# Impact of Biodiesel-Based Na on the Selective Catalytic Reduction (SCR) of $NO_x$ Using Cu-zeolite

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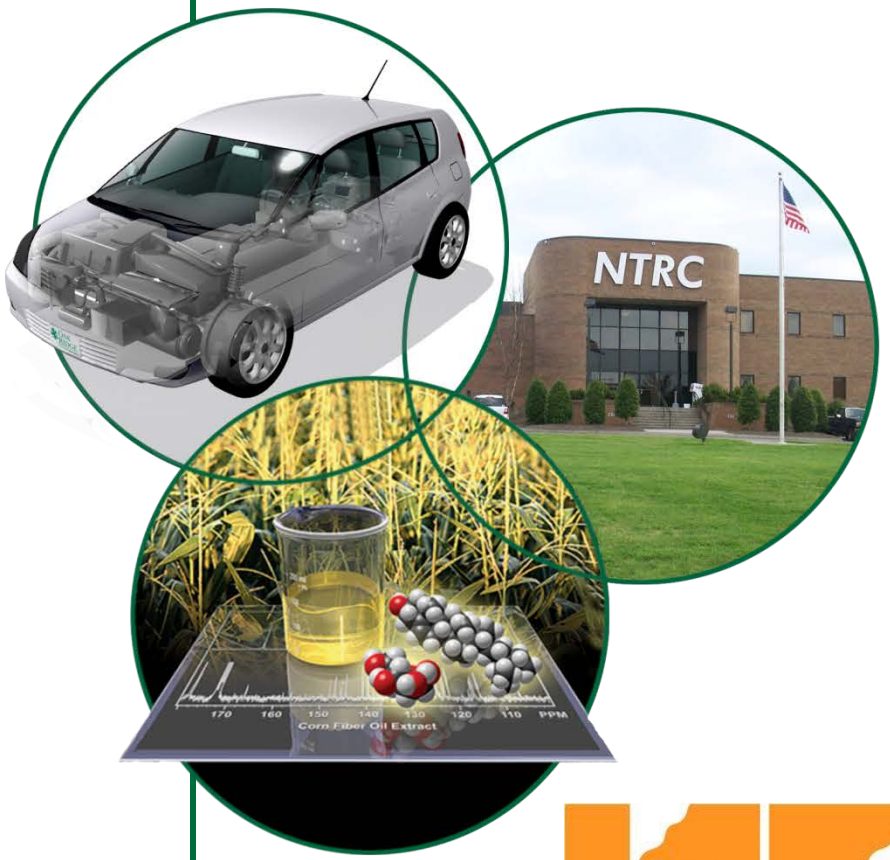


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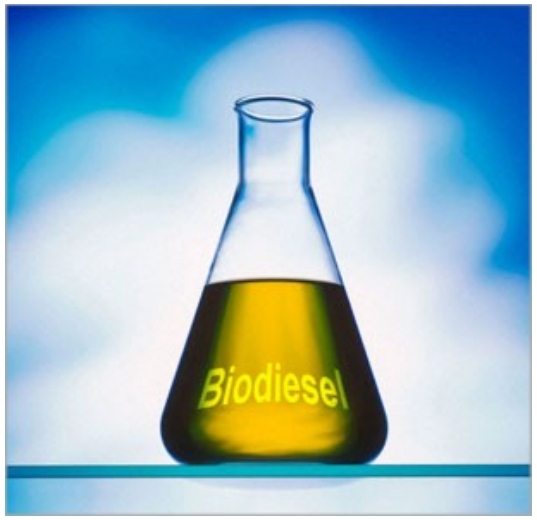
# Motivation to introduce higher levels of biodiesel tempered by the unknown

- Biodiesel: alkyl ester combusts similar to diesel fuel

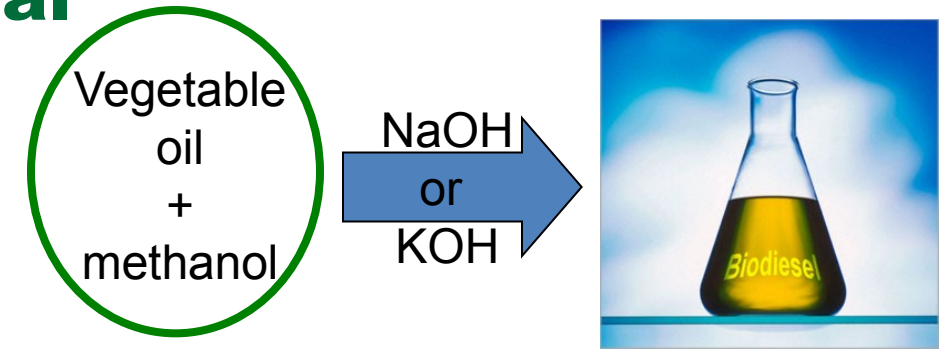
- Domestic renewable energy source synthesized from vegetable oil or animal fat
  - Vegetable: Soybean (~90%), rapeseed, field pennycress, jatropha, etc.
  - Animal sources: Only waste or by-products being converted at this time
  - Currently focus is on waste/excess oil

- Barrier to implementation is the unknowns associated with a new fuel
  - Combusts like diesel, but unknown impact on emissions control devices
  - Trace elements are primary cause of concern in emissions control…particularly Na and K




# Concerns associated with Na and K are mechanical and chemical

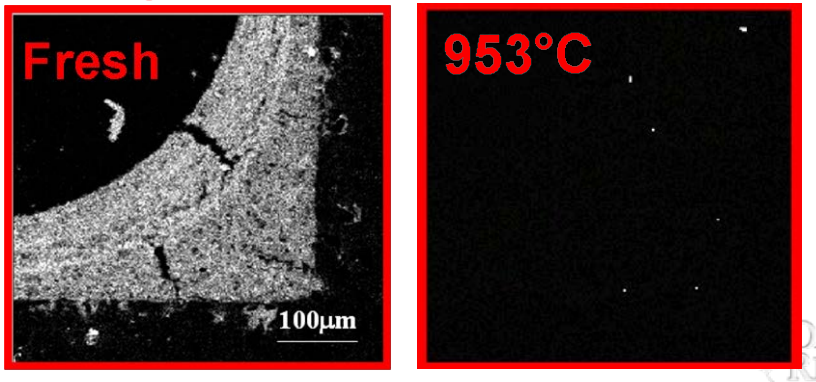
- NaOH or KOH is a liquid-phase catalyst used in biodiesel synthesis
  - NaOH and KOH difficult to separate completely from products
  - Specification set at 5 ppm Na+K in B100




- Potential Na/K emissions control effects
  - Ash accumulation in DPF
  - Alkali absorption into monolith walls
    - possible weakening of monolith
  - Catalyst poisoning/fouling
    - Na-exchanged zeolite is commercial catalyst

