Impact of Biodiesel-based Na on Emission Control Devices

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Motivation to introduce higher levels of biodiesel fueled by many factors

- **Biodiesel: alkyl ester similar to diesel fuel**

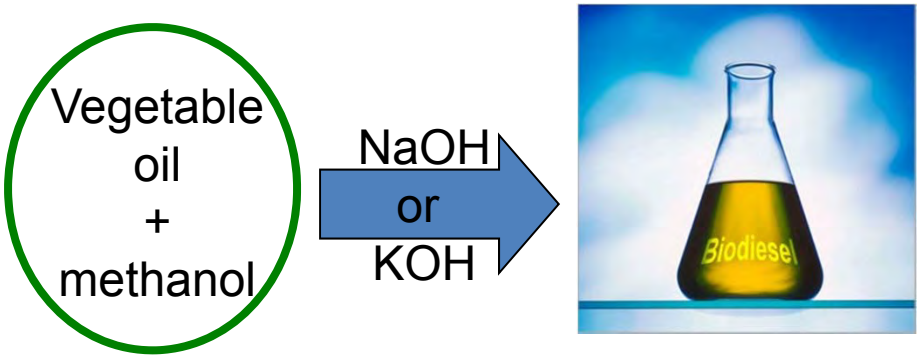
- **Synthesized from vegetable oil or animal fat**
  - **Vegetable: Soybean (~90%), rapeseed, field pennycress, jatropha, etc.**
    - **Several land-use debates/concerns currently ongoing**
  - **Animal sources: Only waste or by-products being converted at this time**

- **Renewable energy source that has the potential to displace a portion of the petroleum that we import from foreign sources**
  - **Maximum is a matter of debate and depends on source**
  - **Peak annual production in US: 13 million barrels (2007)***
  - **Current US capacity: 53 million barrels annually***
  - **2010 Petrodiesel used in US: ~1 billion barrels**

* - source: www.BiodieselMagazine.com

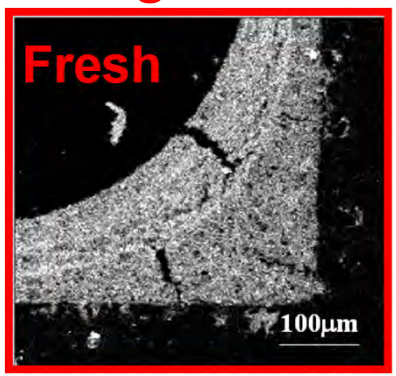
What impact could biodiesel have on emissions control devices?

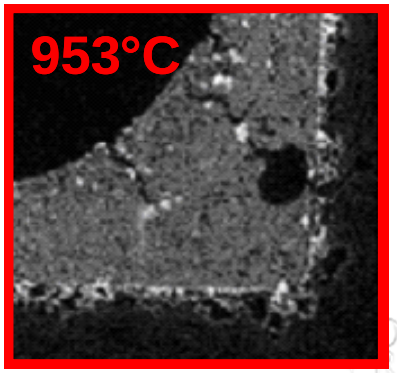
- **NaOH or KOH is a liquid-phase catalyst used in biodiesel synthesis**
  - **NaOH and KOH difficult to separate completely from products**
  - **Specification set at 5 ppm Na/K in B100**
- **Potential Na/K emissions control effects**
  - **ash accumulation**
  - **Alkali absorption into monolith walls**
    - **possible weakening of monolith**
  - **Catalyst poisoning/fouling**
- **Long-term durability requirements set for each on-road system**
  - **Light duty vehicles: 120,000 miles**
  - **Heavy duty vehicles: 435,000 miles**



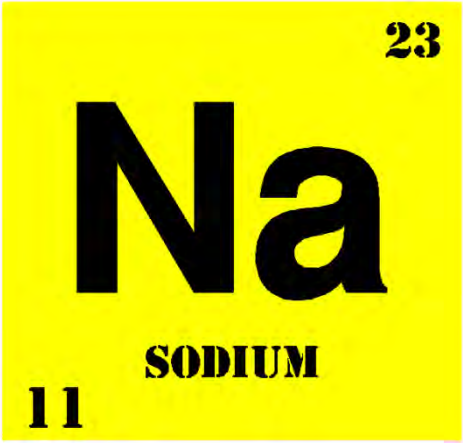
Increased Ash Accumulation

Migration into cordierite



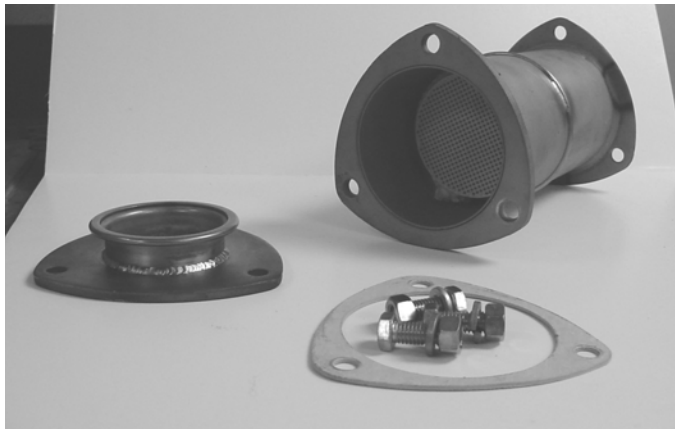


Goals of current project

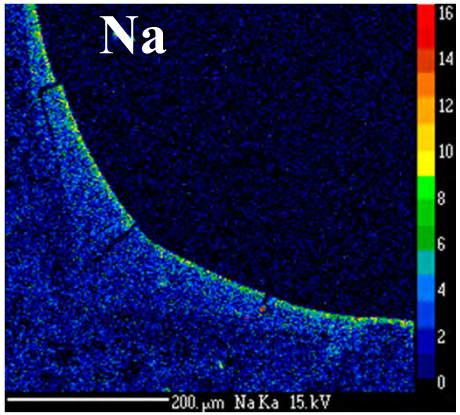


- Determine if accelerated approach mimics behavior and deposition in long-term aging
  - Can accelerated approach be used for evaluation of new formulations?

- Study impact of Na on emissions control devices
  - Field-aged, long-term engine-based aging, and accelerated aging
  - Which devices are most sensitive?



- IF impact is observed, how is it manifested?
  - Performance deactivation? Poisoning?
  - Materials degradation?
  - Ash deposition or fouling layer?

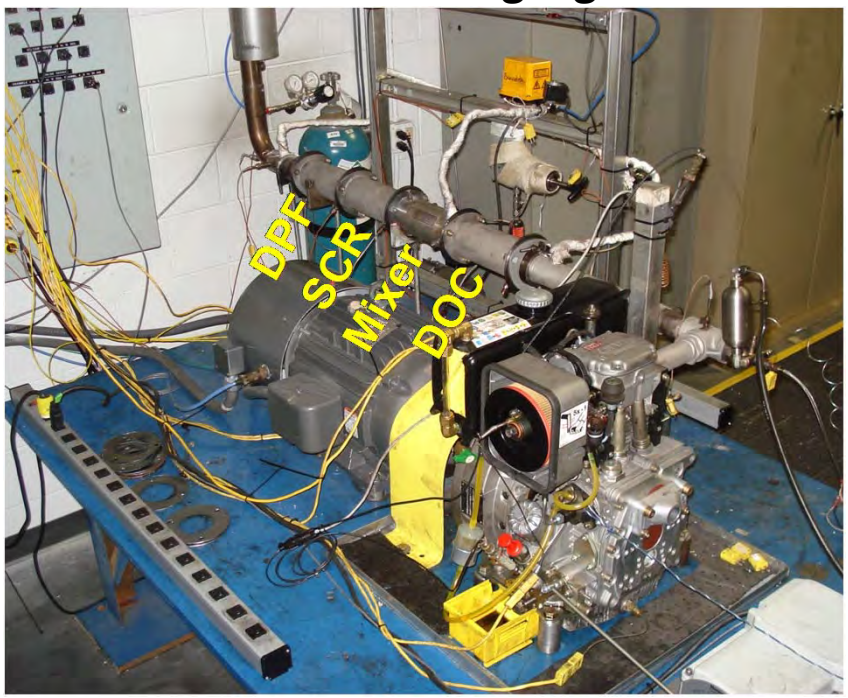


Approach to Na introduction in emissions control devices

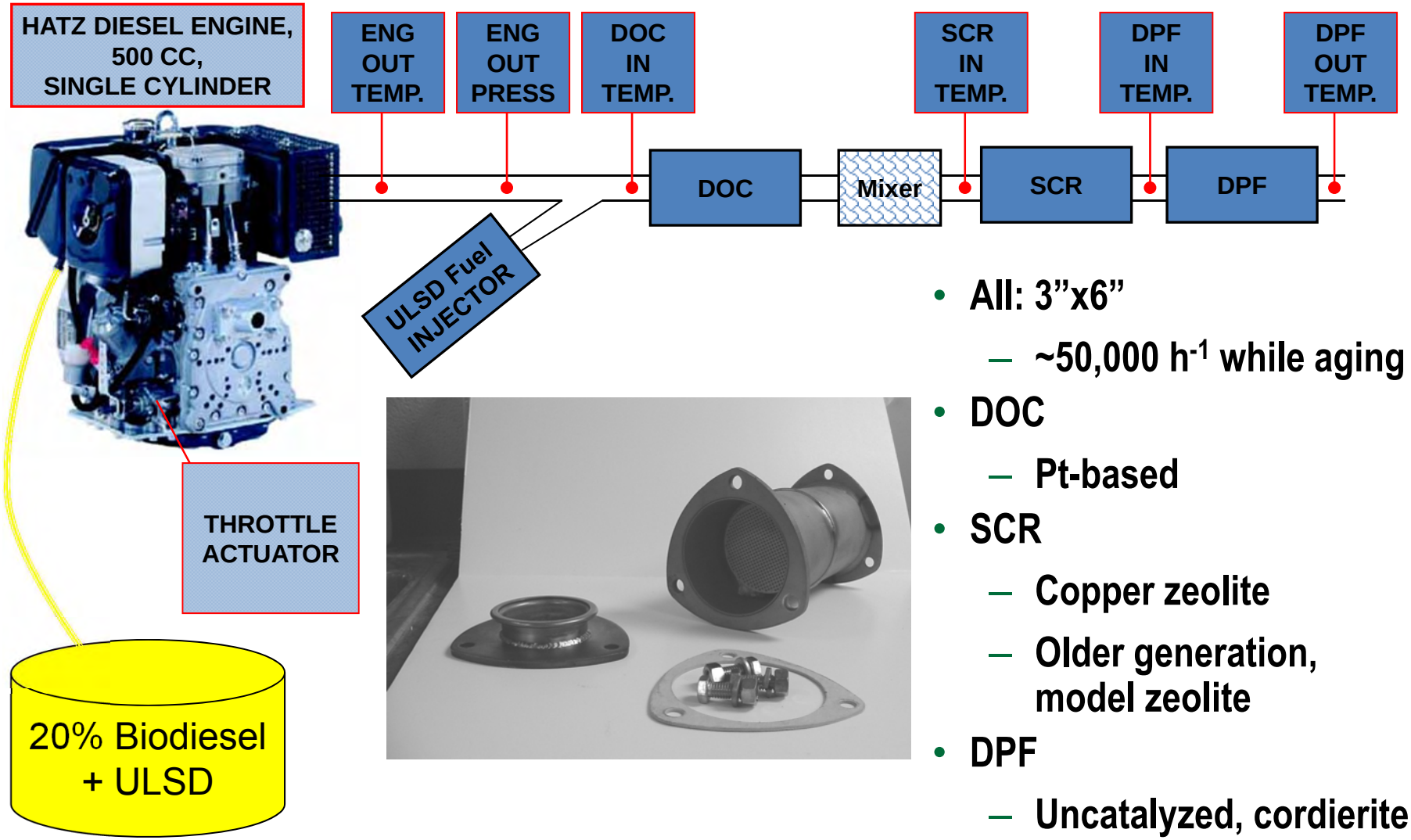
- **Long-term aging studies from our partners**
  - **ORNL received aged parts**
    - **Evaluations and characterization performed**
  - **GM: DOC+DPF system with in-spec B20**
  - **NREL/MECA (partially accelerated) with very low Na-content**
    - **LNT from DOC→LNT→DPF system**

- **Accelerated aging studies looking at Na impact**
  - **Aged at ORNL using high levels of Na to isolate impact**
  - **Studying DOC, SCR and DPF**

ORNL Accelerated Aging Platform



Schematic of engine setup and catalyst information

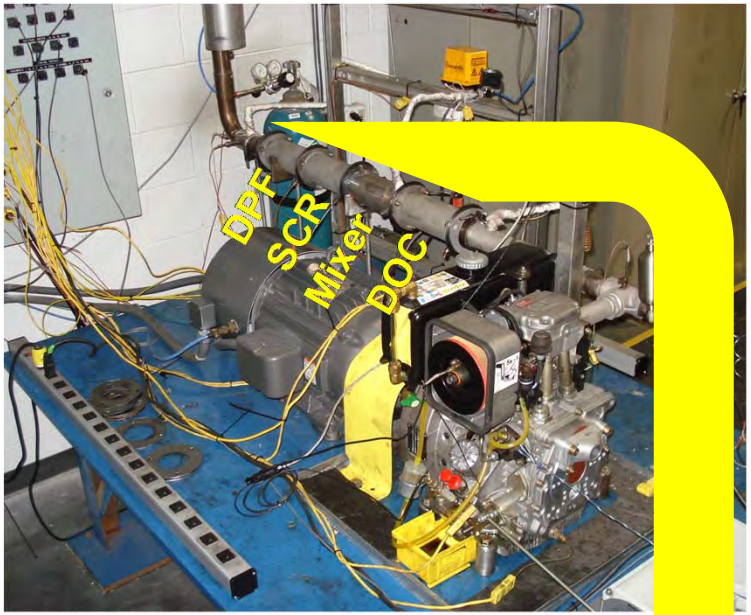


- All: 3”x6”
  - ~50,000 h^{-1} while aging
- DOC
  - Pt-based
- SCR
  - Copper zeolite
  - Older generation, model zeolite
- DPF
  - Uncatalyzed, cordierite

Accelerated aging targets Na-impact

- **Introduce high levels of Na to B20**

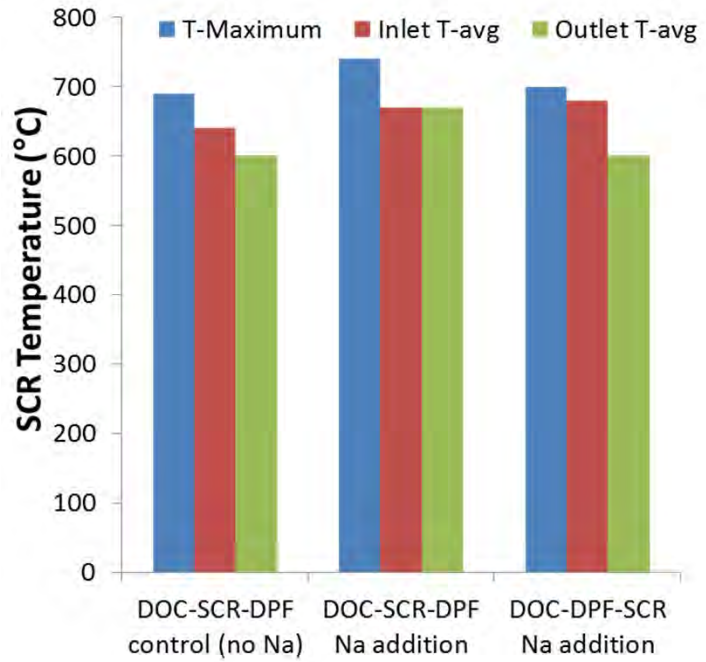
- **Two orientations evaluated**
  - DOC→**SCR**→DPF
    - **"light duty" orientation**
    - **with and without Na (control)**
  - DOC→DPF→**SCR**
    - **"heavy duty" orientation**

