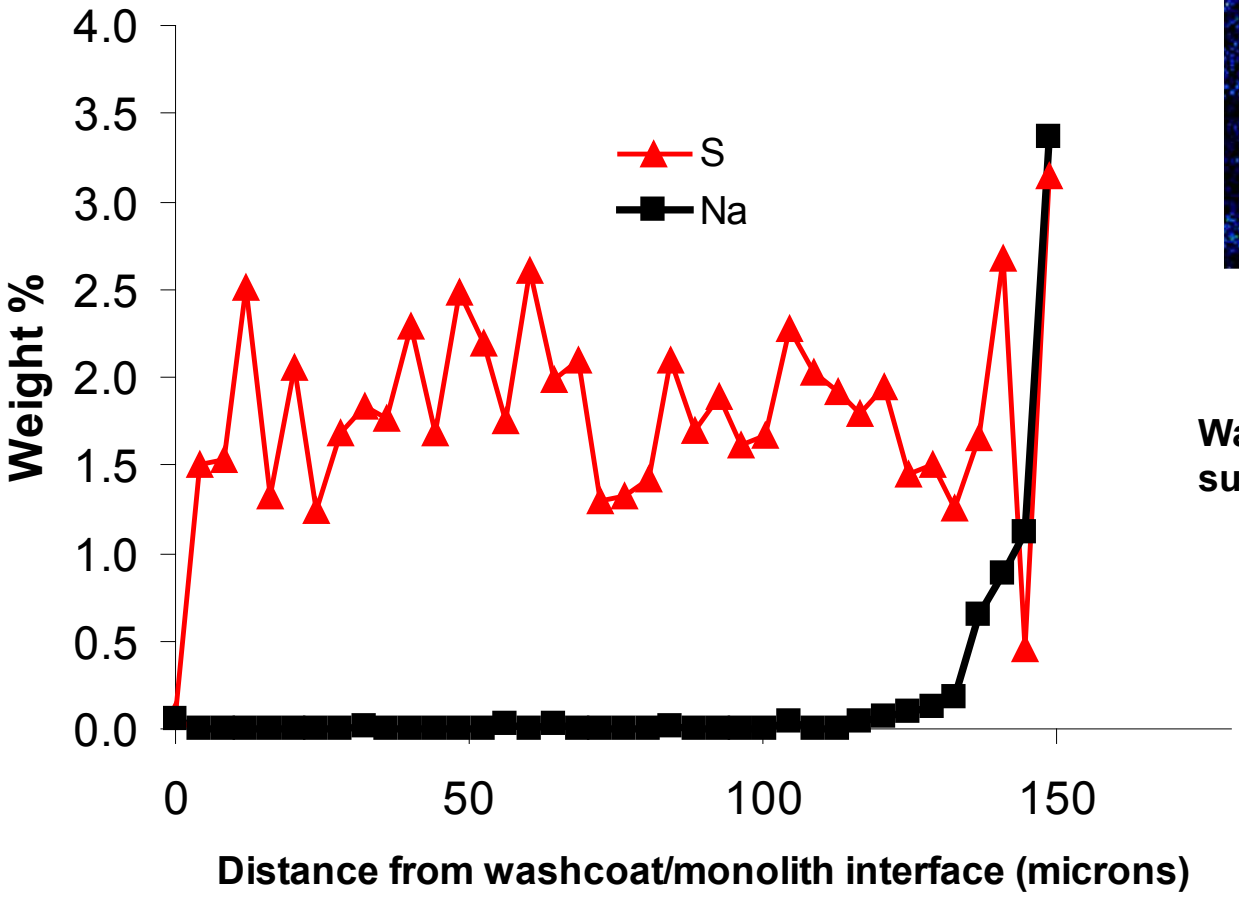
System 2: B20 → DOC → DPF

- Obtained from GM
- Field-aged system with B20
  - 120,000 mile equivalent
- No NOx aftertreatment in system
- Pt/Al_2O_3-based DOC
- SiC-based DPF

LNT-1 EPMA Line Scan

- Na penetration depth is approximately 30 microns and up to 1-3%wt locally
- S poisoning penetrates entire washcoat





Washcoat surface