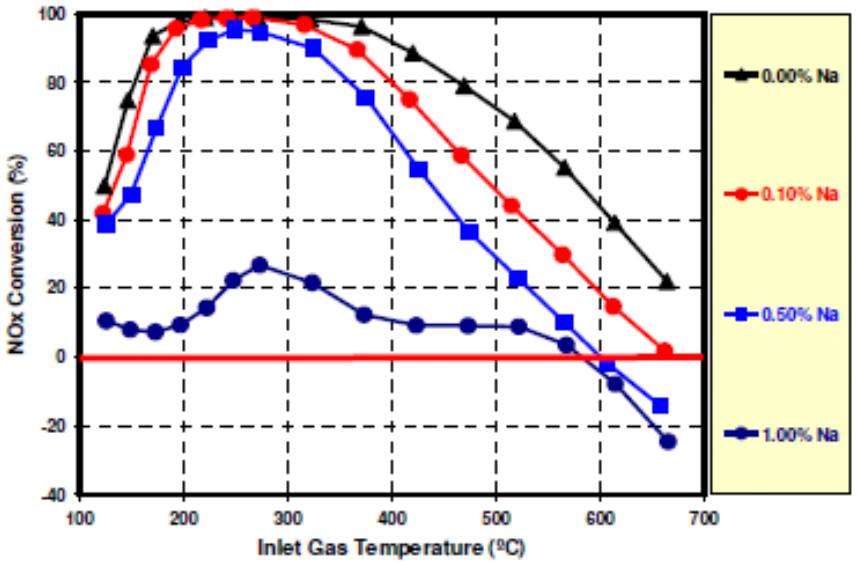
Increased ash accumulation

Migration into cordierite

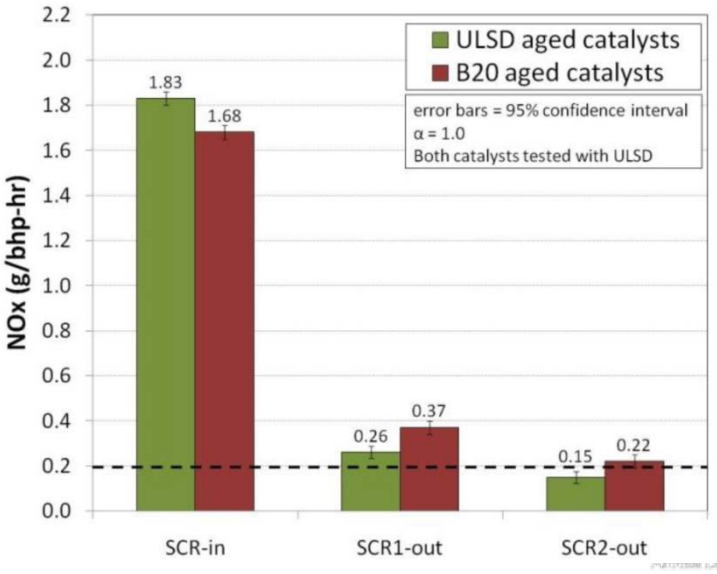


# Recent research illustrates potential Na impact on SCR and DPF cordierite walls

- Cavataio et al. (SAE 2009-01-2823)
- Aqueous addition of Na to SCR and DOC using incipient wetness technique
  - Investigated Na and K
  - Multiple DOC and SCR formulations
- Dramatic deactivation observed
- Na and K accelerated zeolite structure collapse

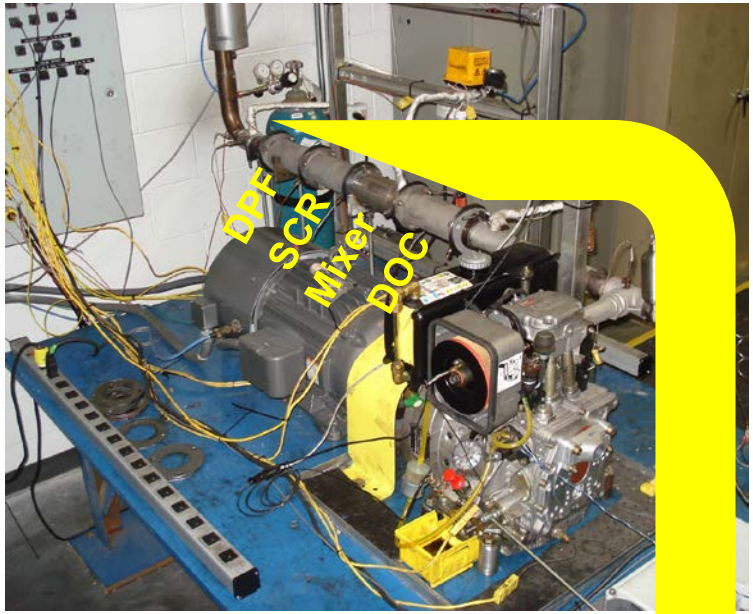



- Williams et al. (SAE 2011-01-1136)
- Accelerated full-size engine approach
  - DOC→DPF→SCR approach
  - Both Na and K added to fuel
  - 150k and 435k mile equivalent
- Na+K penetrate wall of DPF
- Small but significant decrease in NOx performance



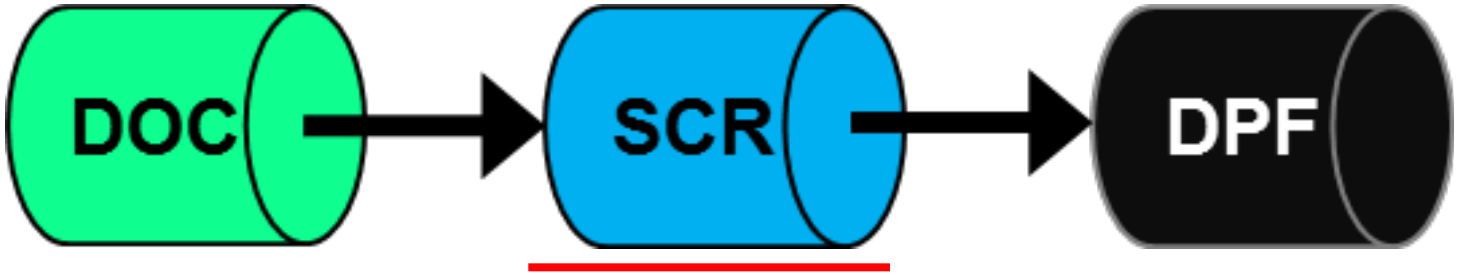
# Accelerated aging targets Na-impact

- Introduce high levels of Na to B20
- Two configurations evaluated
  - DOC→**SCR**→DPF
    - "light duty" configuration
    - with and without Na (control)
  - DOC→DPF→**SCR**
    - "heavy duty" configuration




- Levels elevated to achieve 435,000 mile Na exposure
  - Dioctyl sulfo-succinate sodium salt with Na:S = 1
  - 5000+ ppm Na in B20
  - Periodic soot regeneration performed at 700°C
  - Measure performance in bench-core reactor
    - First 3" of catalysts studied
    - Employ portions of the CLEERS SCR protocol
    - SV = 30,000 $h^{-1}$, $NH_3$/NO = 0.8-1.0, $NO_2$:NO = 0 or 1

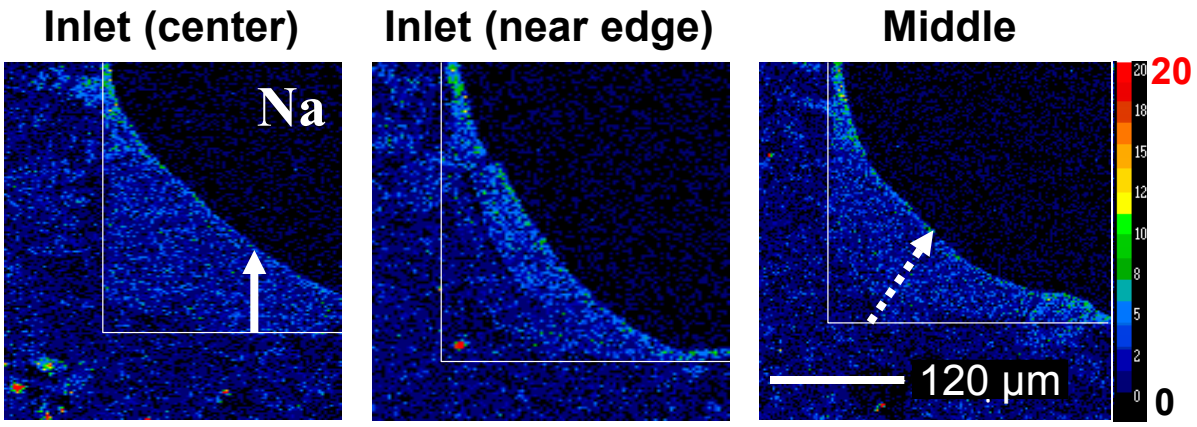
# DOC-SCR-DPF (LIGHT-DUTY) Na ACCELERATED-AGING