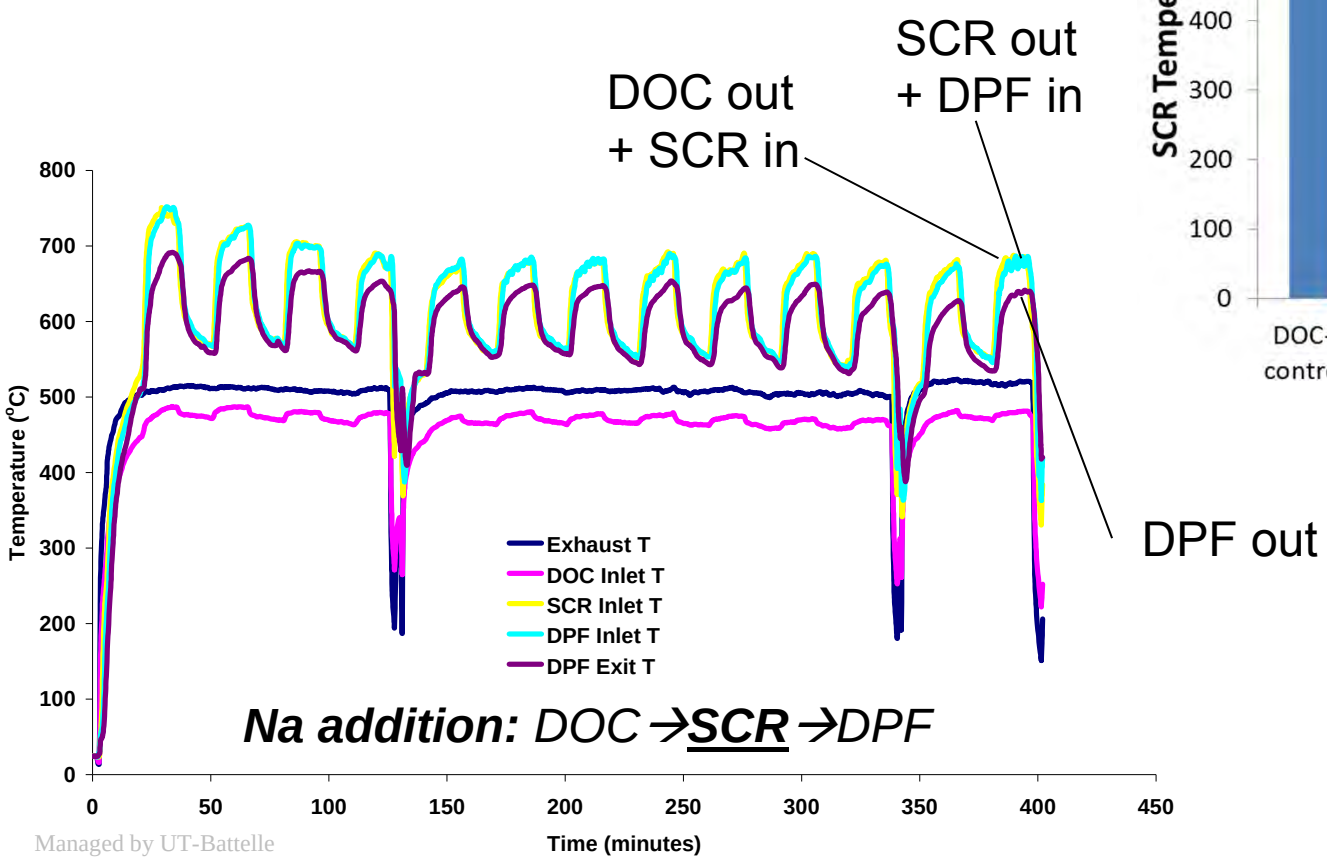


- **Levels elevated to achieve 435,000k mile Na exposure**
  - **Dioctyl sulfo-succinate sodium salt with Na:S = 1**
  - **5000+ ppm Na and S in B20**
  - **Periodic soot regeneration performed**
  - **Measure performance in bench-core reactor**
    - **First 3" of catalysts studied**
    - **Employ portions of the CLEERS SCR protocol**
    - **SV = 36,000 h^{-1}, alpha = 0.8-1.0, NO_2:NO = 0 or 1**

Temperature profiles during accelerated engine-aging: DOC→SCR→DPF (light duty)

- **Exotherm generated over DOC**
- **SCR inlet and outlet similar**
- **DPF temperature decreases from inlet**





COMPARISON OF ACCELERATED APPROACH TO LONG-TERM AGING

Field-aged systems used for comparison when possible

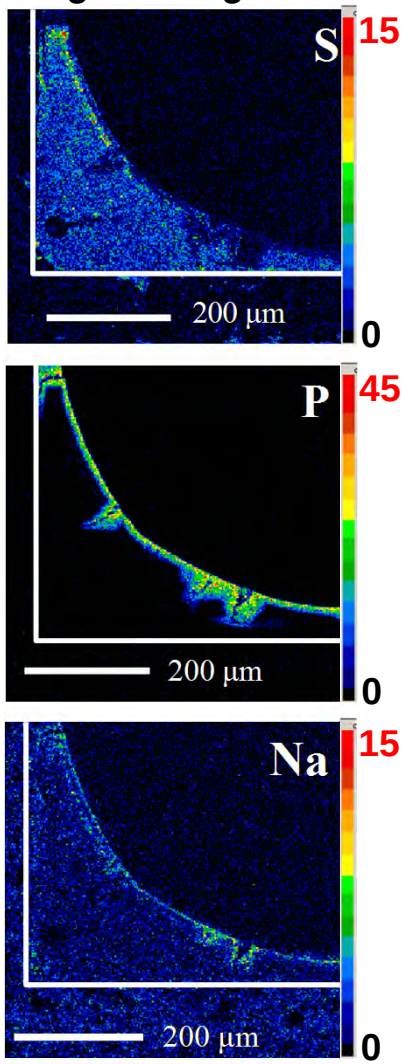
B20 → DOC → DPF

- **Obtained from GM**
  - **Pt/Al_2O_3-based DOC**
  - **SiC-based DPF**
- **Field-aged system with B20**
  - **120,000 mile equivalent**
- **Minimal knowledge about aging details**
  - **Na content was below specification**
    - **Exact value unknown**
  - **Temperature history unknown**

- **Unfortunately unable to secure any B20-aged SCR catalysts**

Biodiesel and lube oil components observed in DOC; accelerated- and engine-aged results similar

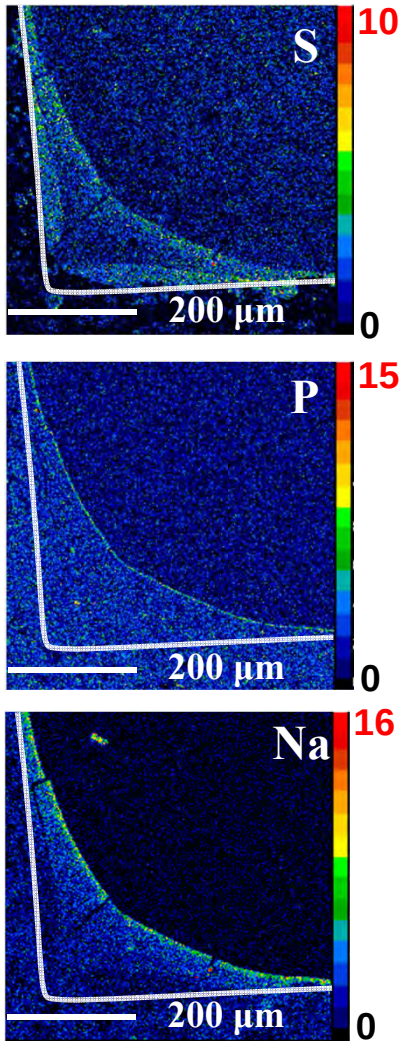
Long-term aged DOC



- Na, S and P observed in DOC
  - Inlet cross-sections shown with EPMA
- Long –term aged
  - S throughout washcoat
  - P at surface of washcoat
  - Na observed primarily at surface
    - Primarily at inlet of DOC
- Accelerated aged
  - S throughout washcoat
  - Minimal lube oil phosphorous detected
  - Na observed throughout DOC
    - Equally in front and rear of DOC

	Long-term Aging			Accelerated Aging		
	Average	Maximum	Penetration	Average	Maximum	Penetration
S	0.70%	1.00%	throughout	0.40%	0.60%	throughout
P	n/a	8%	30 µm	n/a	<0.1%	<10 µm
Na	n/a	0.40%	30 µm	n/a	0.40%	30 µm

Accelerated-Aged DOC

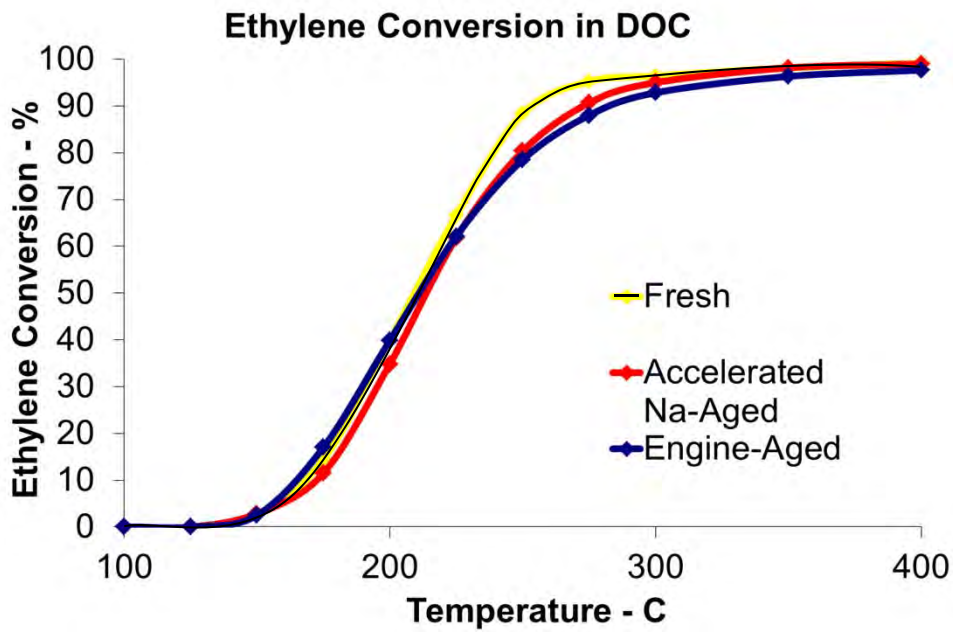


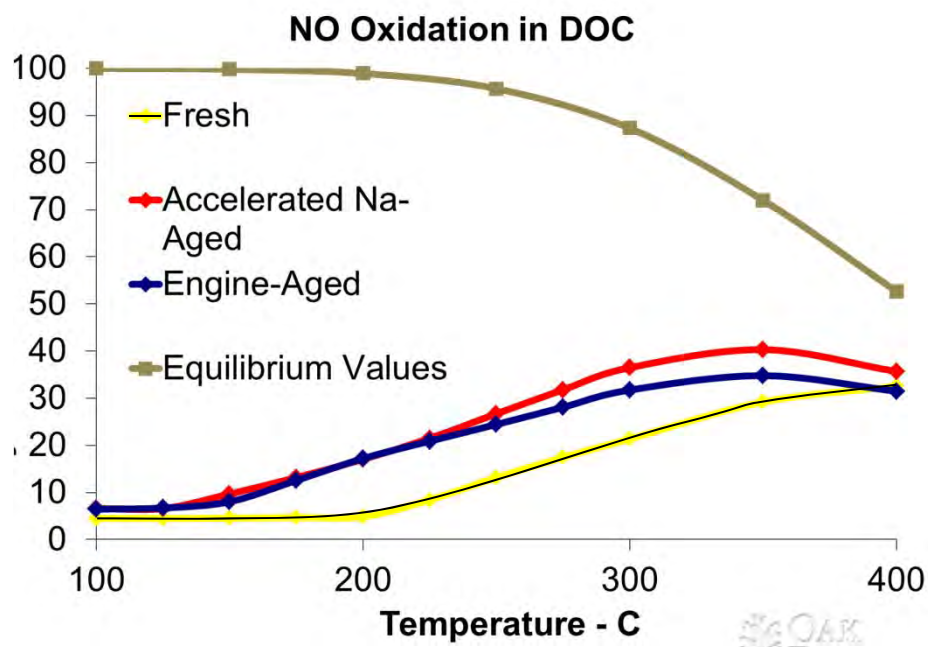
DOC minimally affected; similar effects shown for both accelerated- and engine-aged devices

- **Analysis of fresh, engine-aged and accelerated Na-aged DOCs**
- **Both aged samples show slight decrease between 225°C and 300°C**
  - **Conversion decreases by <12%**

- **Oxidation of NO to NO_2 is as much as 12% higher in engine-aged DOC samples than in fresh**
  - **Stay for Louise's talk on Thursday**

    "The Beneficial Effect of SO_2 on Platinum Migration and NO Oxidation over Diesel Oxidation Catalysts"



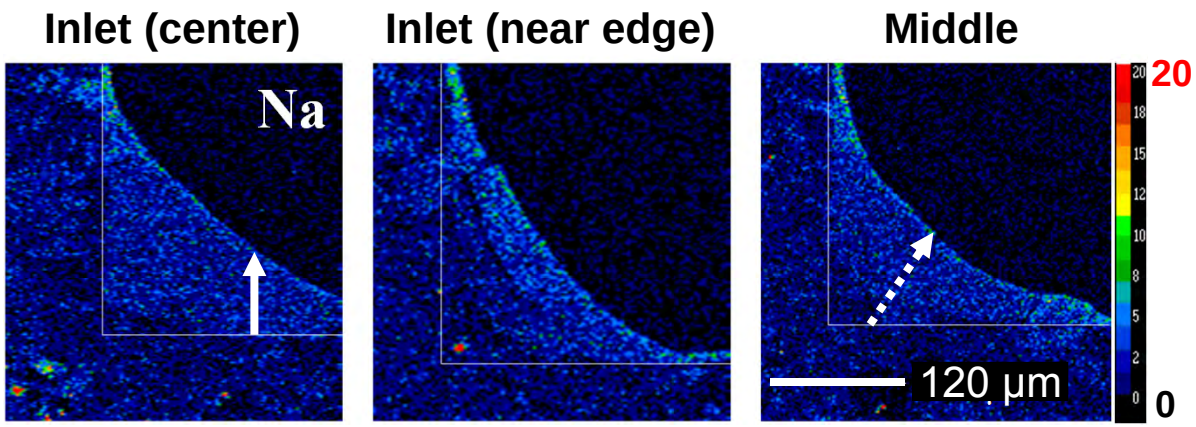


SODIUM IMPACT ON SCR DOC → SCR → DPF ARRANGEMENT

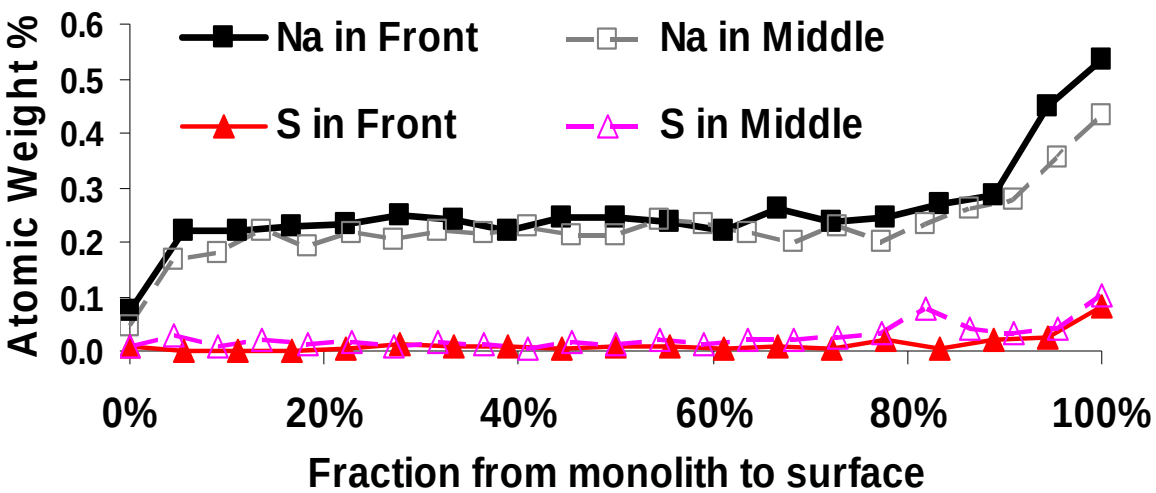
Na observed after accelerated aging throughout SCR washcoat

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

Accelerated Na-Aged SCR (from DOC→<u>SCR</u>→DPF)

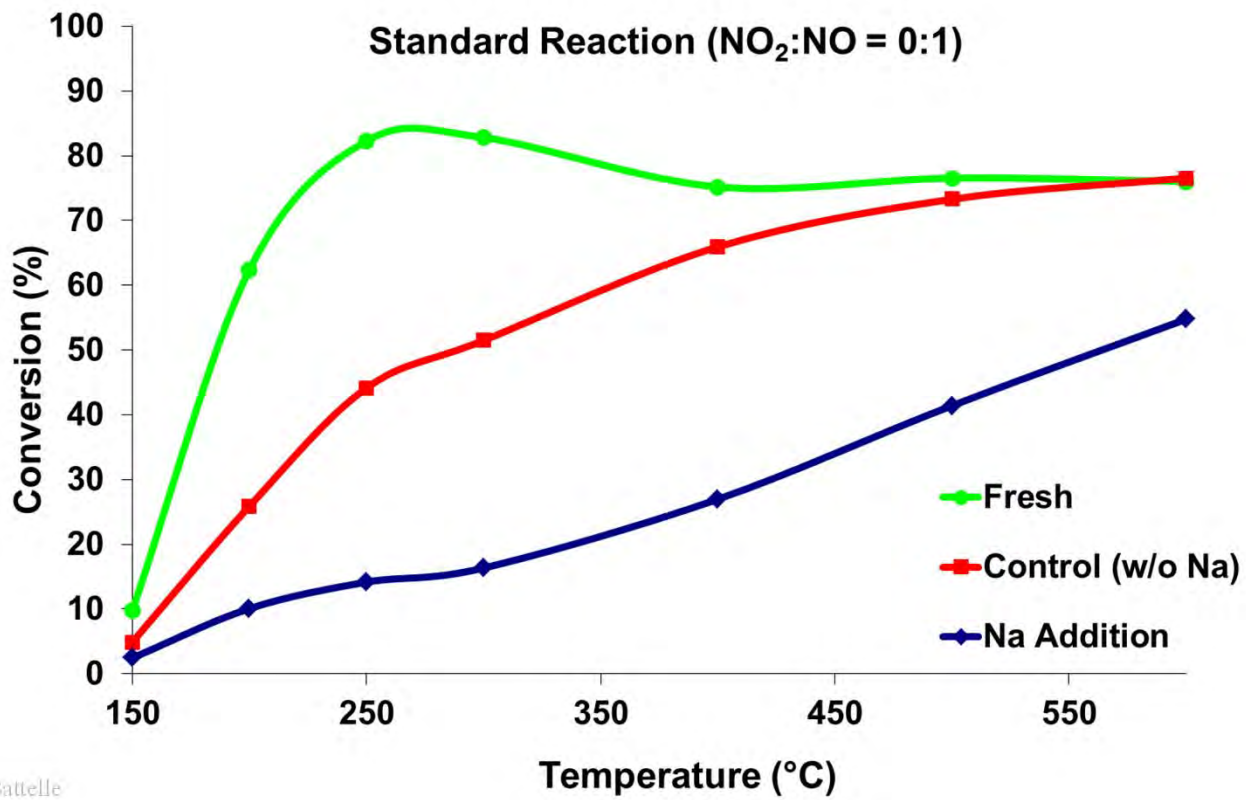


EPMA line scans



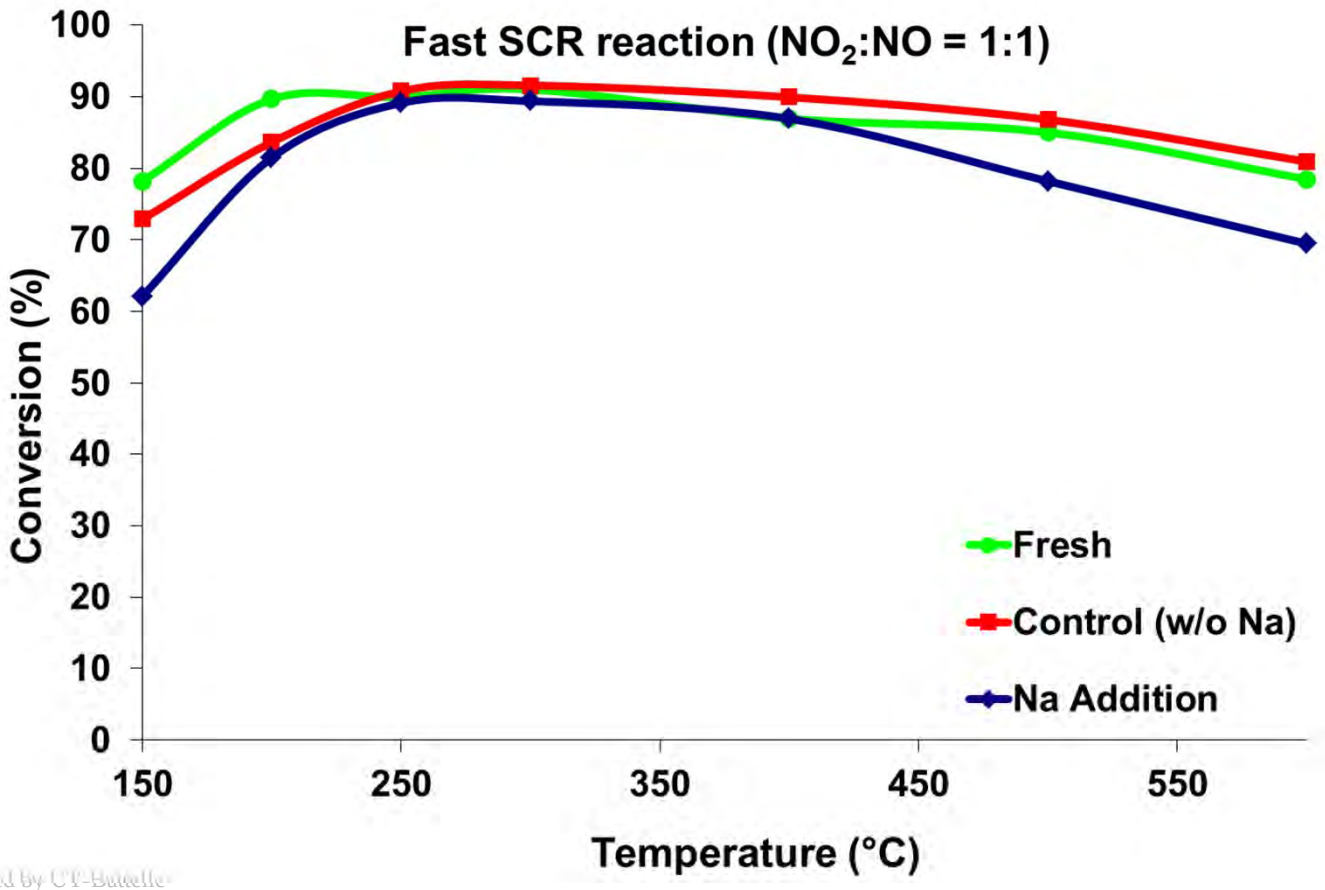
Standard SCR reaction significantly inhibited with Na addition

- **Some aging observed for both the control and Na addition**
  - **Illustrates some thermal effects on this model Cu zeolite SCR catalyst**
- **SCR with Na has significantly less activity for the standard SCR reaction**



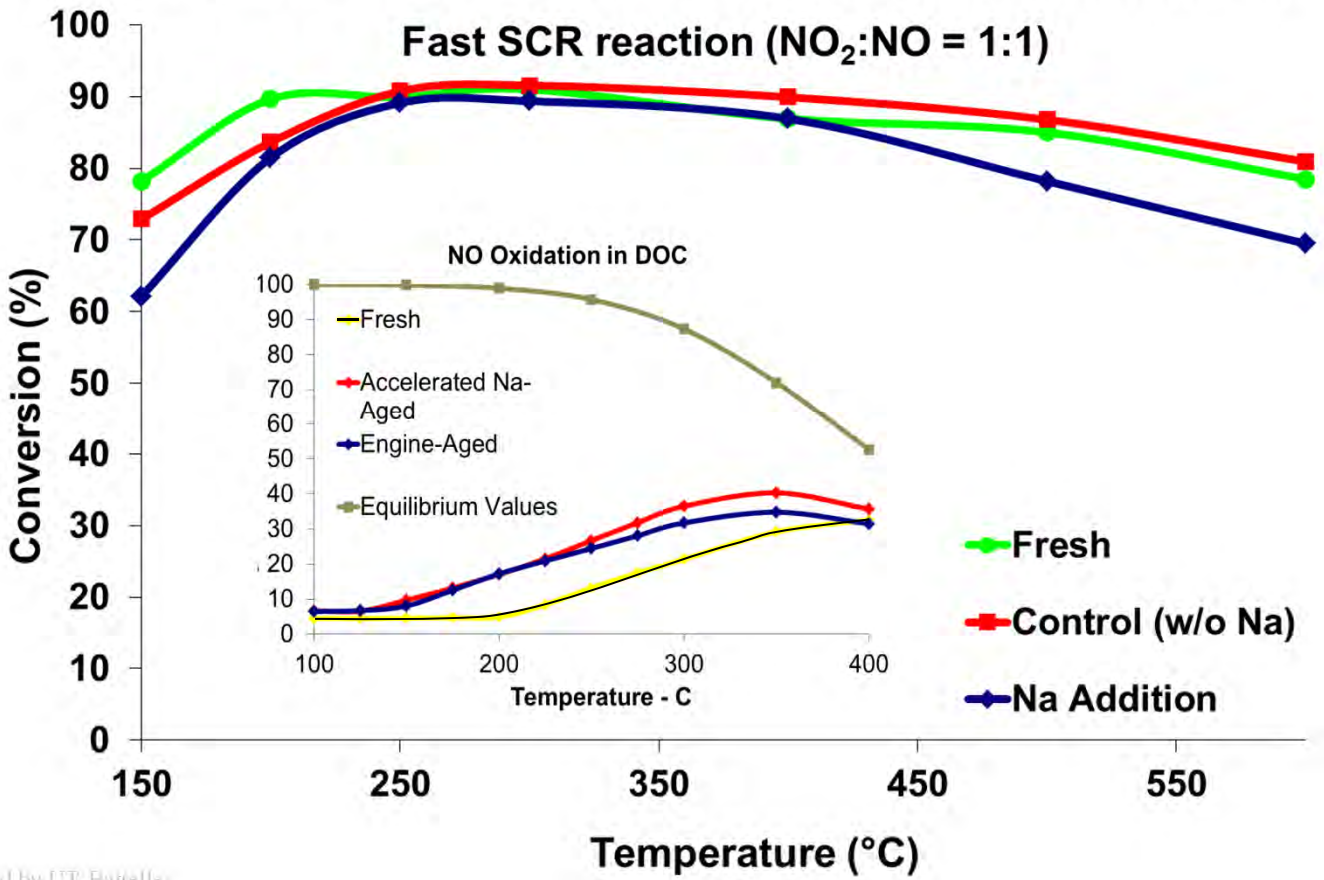
Minimal impact when feeding equimolar NO_2:NO (fast SCR reaction)

- **Minimal effects when feeding both NO_2 and NO**
  - **However, the catalyst most effected is the SCR with Na addition**



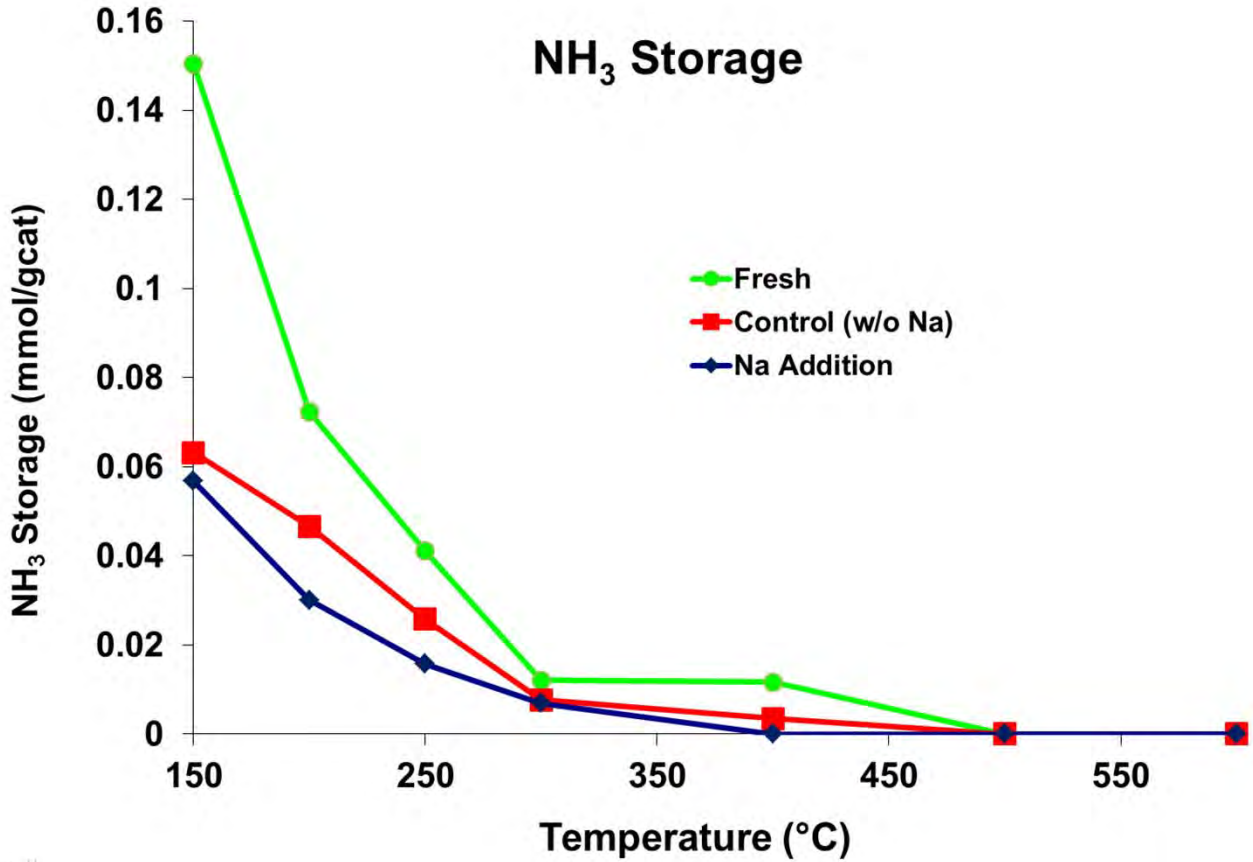
Minimal impact when feeding equimolar NO_2:NO (fast SCR reaction)

- **Minimal effects when feeding both NO_2 and NO**
  - **However, the catalyst most effected is the SCR with Na addition**
  - **Additional DOC consideration…max NO to NO_2 conversion was only ~40%**



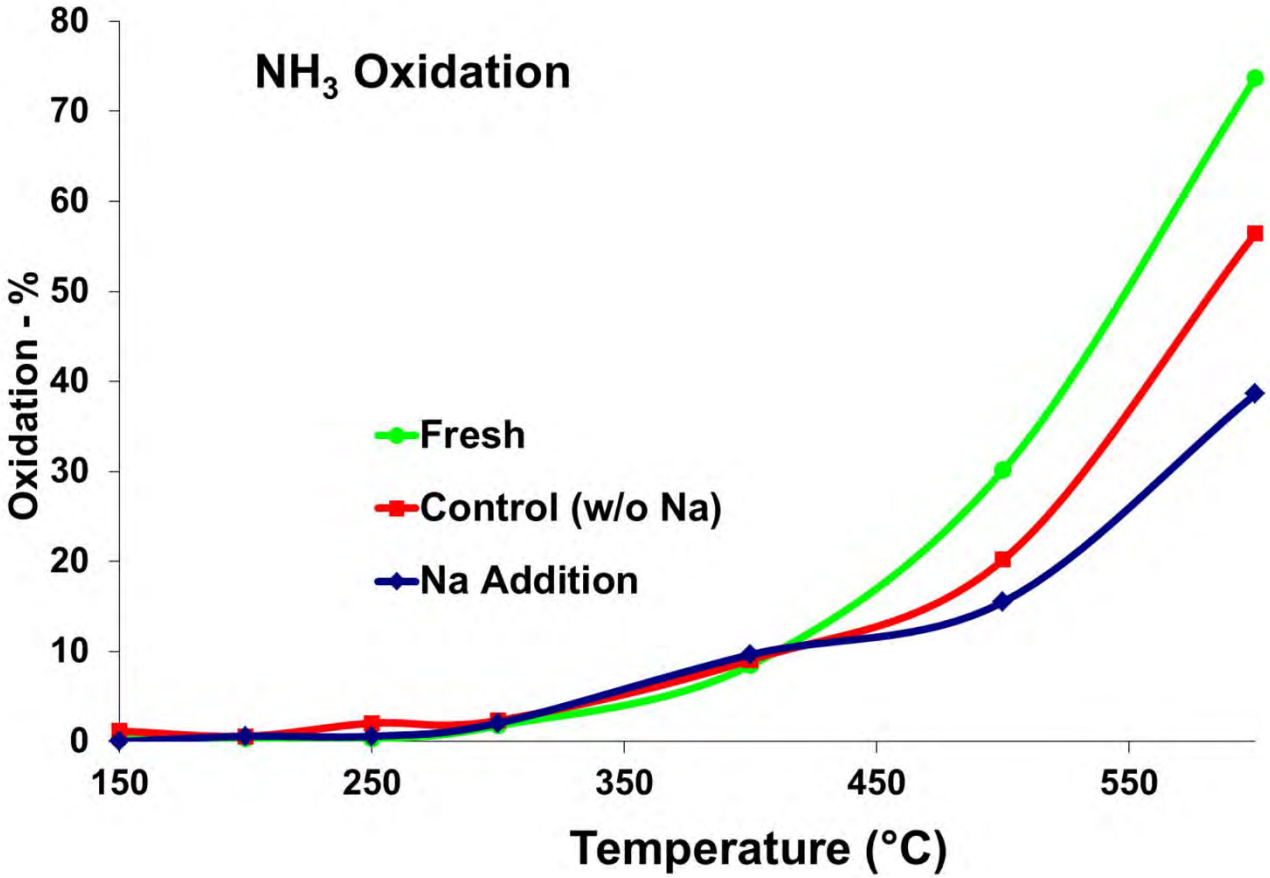
NH_3 storage decreases with aging; control and Na-aged show similar impact

- **Significant impact on NH_3 storage for both aged samples**
  - **Similar impact suggests thermal effect is more responsible than Na**



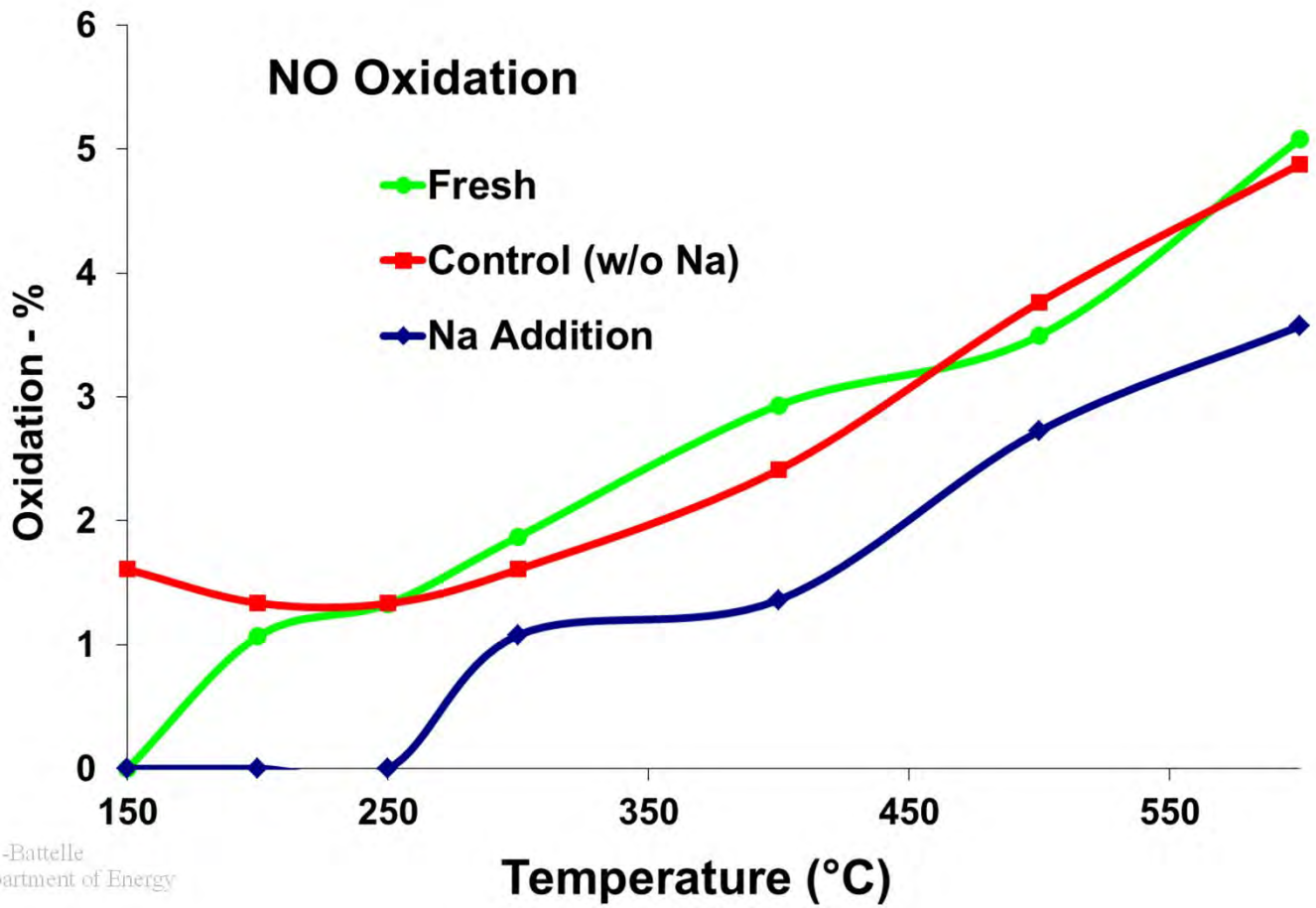
NH_3 oxidation decreases with aging

- **NH_3 oxidation reduced above 400°C in both aged samples**
  - **Oxidation associated with Cu sites**
  - **Significant difference between control and Na-aged SCR suggests Na effect**