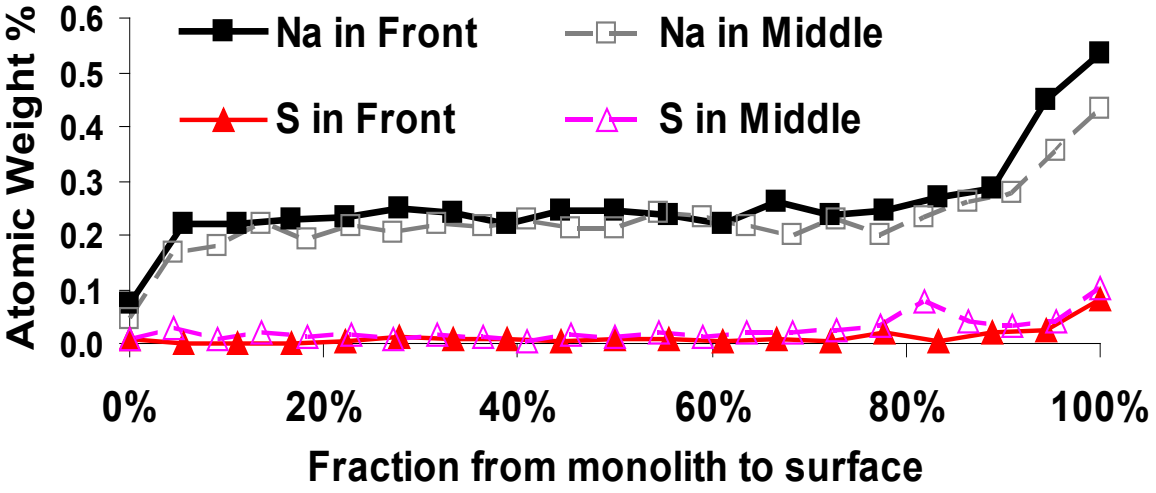
# Na observed after accelerated aging throughout SCR washcoat

- Na throughout washcoat
  - In bulk ~0.2%wt
- Elevated Na levels also observed at surface
  - 0.3-0.6%wt
- Concentration of Na axially uniform
- Low sulfur levels detected in SCR washcoat
  - Near detection limit
  - Increased level at surface ~0.1%wt
  - Na:S ≠ 1

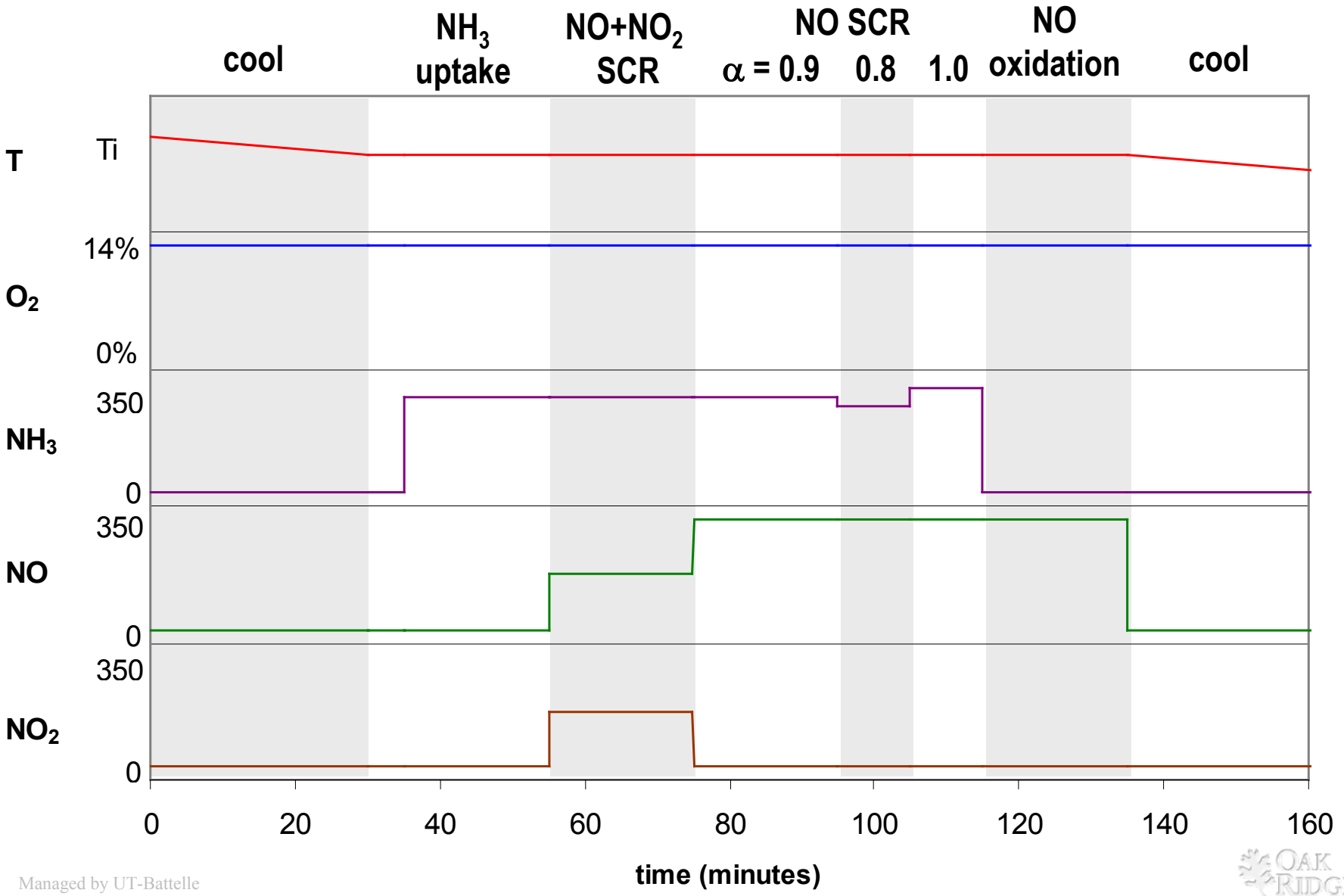
**Accelerated Na-Aged SCR (from DOC→SCR→DPF)**