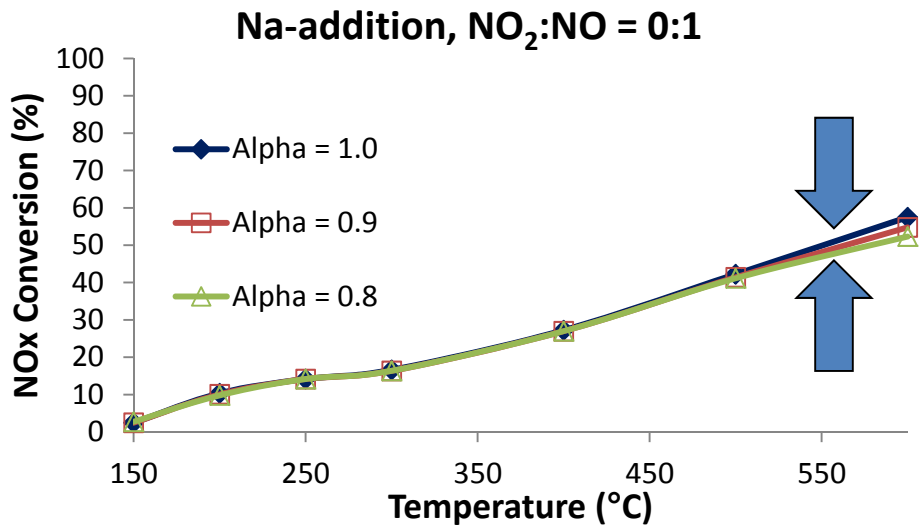
Further evidence of Na impact on Cu-sites with decreased NO oxidation

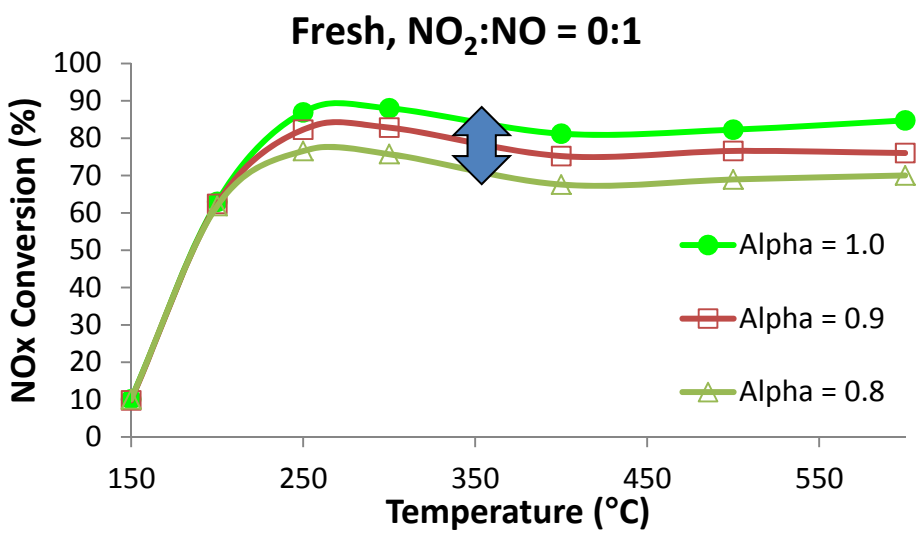
- **Na-aged samples show less oxidation of NO to NO_2 over entire temperature range**
- **Fresh and control show similar, albeit low reactivity**

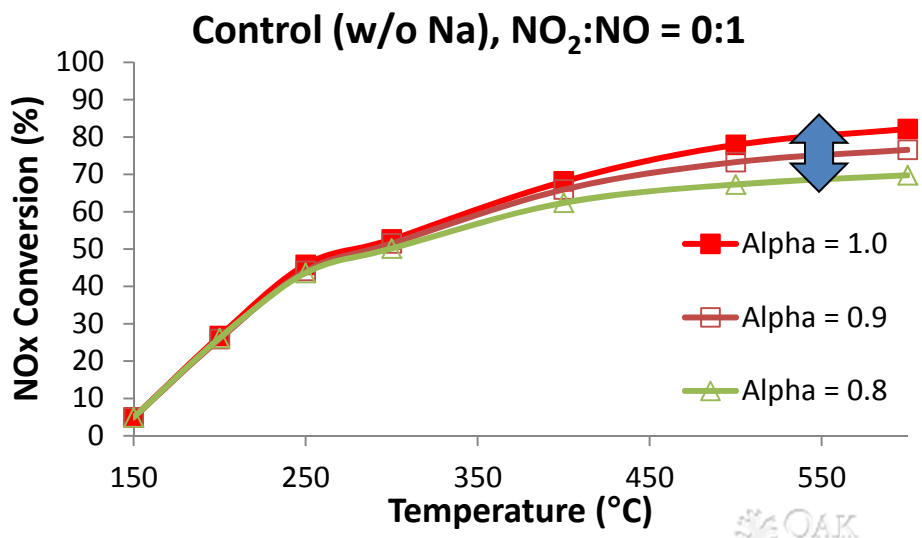


Increasing NH_3 does not improve performance on Na-aged SCR

- Indicates NH_3 oxidation does not limit performance
  - NH_3 breakthrough observed
- Further illustrates NO to NO_2 oxidation is limiting performance in Na-aged sample
  - Oxidation sites are most impacted
- Impact on control is less pronounced



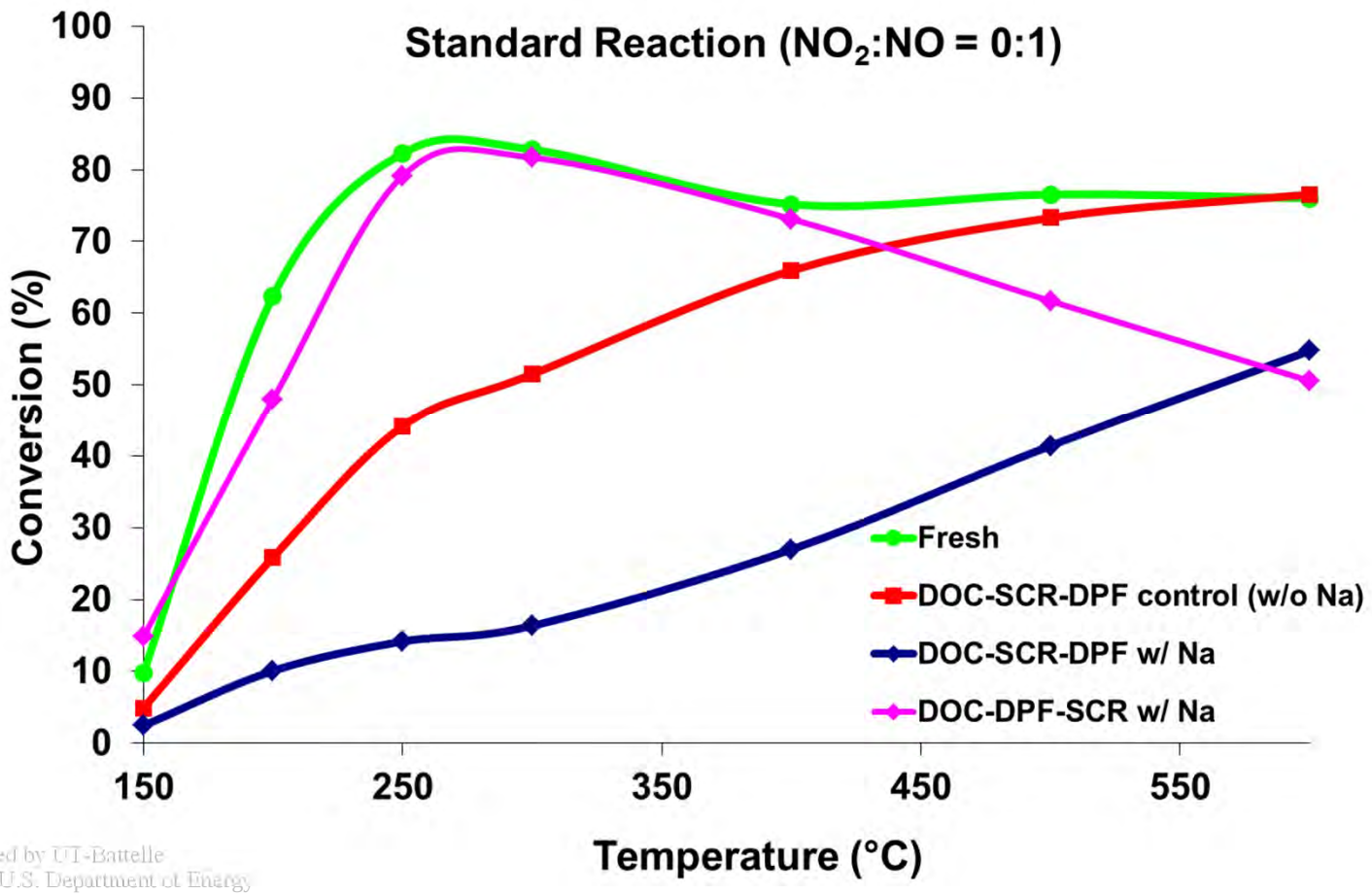




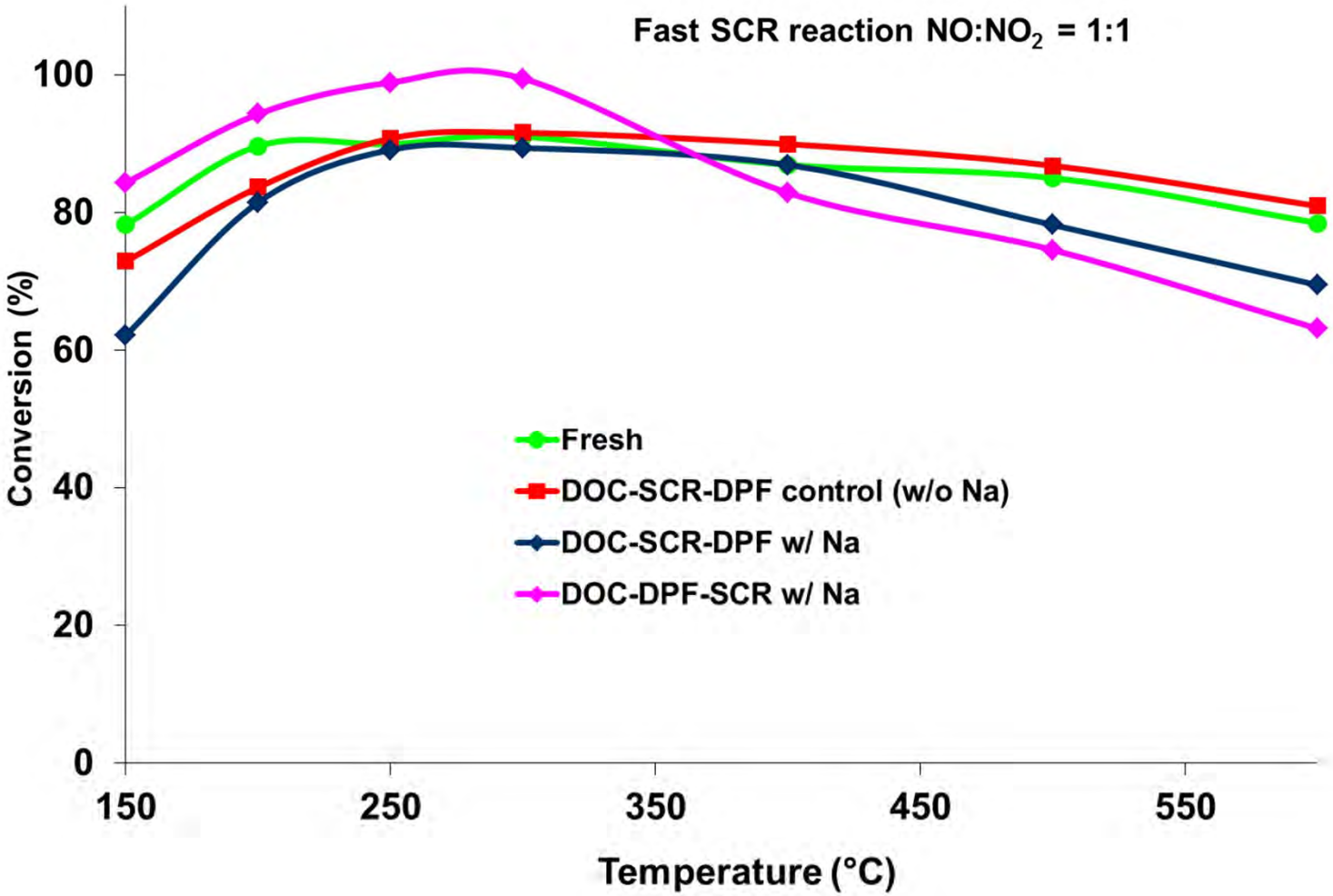
IMPACT ON SCR IN DOC → DPF → SCR ARRANGEMENT

When DPF is in front of SCR, catalyst is protected from Na and its effects

- **Below 400ºC, no significant effect from accelerated Na-aging if DPF is in front of SCR**
  - **Some thermal protection is gained from being down stream of DPF**



Similar good behavior observed with fast SCR conditions



Modeling considerations of Na-impact

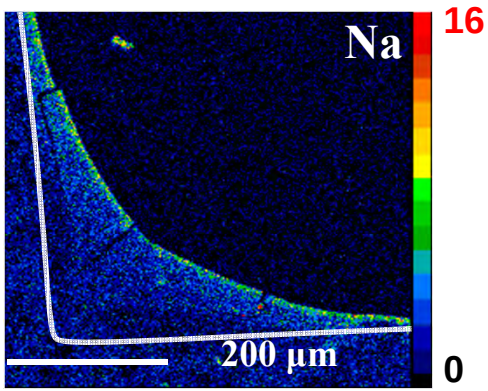
- **What sites are being impacted?**
  - **Results suggest oxidation sites being targeted**
  - **If only adsorbing on oxidation sites, it may be possible to employ Na to selectively poison sites for kinetic studies**

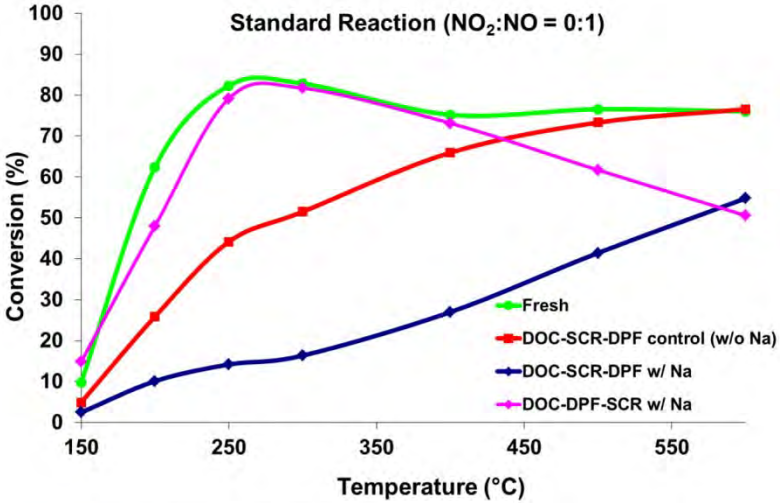
- **Need to measure total surface area**
  - **Is Na penetrating zeolite and causing structural collapse?**
    - **Evidence shown by Ford using aqueous incipient wetness Na addition method (SAE 2009-01-2823)**

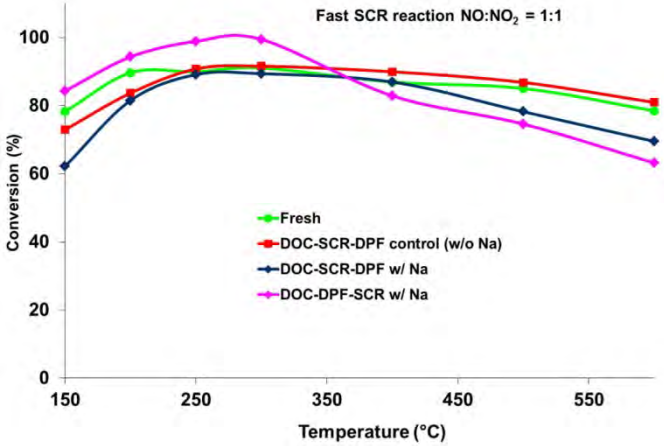
- **Other ongoing efforts looking at DPF integrity especially with respect to Na penetration into the walls**
  - **Evidence shown by NREL and MECA collaboration and in our additional slides**
  - **Highly temperature/material dependent**

Summary

- Na can significantly impact the chemistry of SCR catalysis
- When placed behind a DPF the impact is significantly muted
- Impact of both thermal and Na aging less severe when feeding equimolar amounts of NO and NO_2
- Future directions
  - Is this the case for newer generation of zeolites?
    - Focus of NREL/MECA/Ford/ORNL collaboration
  - What is the effect at lower Na doses
    - What is the limit?
    - Does ASTM standard need to be decreased?







Acknowledgements

- **Funding provided by DOE – Vehicles Technology Program**
  - **Kevin Stork: Fuels & Lubricants – Non-Petroleum Based Fuels**

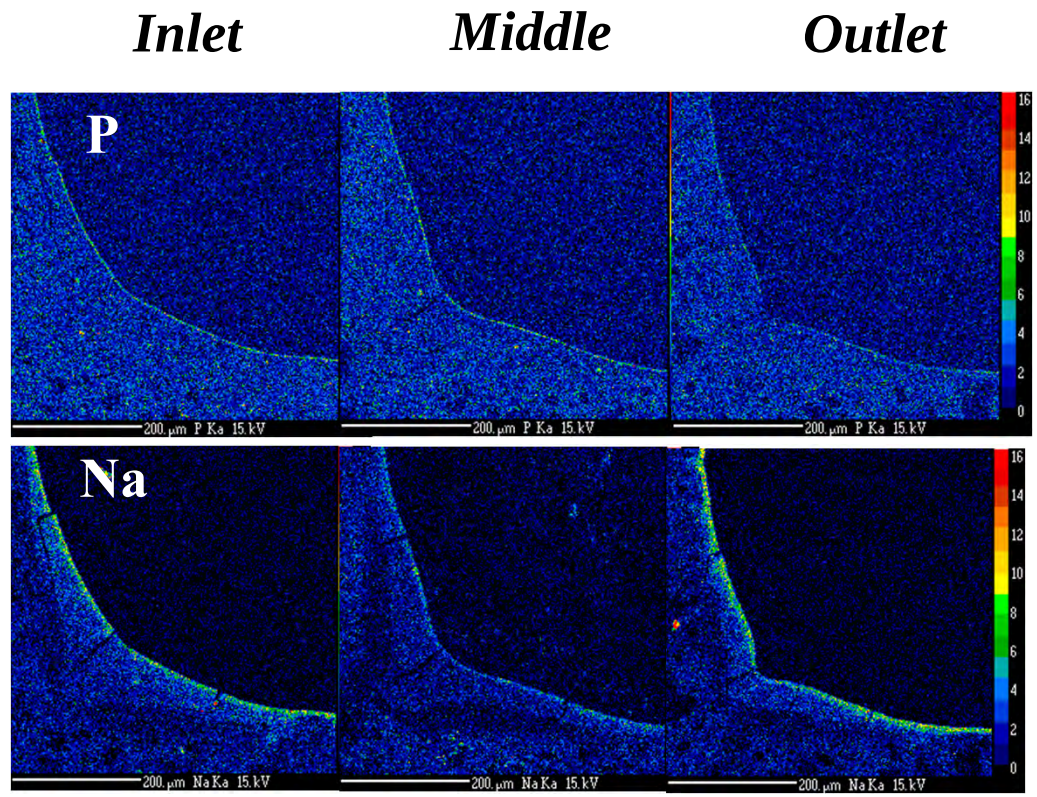
- **Long-term aged emissions control parts**
  - **General Motors**
  - **Umicore, MECA**

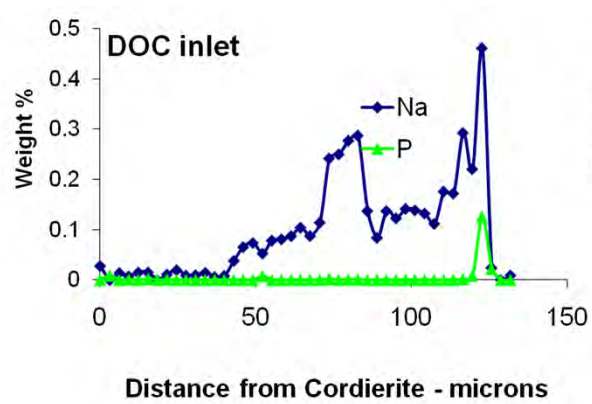
- **Discussions and project development**
  - **Bob McCormick, Matt Thornton, Aaron Williams – NREL**
  - **Rasto Brezny – MECA**

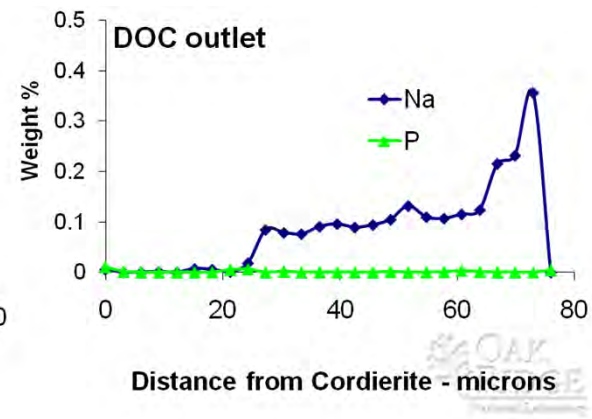
Additional slides

DOC from Accelerated Na-introduction

- DOC used to generate DPF inlet temperature of 650C
  - Incurs thermal aging
- Minimal lube oil phosphorous detected
  - Less than 0.05%wt
  - Penetration < 10 µm
- Na observed throughout DOC
  - Equally in front and rear
  - Penetration through washcoat
  - EPMA line scans
    - Maximum: 0.4%wt
    - Penetration: 30 µm

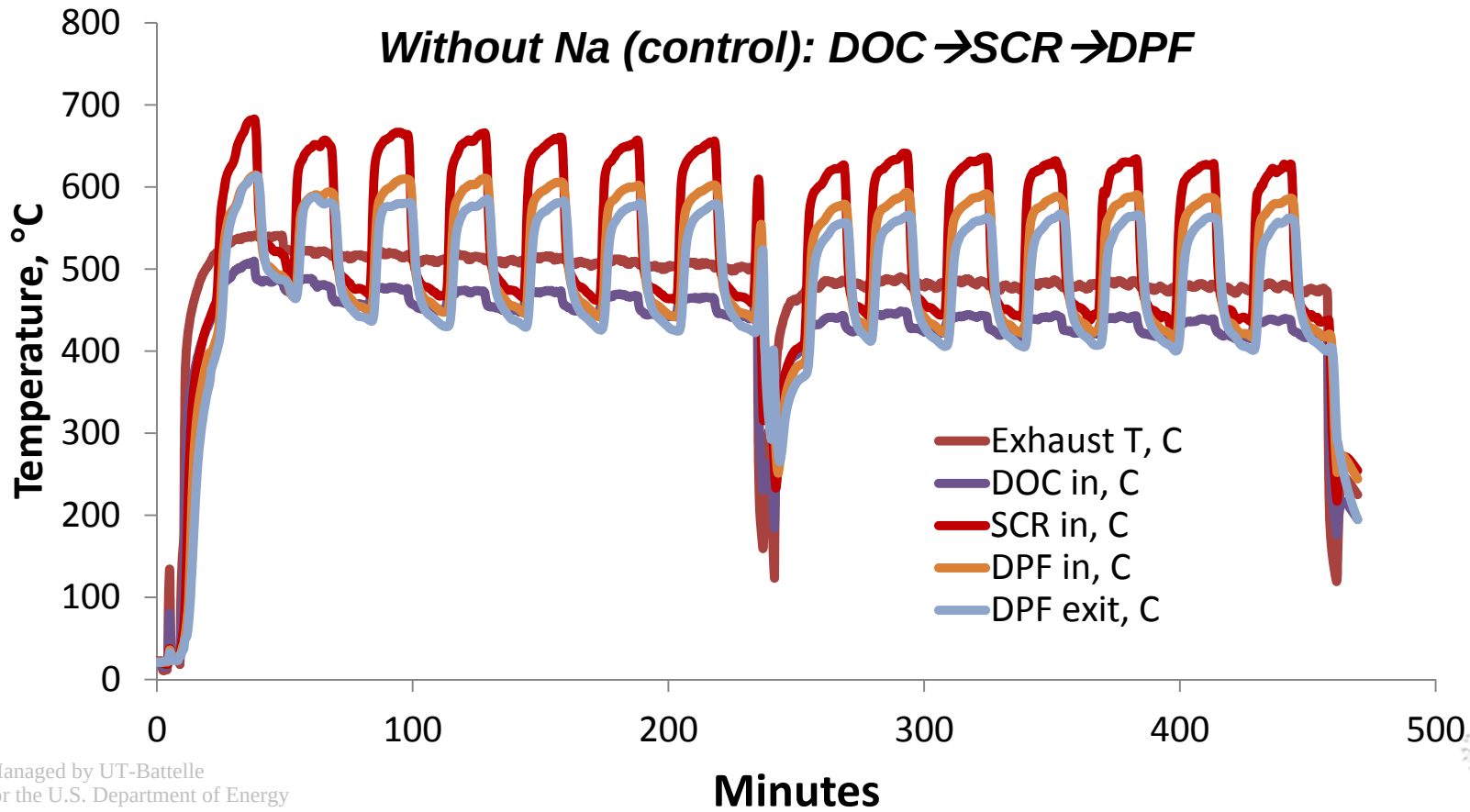






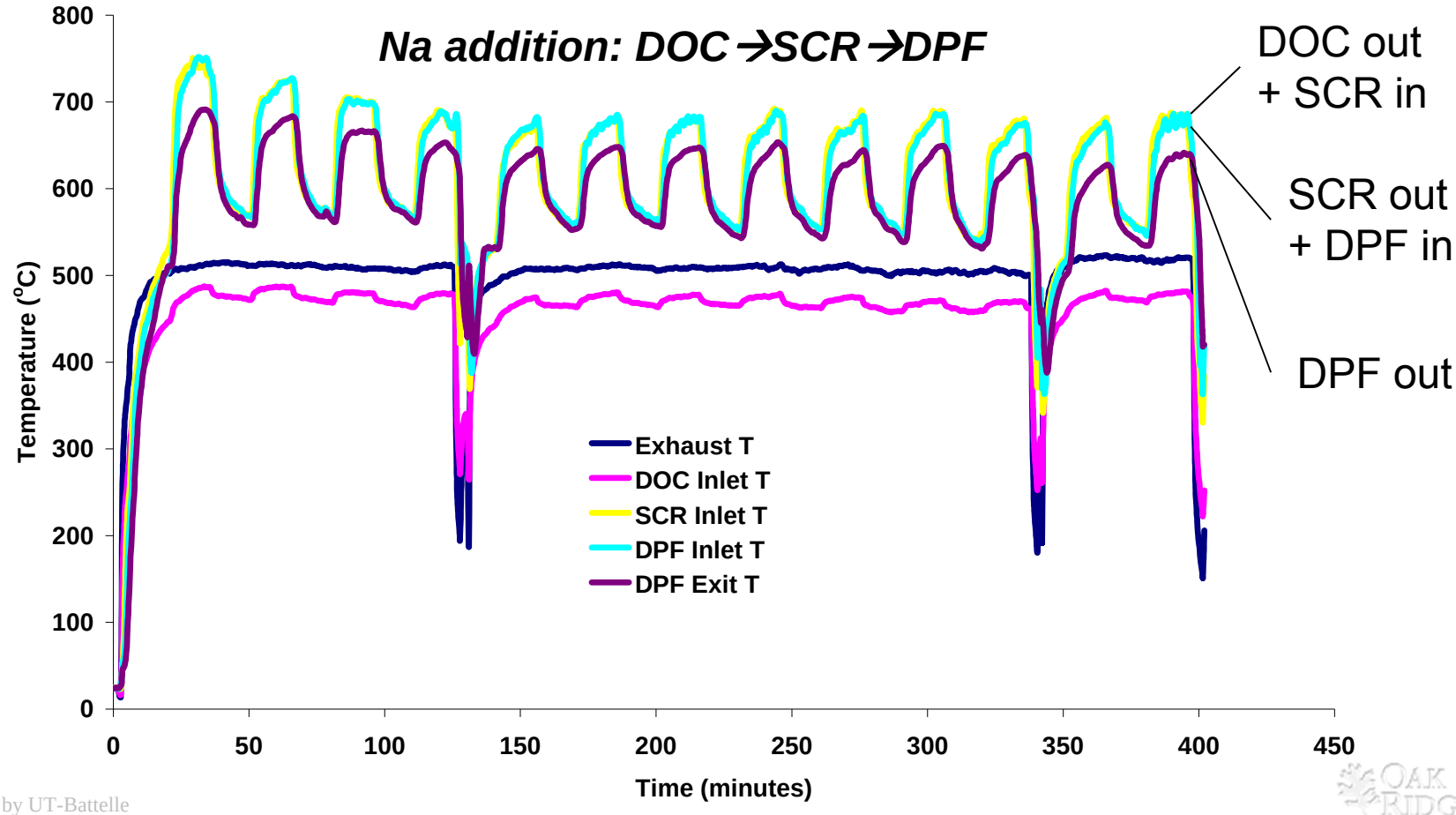
Temperature profiles during accelerated engine-aging: DOC→SCR→DPF (light duty)

- **Exotherm generated over DOC (inlet 450-490°C; outlet 650-680°C)**
- **SCR temperature decrease from inlet to outlet**
  - **Inlet: average 650°C, maximum 690°C; Outlet: average 600°C**
- **DPF temperature decreases from inlet (average 580°C) to outlet (average 580°C)**



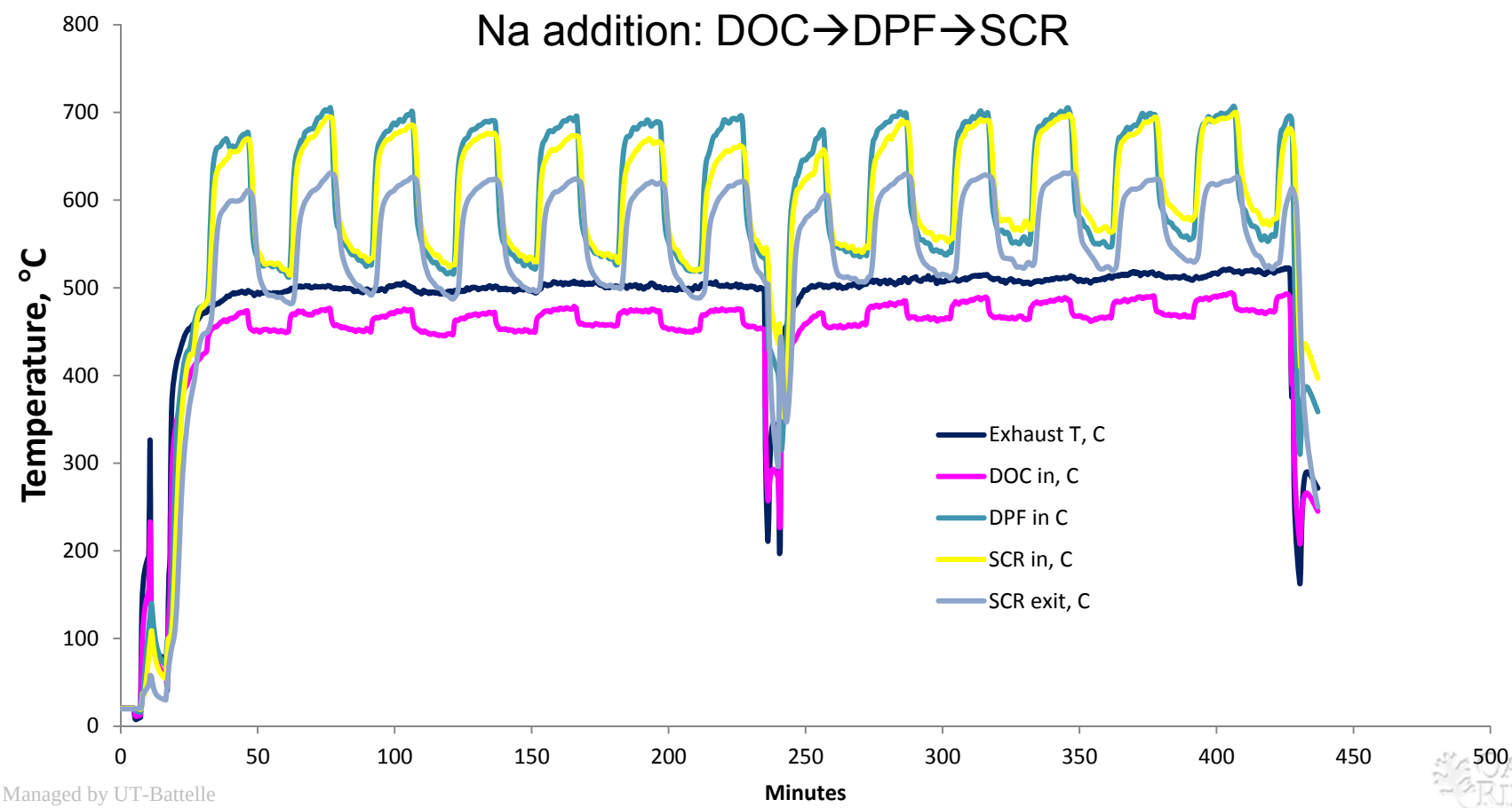
Temperature profiles during accelerated engine-aging: DOC→SCR→DPF (light duty)