**EPMA line scans**

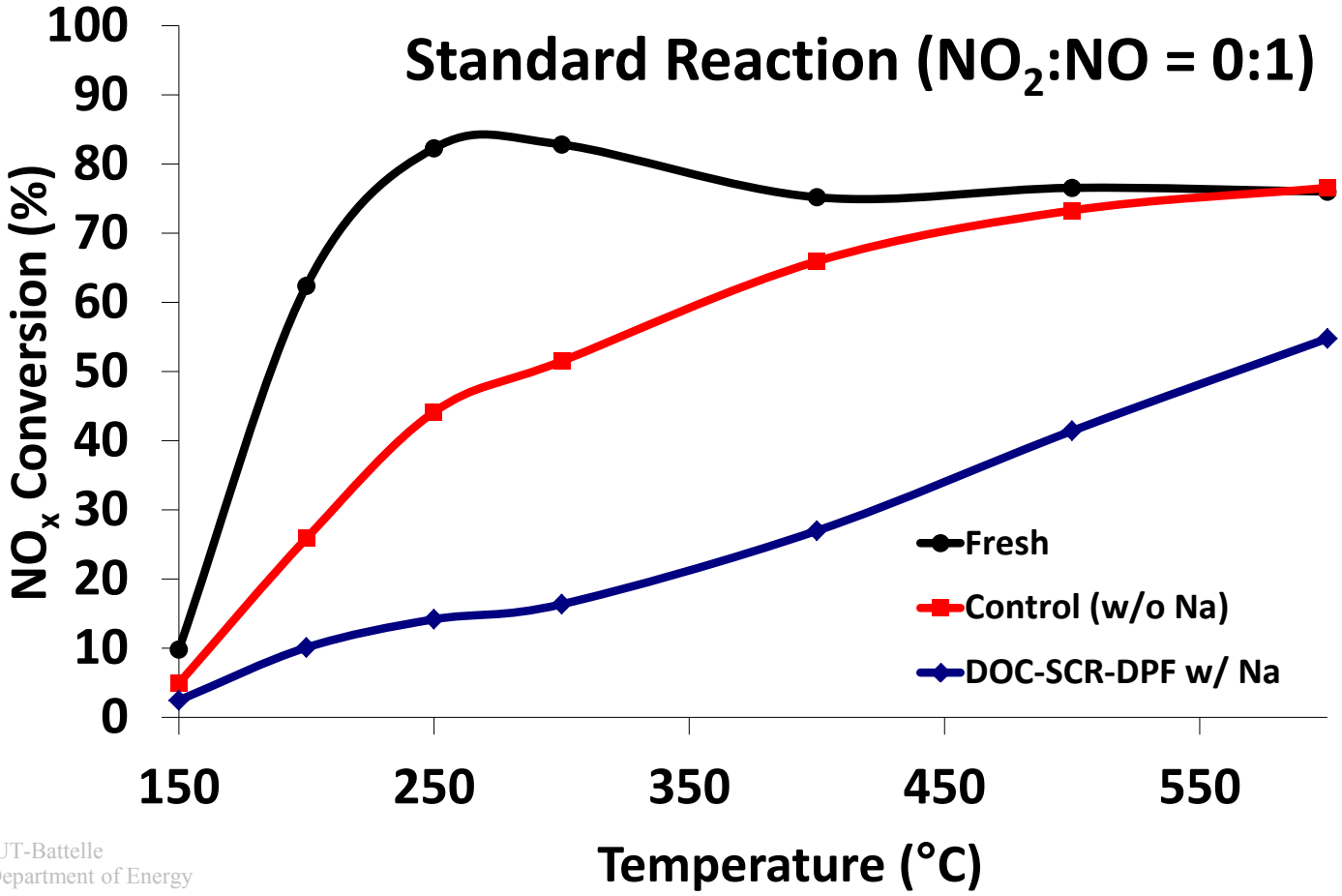


# A version of the CLEERS transient SCR protocol utilized to probe behavior



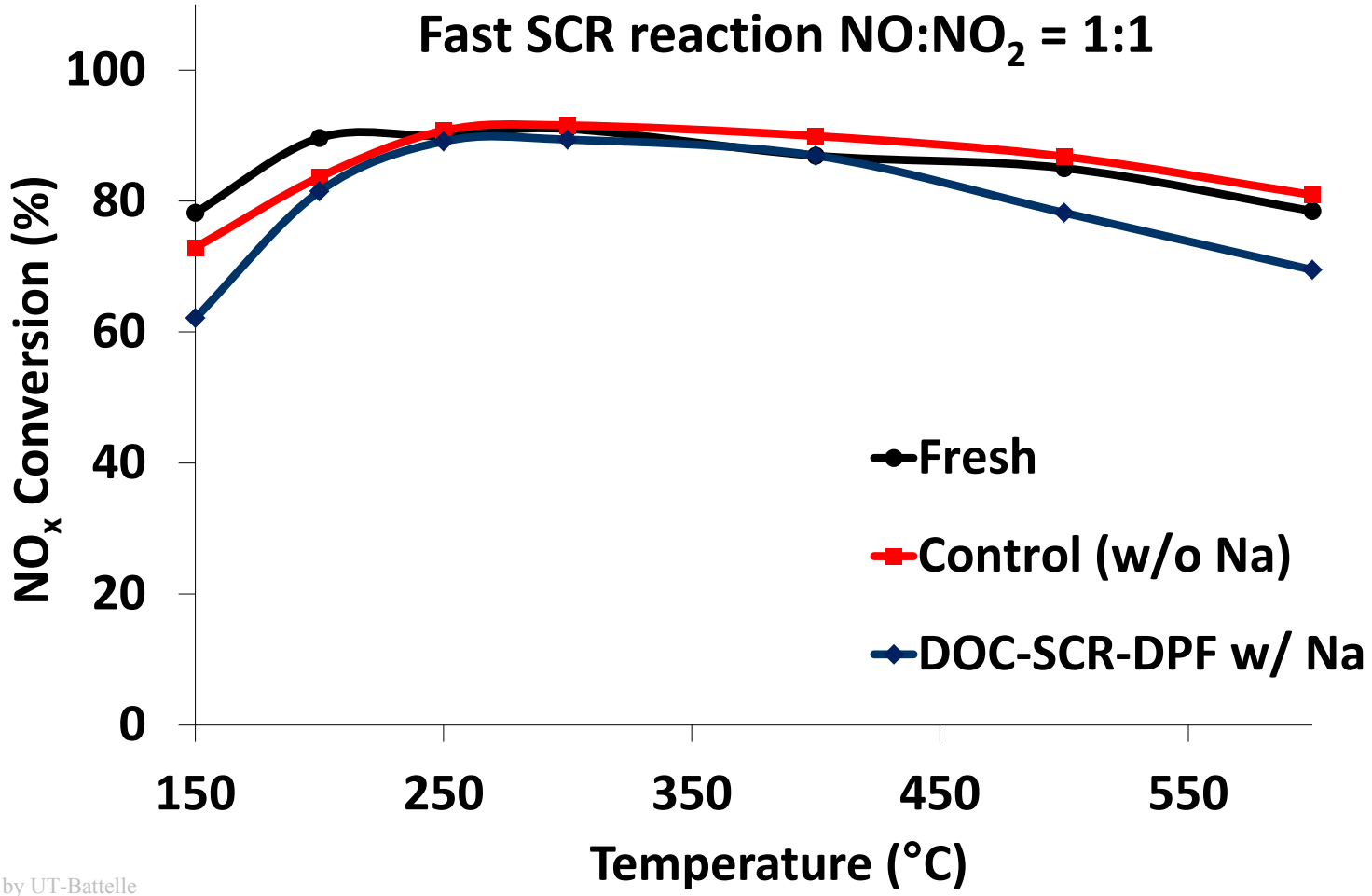
# Standard SCR reaction significantly inhibited with Na addition

- 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



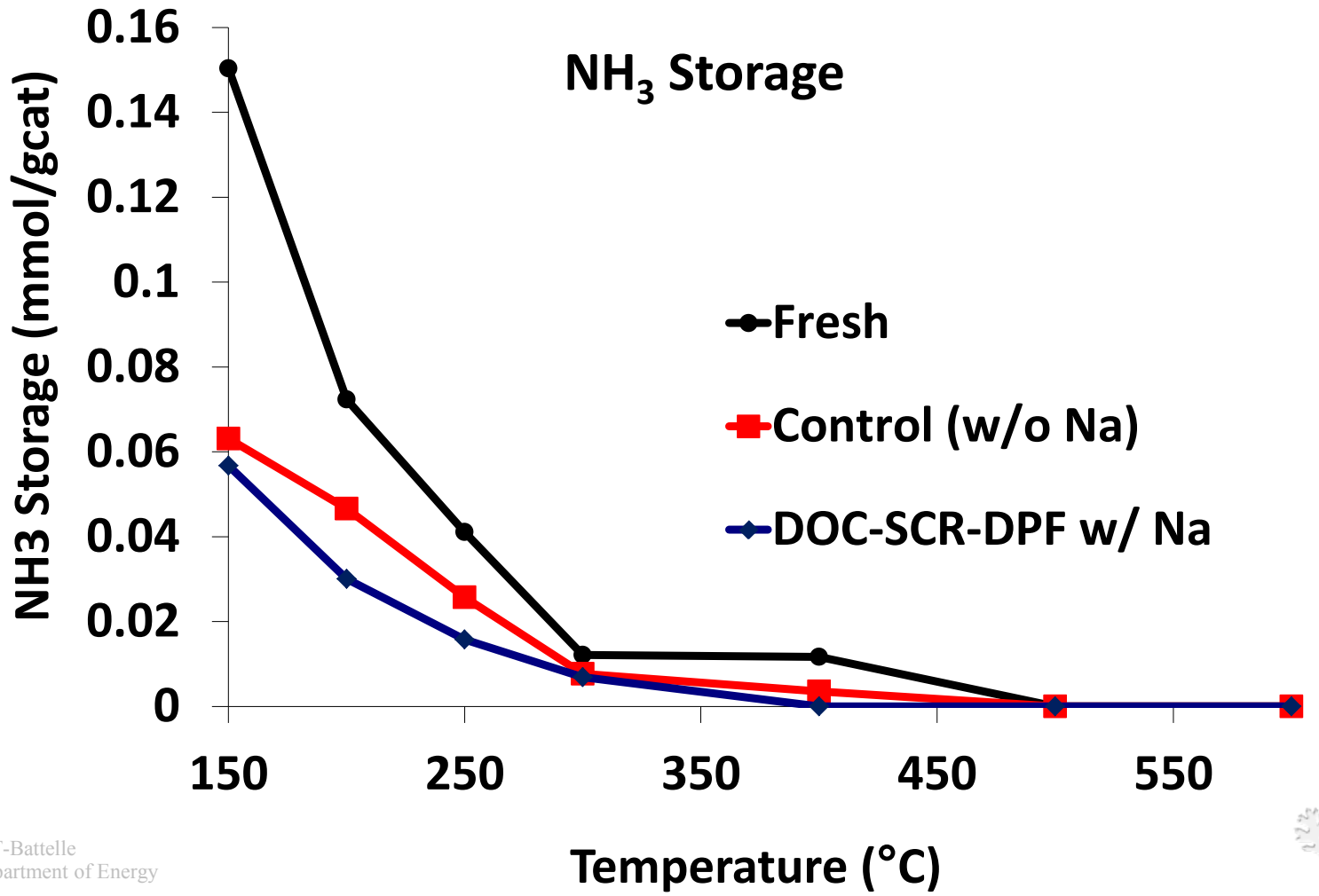
# Minimal impact when feeding equimolar $NO_2$:NO (fast SCR reaction)

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



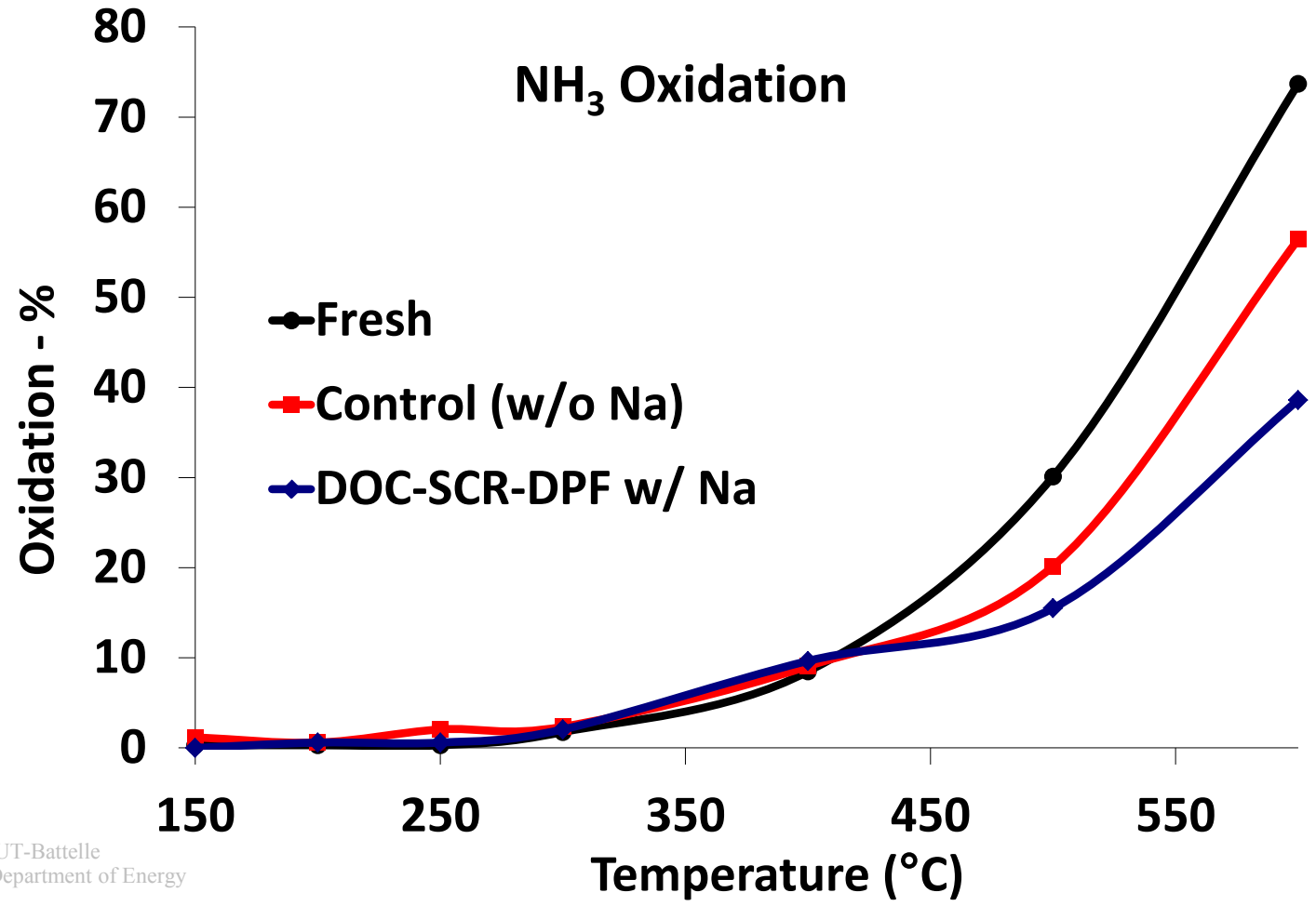
# $NH_3$ storage decreases with aging; control and Na-aged show similar impact