- **Exotherm generated over DOC (inlet 450-480°C; outlet 670-740°C)**
- **SCR inlet and outlet approximately equal (average 670°C, maximum 740°C)**
- **DPF temperature decreases from inlet (average 670°C) to outlet (average 640°C)**



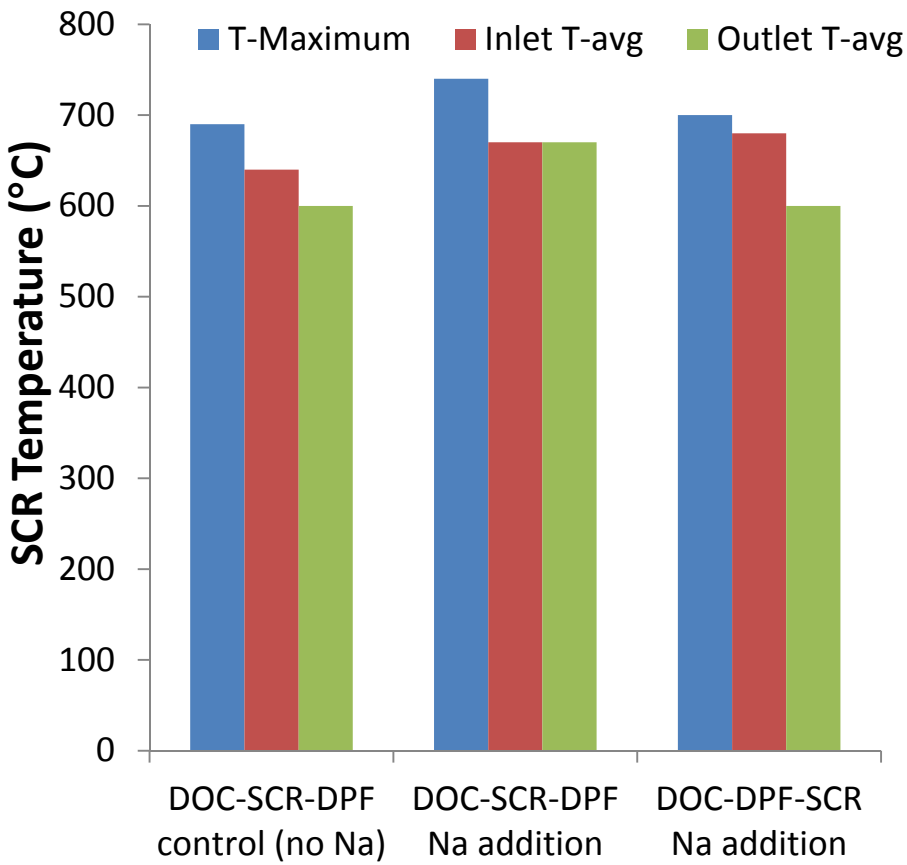
Temperature profiles during accelerated engine-aging: DOC→DPF→SCR (heavy duty)

- **Exotherm generated over DOC (inlet 450-480°C; outlet 650-700°C)**
- **DPF inlet and outlet approximately equal (average 680°C, maximum 700°C)**
- **SCR temperature decreases from inlet (average 680°C) to outlet (average 600°C)**

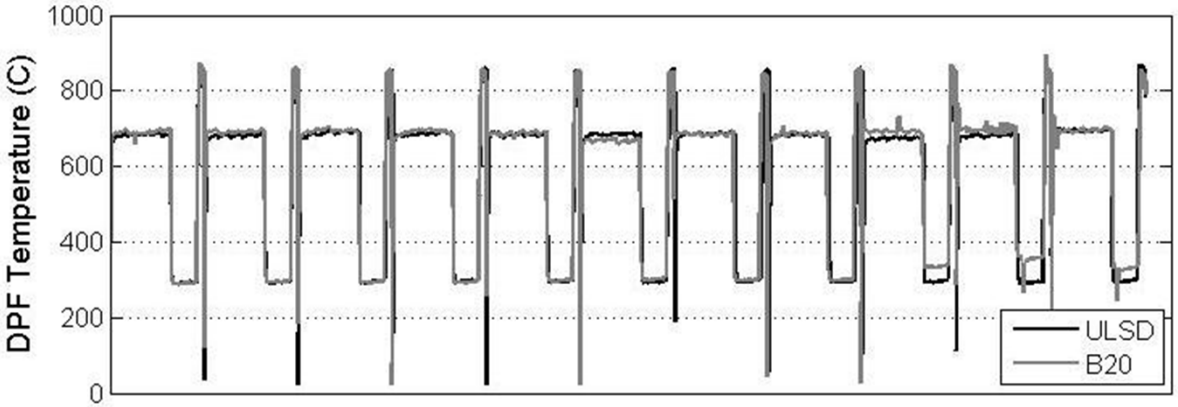


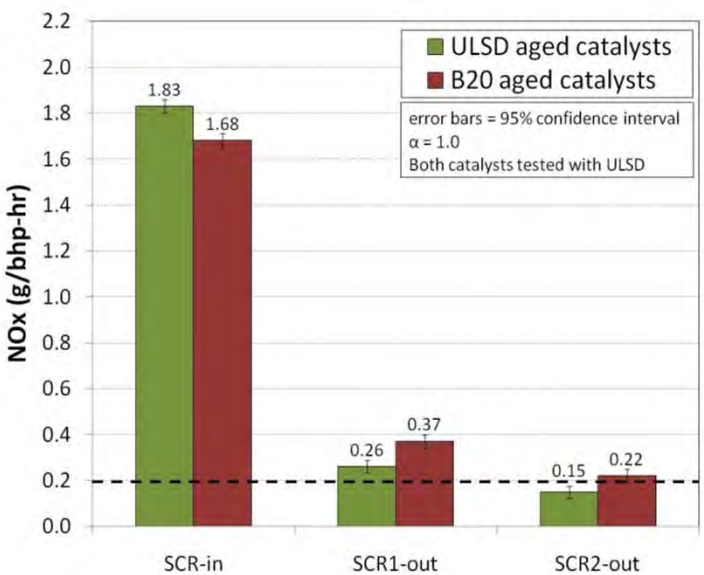
SCR Temperatures during aging

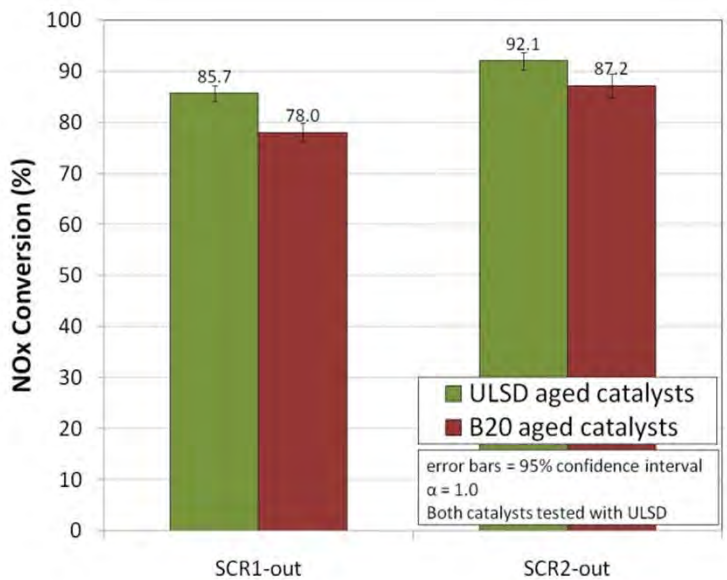
- **Without Na addition DOC→SCR→DPF (light duty - control)**
  - **SCR temperature decreases from inlet to outlet**
  - **$T_{maximum}$ = 690°C**
- **Na addition DOC→SCR→DPF (light duty)**
  - **SCR inlet and outlet equal**
  - **$T_{maximum}$ = 740°C**
- **Na addition DOC→DPF→SCR (heavy duty)**
  - **SCR temperature decreases from inlet to outlet**
  - **$T_{maximum}$ = 700°C**



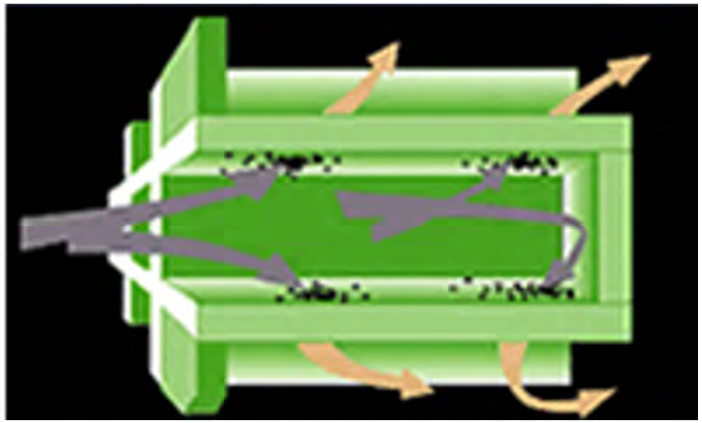
NREL


DPF Temperature (C)
1000
800
600
400
200
0
ULSD
B20


NOx (g/bhp-hr)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
ULSD aged catalysts
B20 aged catalysts
error bars = 95% confidence interval
α = 1.0
Both catalysts tested with ULSD
1.83
1.68
0.26
0.37
0.15
0.22
SCR-in
SCR1-out
SCR2-out

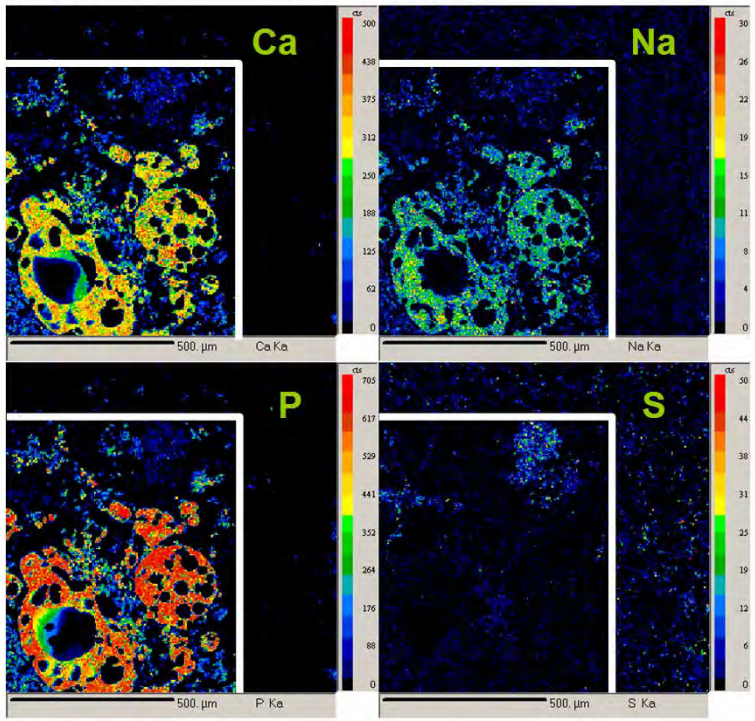

NOx Conversion (%)
100
90
80
70
60
50
40
30
20
10
0
85.7
78.0
92.1
87.2
ULSD aged catalysts
B20 aged catalysts
error bars = 95% confidence interval
α = 1.0
Both catalysts tested with ULSD
SCR1-out
SCR2-out

DPF



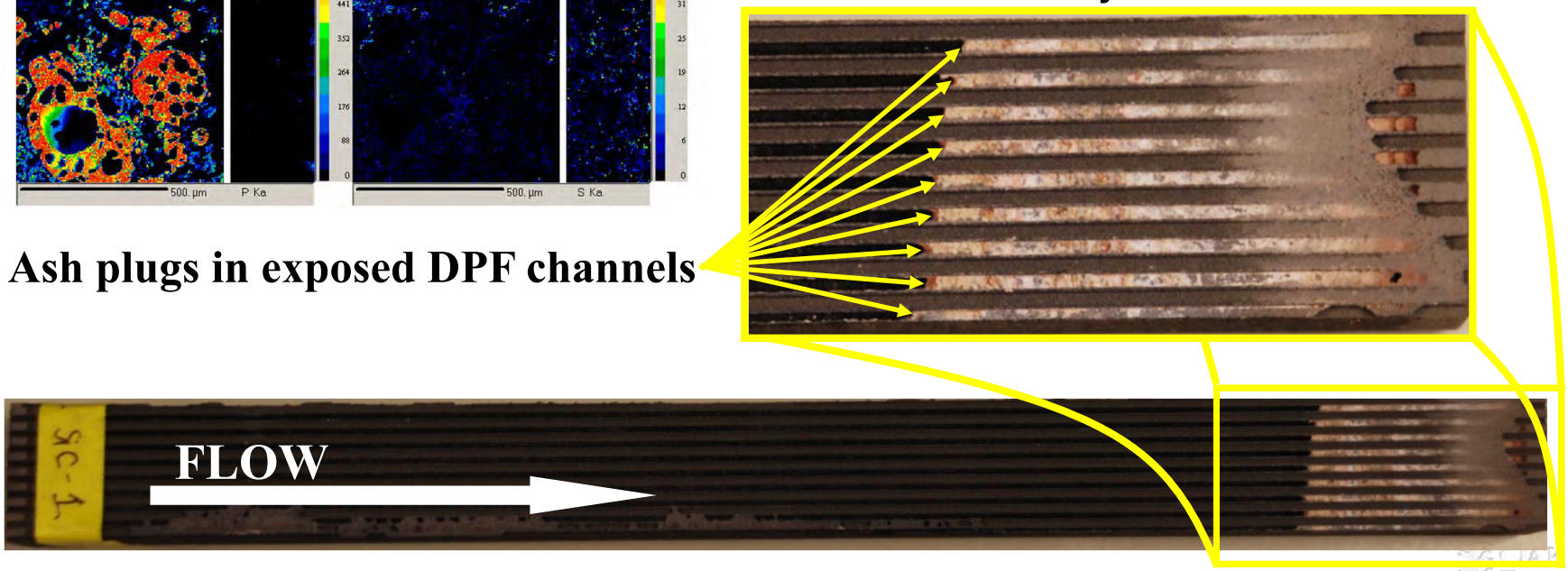
Ash in GM-aged DPFs – 20:1 for Ca:Na

EPMA of ash plugs in DPF



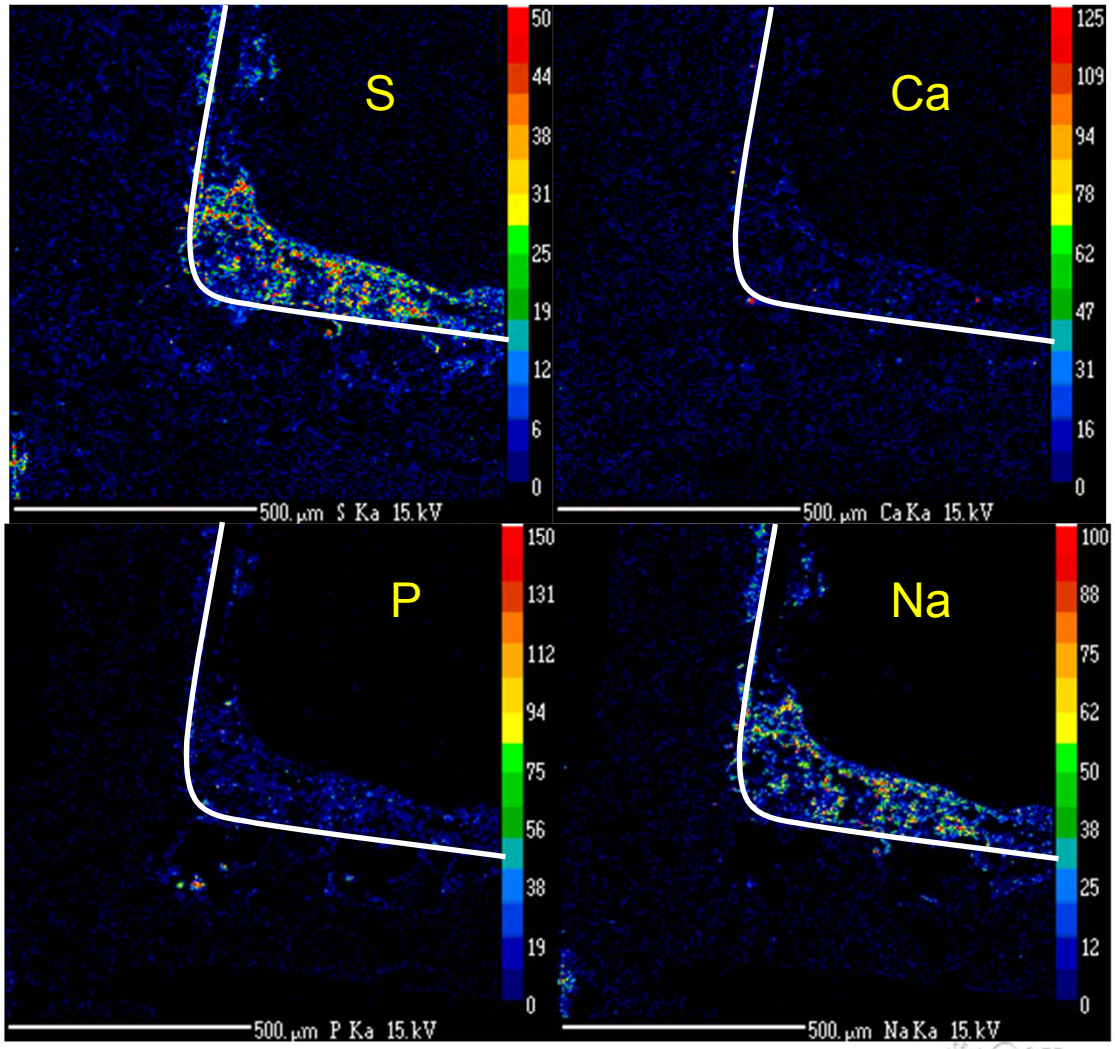
- Ash plugs apparent in rear of DPF
- 20x more Ca than Na detected in ash
  - Ca associated with standard lube oil
- Na not detected in wall of SiC DPF
- For GM-DPF major ash contribution is from oil consumption
  - Unknown Na level in fuel makes further conclusions difficult
  - Could be very low Na level in fuel

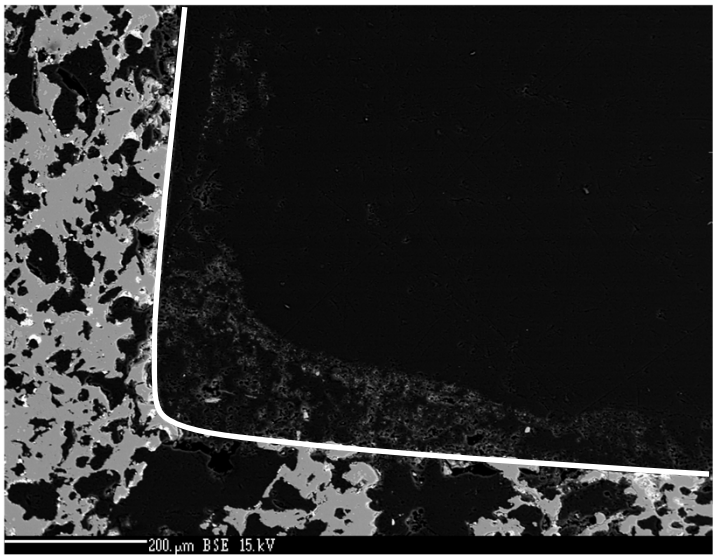
Ash plugs in exposed DPF channels



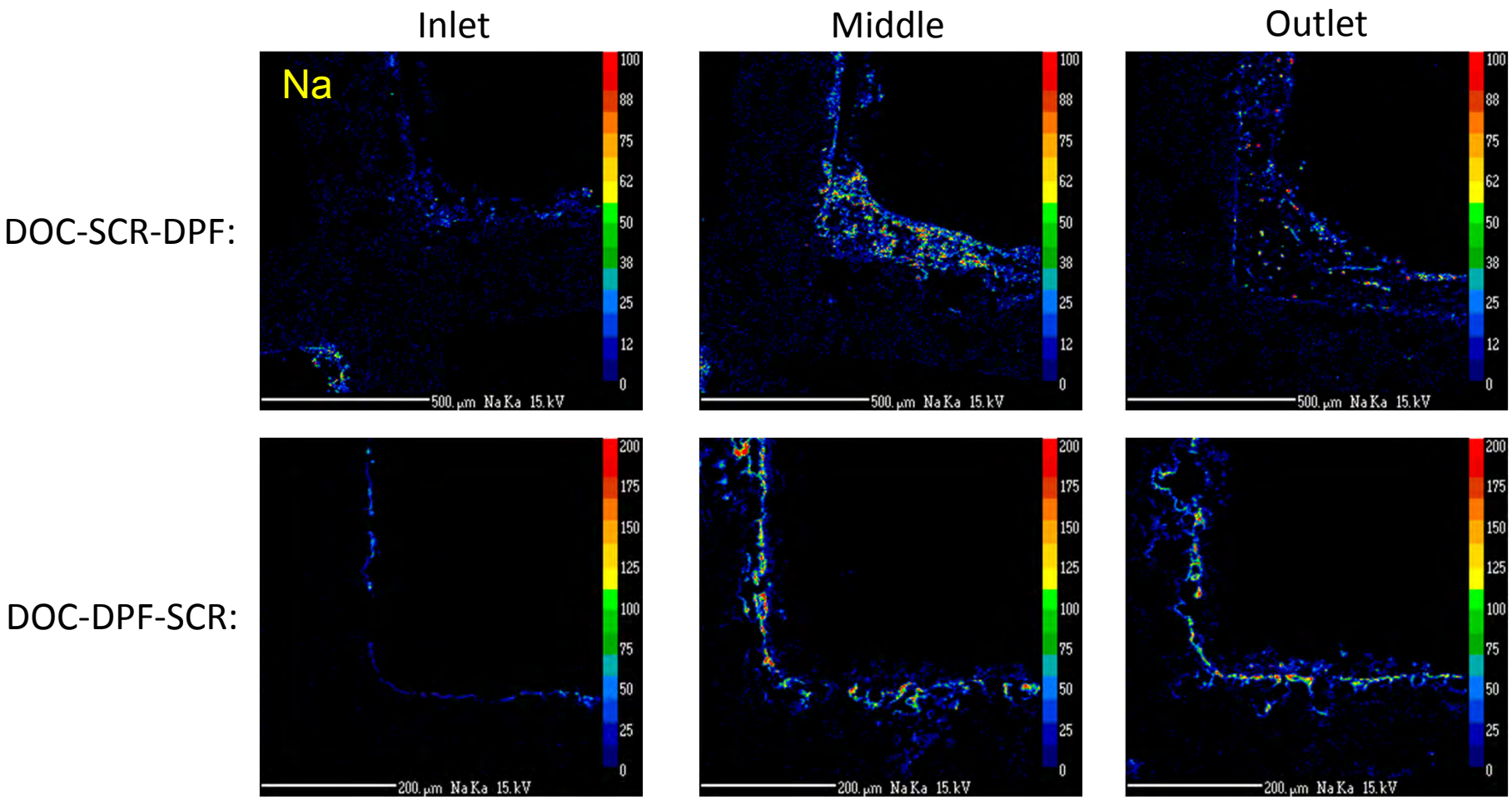
Na is primary ash component in accelerated study; no wall penetration

- **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_{avg}=650°C**





Na in Accelerated Na-Aged DPFs

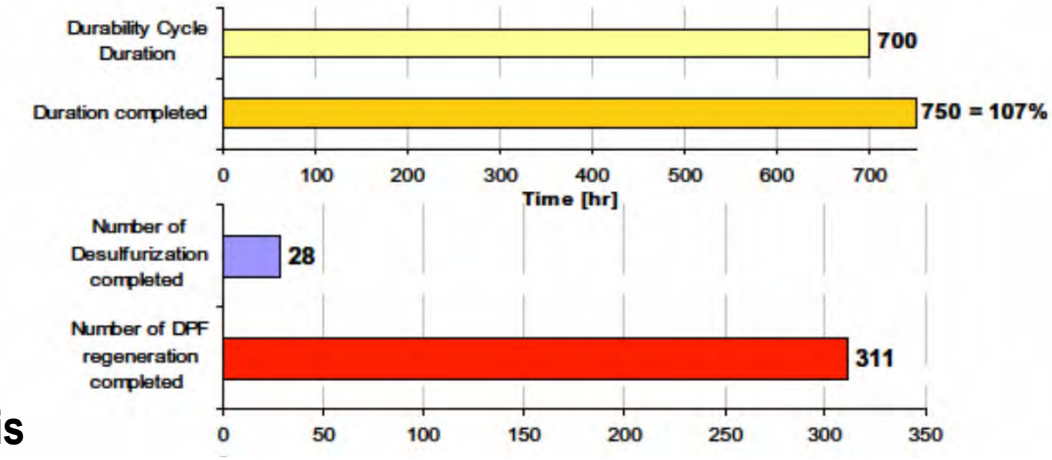


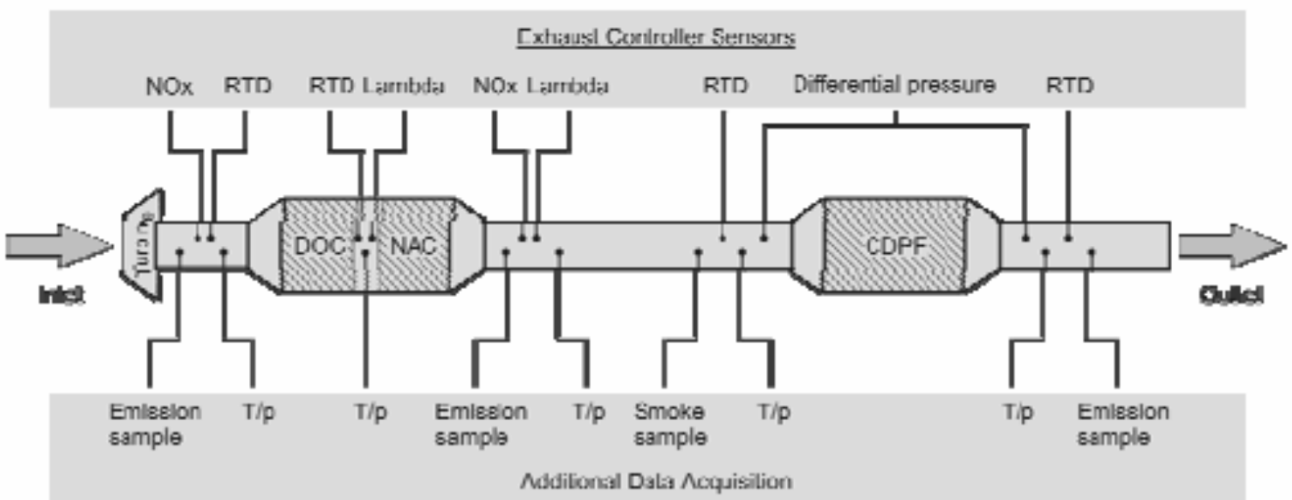
- **In DOC-DPF-SCR configuration, level of Na contamination is doubled and penetrates into substrate**
- **Penetration into DPF substrate observed; max temperature recorded =**

LNT

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 <u>LNTs</u> provided to ORNL for analysis**
- **Final state was before desulfation**

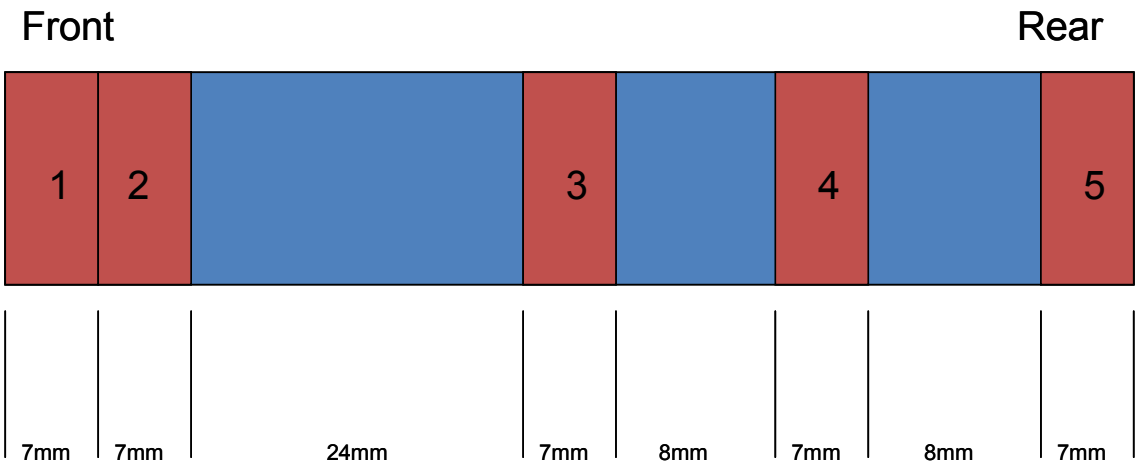


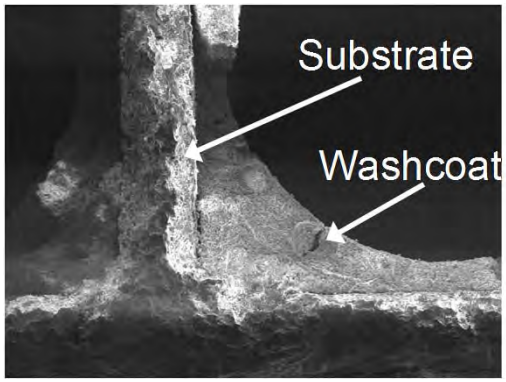


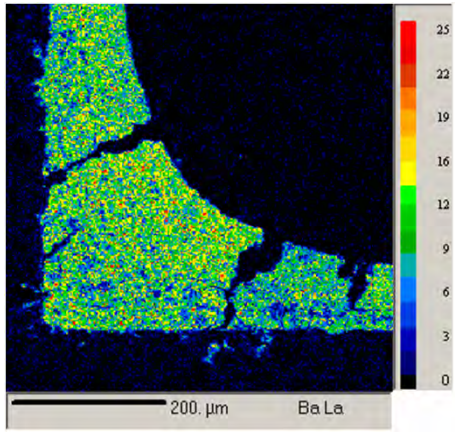
NREL References: SAE 2008-01-0080, SAE 2009-01-0281 & SAE 2009-01-1790

EPMA Study of LNT-1

- **Five samples obtained from front field-aged LNT**
  - **Dual LNT system; Rear LNT not analyzed**
- **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**