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



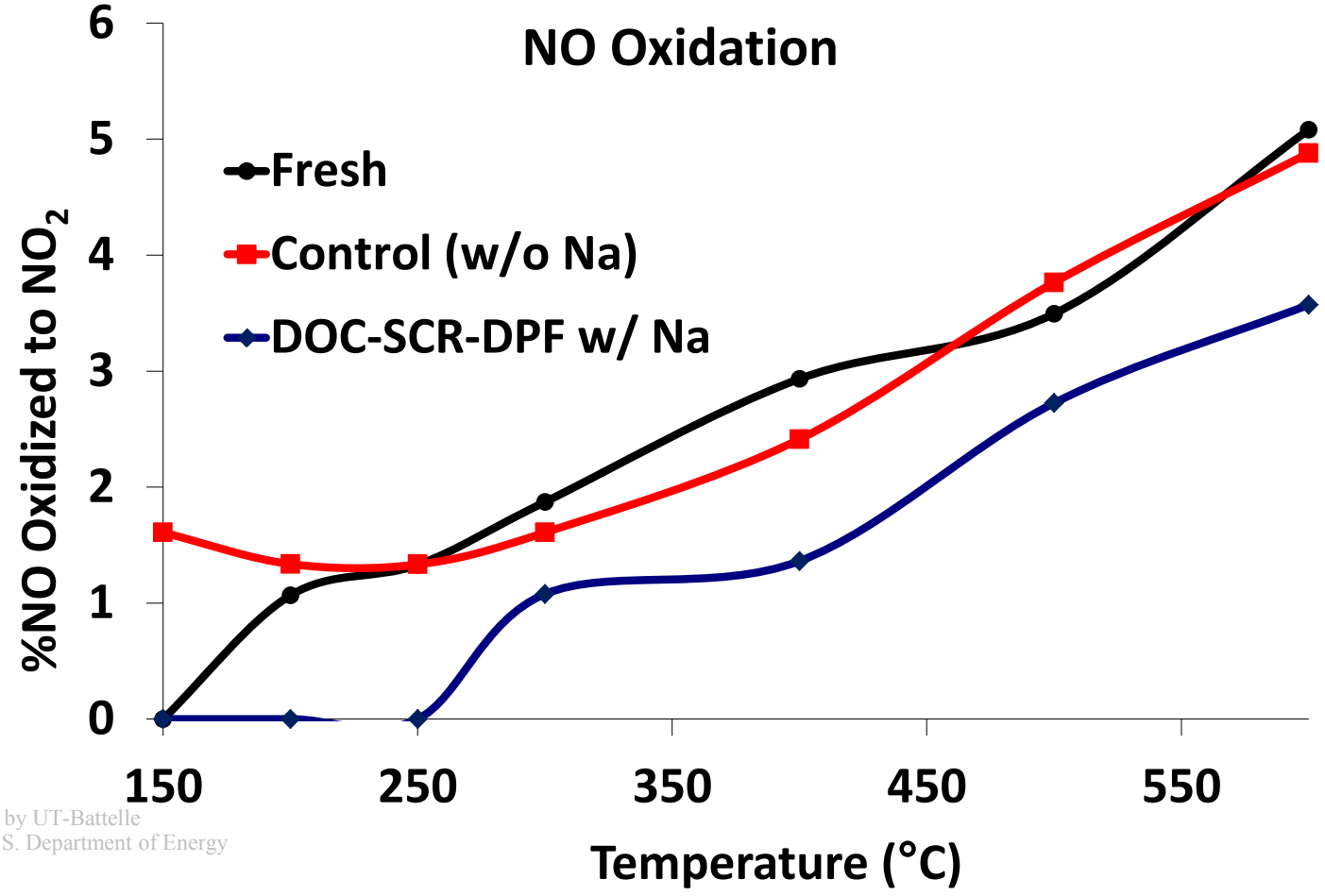
# $NH_3$ oxidation decreases with aging

- $NH_3$ 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



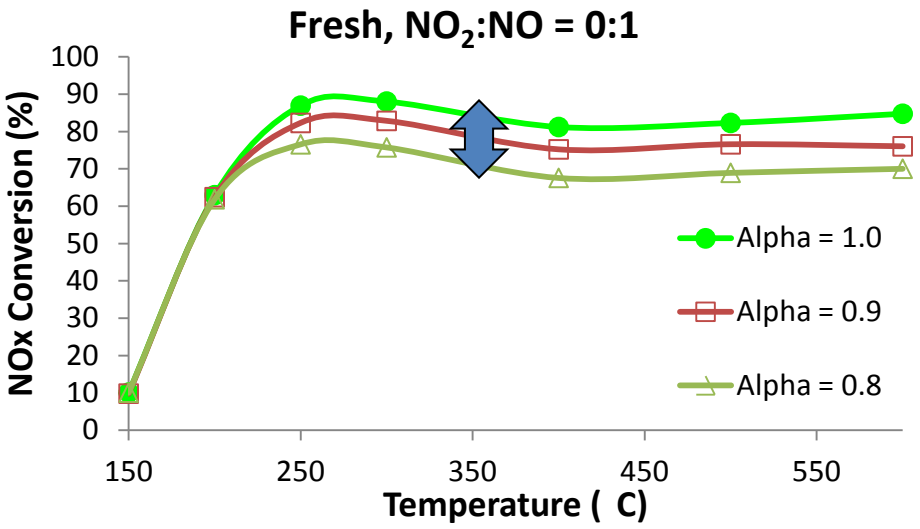
# Further evidence of Na impact on Cu-sites with decreased NO oxidation

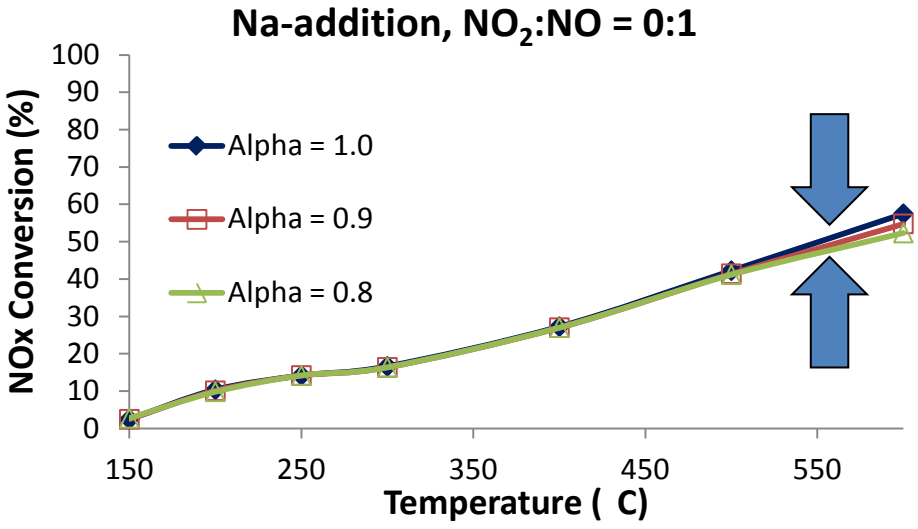
- Na-aged samples show less oxidation of NO to $NO_2$ over entire temperature range
- Fresh and control show similar, albeit low reactivity

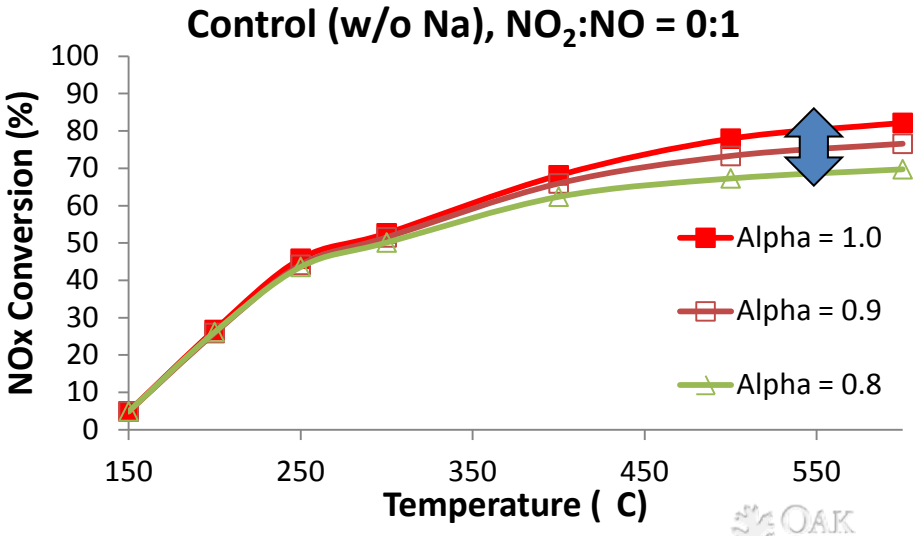


# Increasing $NH_3$ does not improve performance on Na-aged SCR

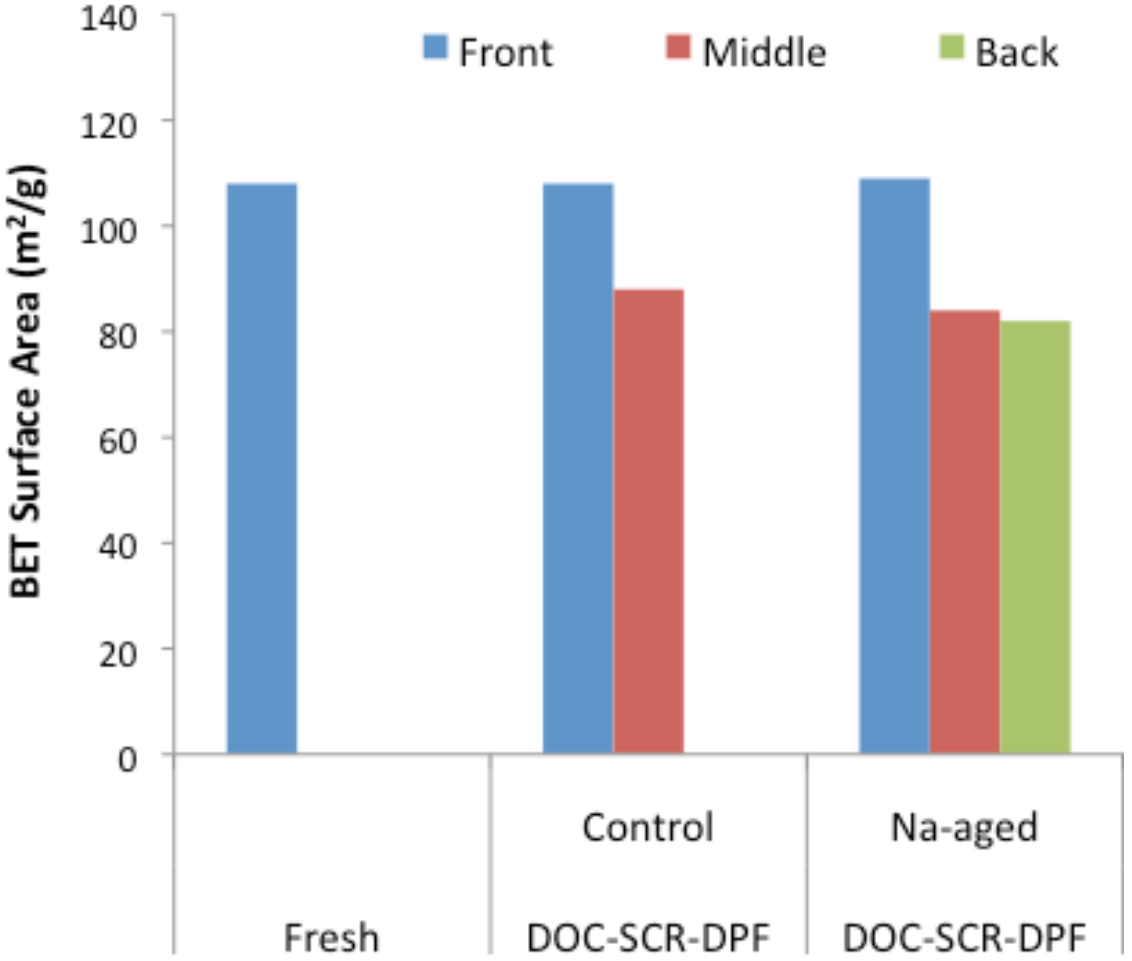
- Indicates $NH_3$ oxidation does not limit performance
  - $NH_3$ breakthrough observed
- Further illustrates NO to $NO_2$ oxidation is limiting performance in Na-aged sample
  - Oxidation sites are most impacted
- Impact on control is less pronounced