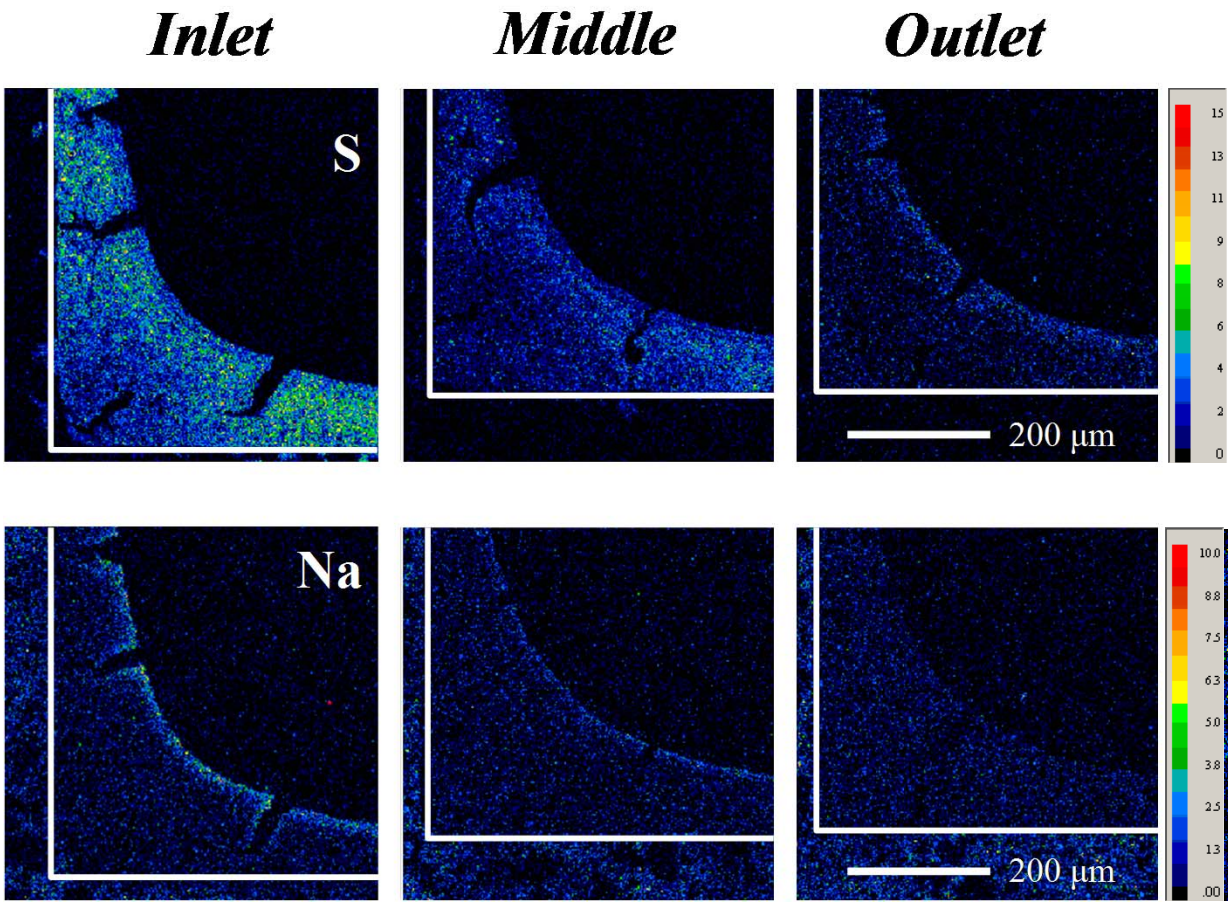


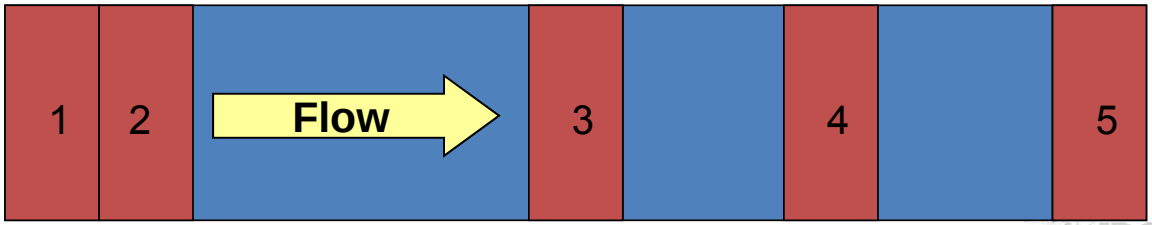




Cross-Sectional EPMA of LNT-1

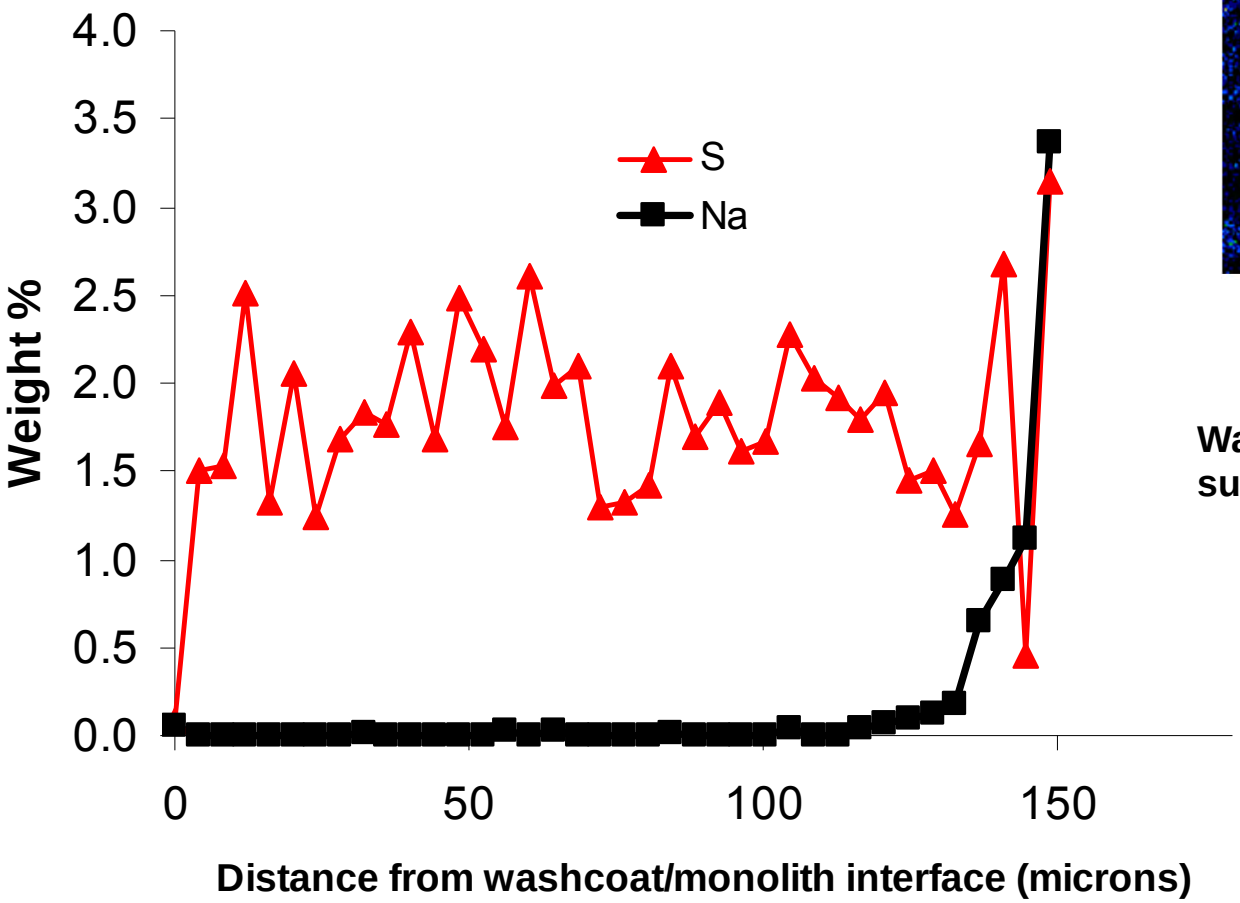
- Five samples obtained from front NREL-aged LNT
  - Dual LNT system
  - Rear LNT not analyzed
- Na, S, Ba, and K EPMA micrographs were obtained from each sample
- Sulfur content is highest in first 10mm of front section
- Na layer on washcoat surface diminishes front to rear
  - Top 30 microns has up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

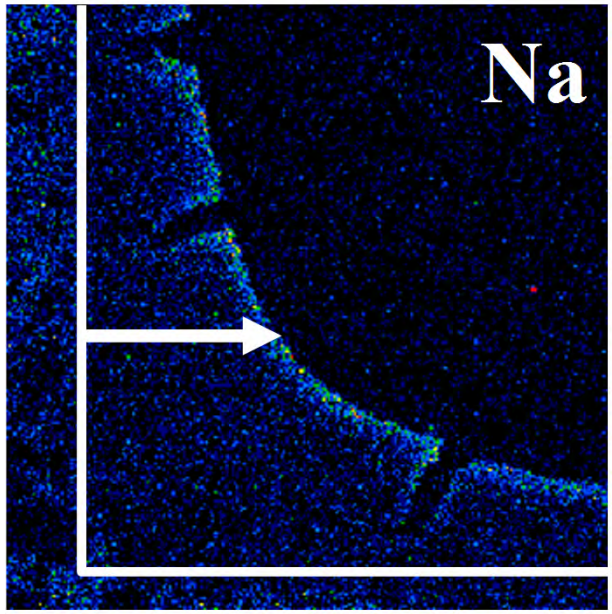




LNT-1 EPMA Line Scan

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

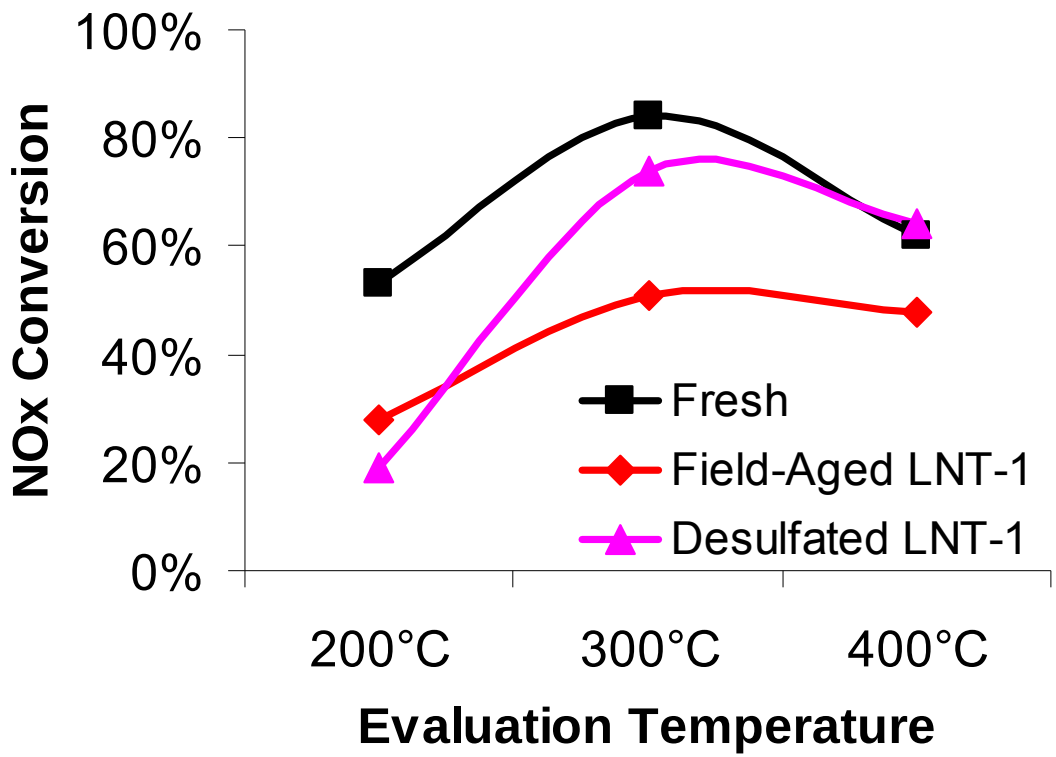




Washcoat surface

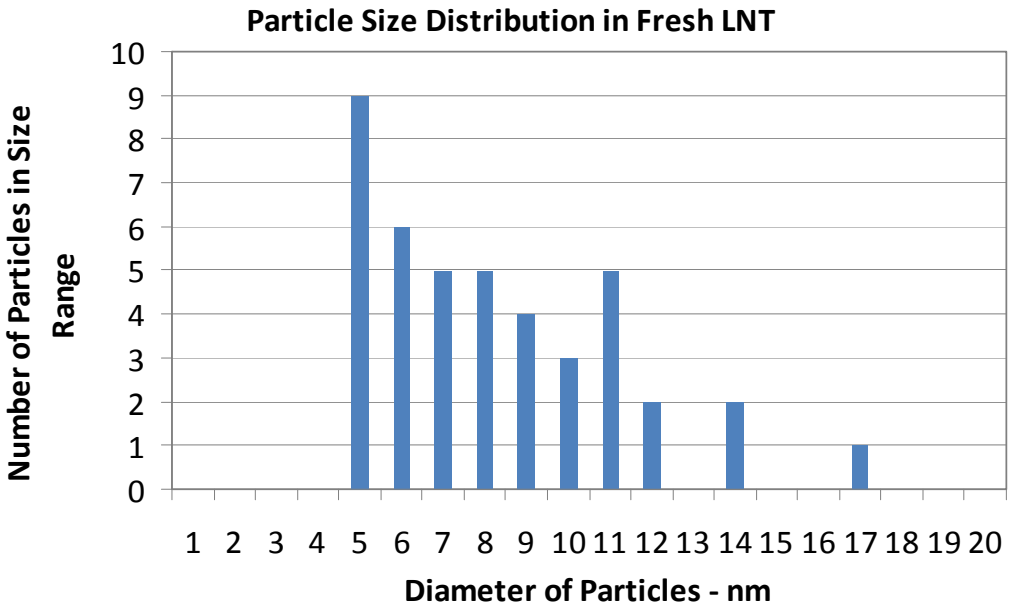
LNT performance primarily affected by S

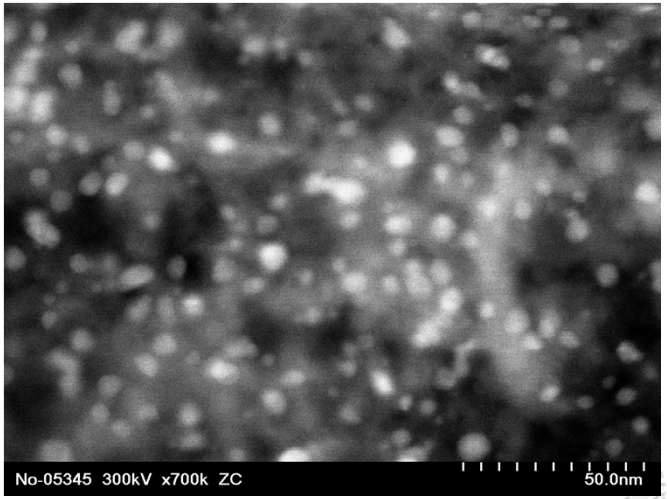
- **Sulfur primary deactivation mechanism**
- **Performance recovered at 400°C after bench desulfation (at 700°C)**
- **Materials characterization suggests thermal effects impact performance at 200 and 300°C**
  - **i.e., B20 is not suspected to impact LNT**
  - **Not surprising, Na will adsorb NOx**



Fresh LNT

- **Average particle size in fresh LNT samples is 9 nm**
- **In fresh sample, Pt appears in large clusters containing numerous particles**

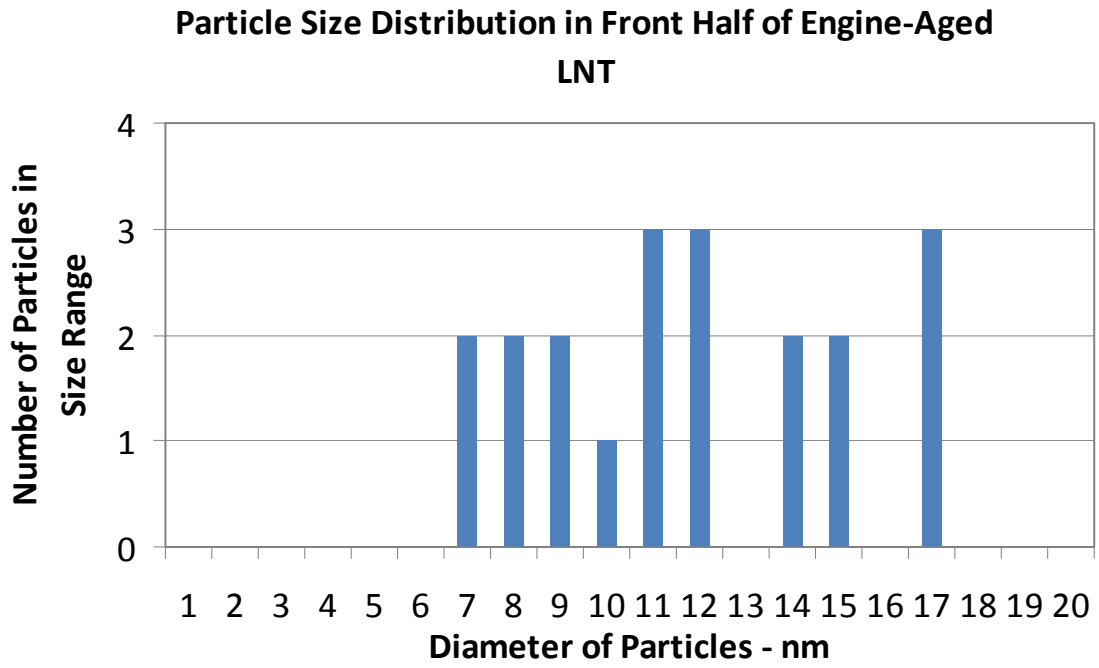


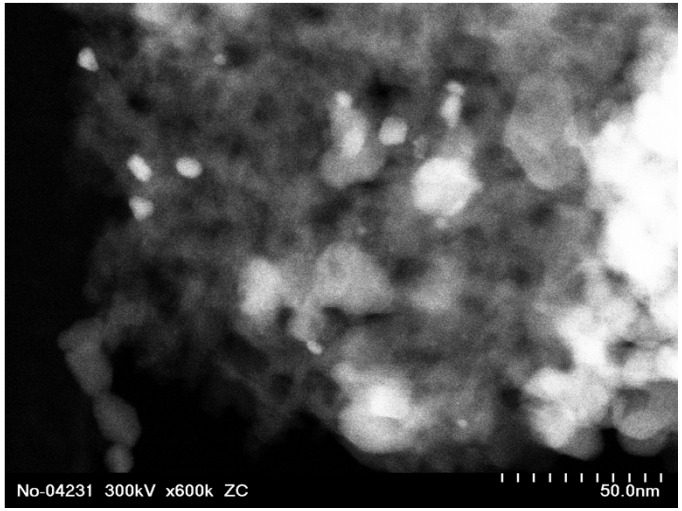


Fresh LNT TEM Image

Engine-Aged LNT: Front

- **Average particle size in engine-aged front LNT samples is 11.65 nm**
- **PGM sintering apparent as reduction in number of small particles and increase in average size**

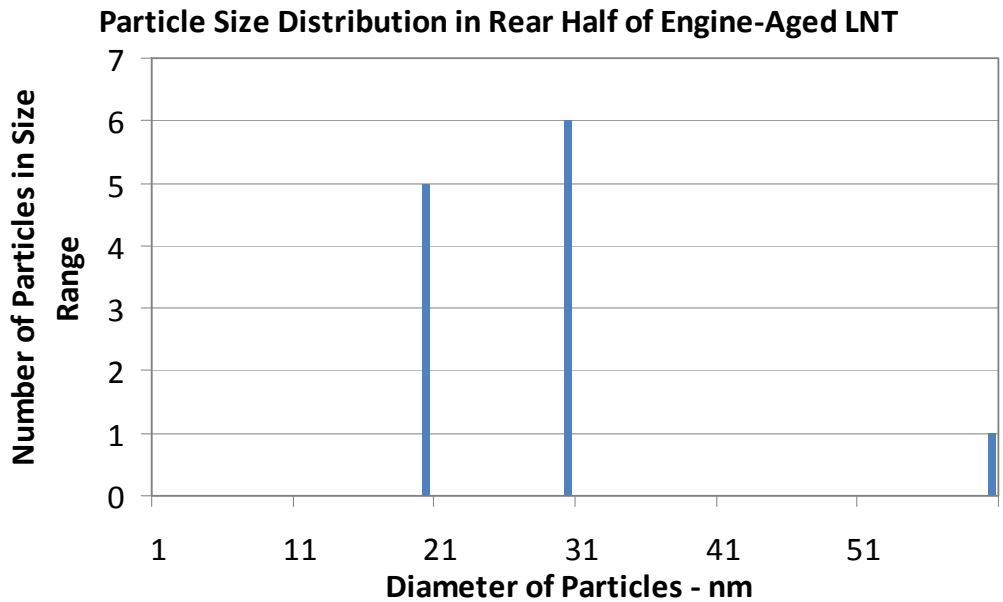


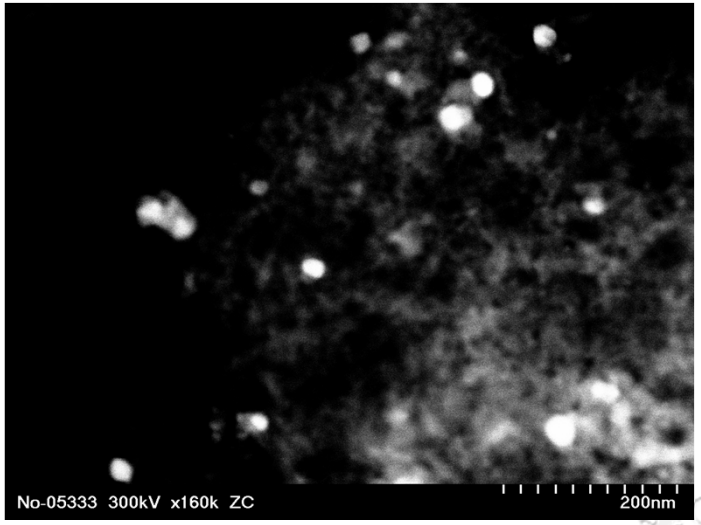


Engine-Aged LNT Front TEM Image

Engine-Aged LNT: Rear

- **Average particle size in rear of engine-aged LNT samples is 34.66 nm**
- **Extremely large Pt particles present at rear of engine-aged LNT indicate severe PGM sintering**





Engine-Aged LNT Rear TEM Image