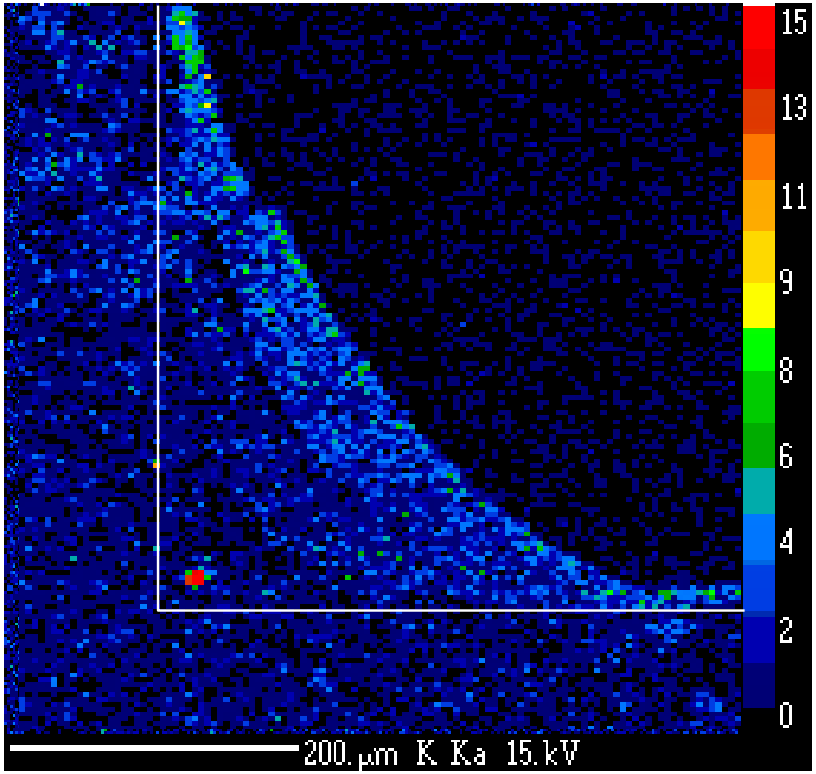



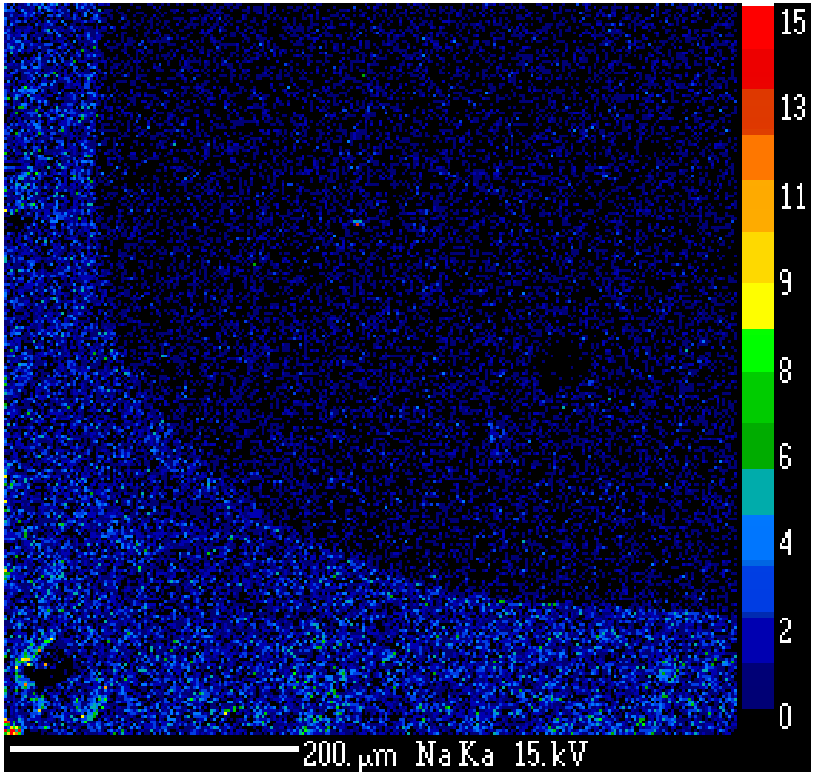
# Control-SCR and Na-aged SCR have similar BET profiles



# DOC → DPF → SCR (HEAVY-DUTY) Na ACCELERATED-AGING

# Minimal Na Contamination SCR when placed after DPF

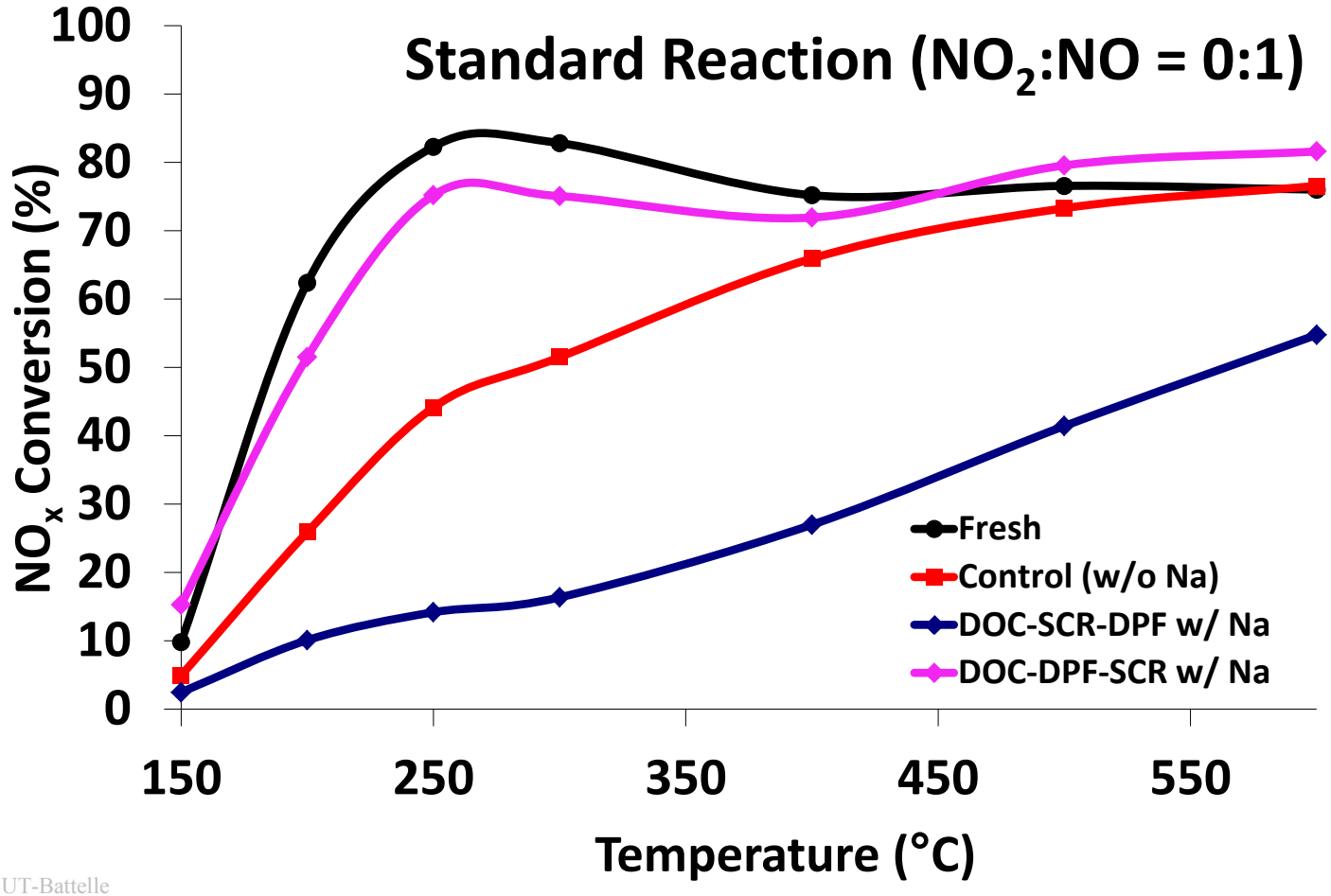


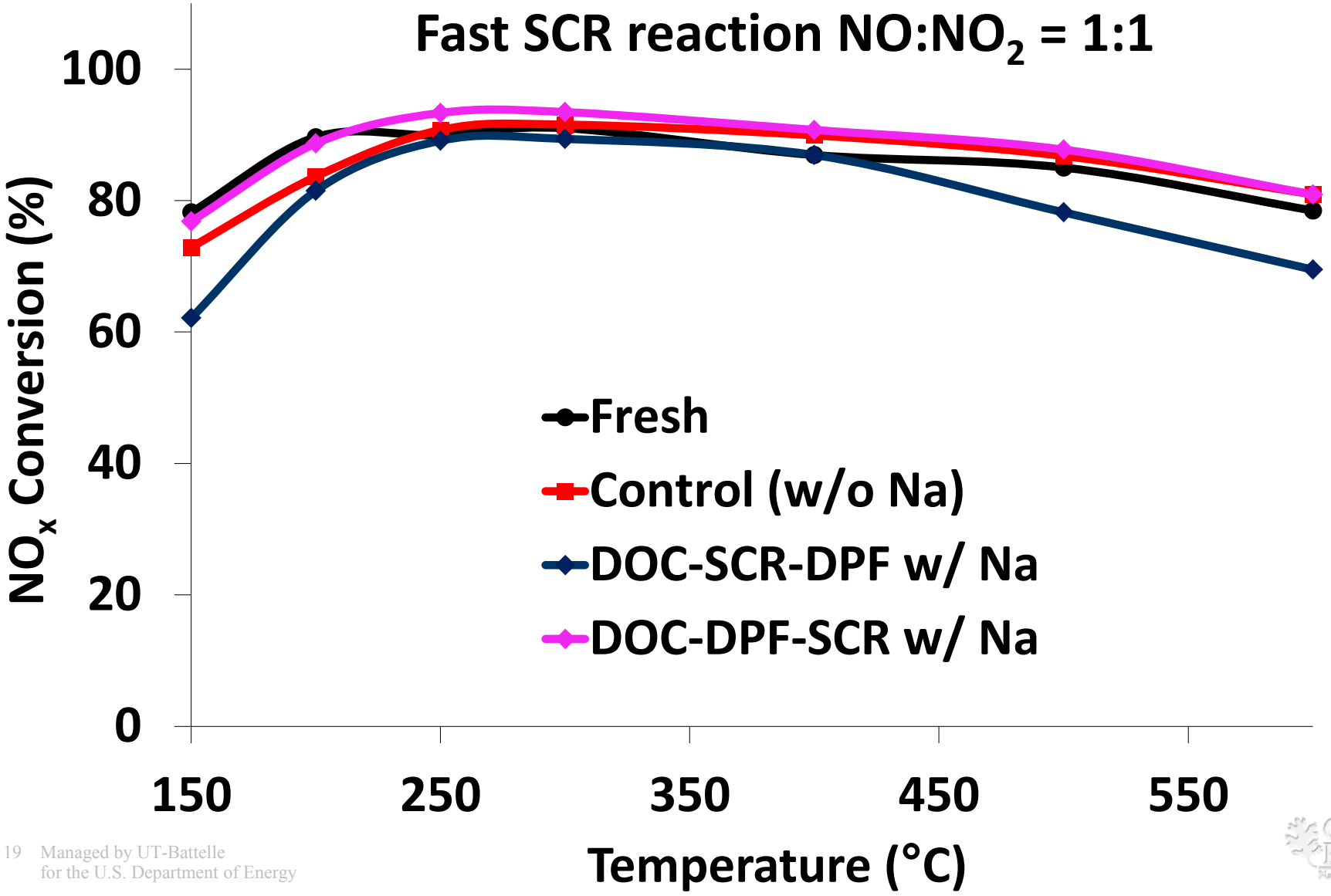


# When DPF is in front of SCR, catalyst is protected from Na and its effects

- No significant effect from accelerated Na-aging if DPF is in front of SCR
  - Some protection from thermal effects also gained with DPF upstream of SCR

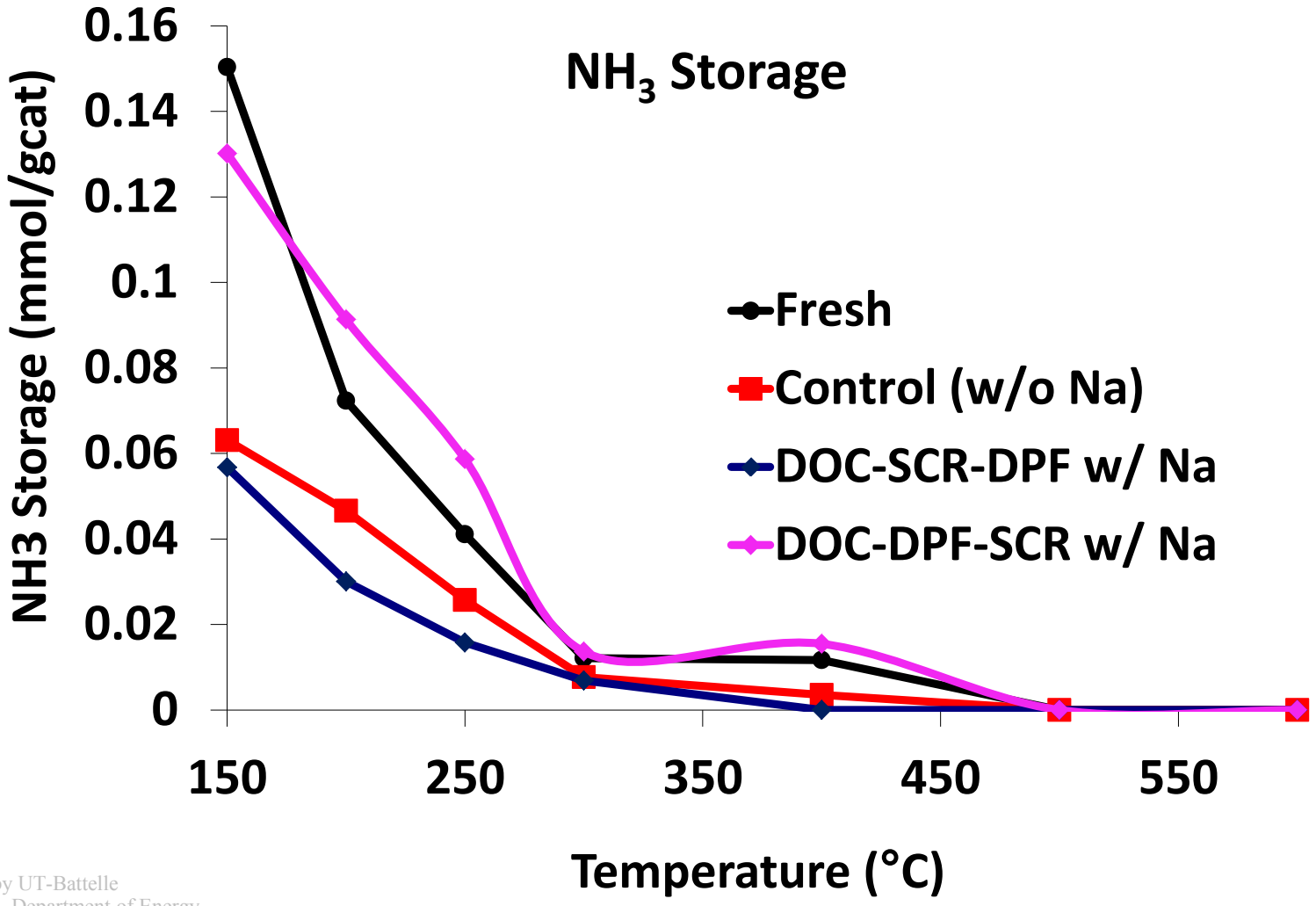


# Similar good behavior observed with fast SCR conditions



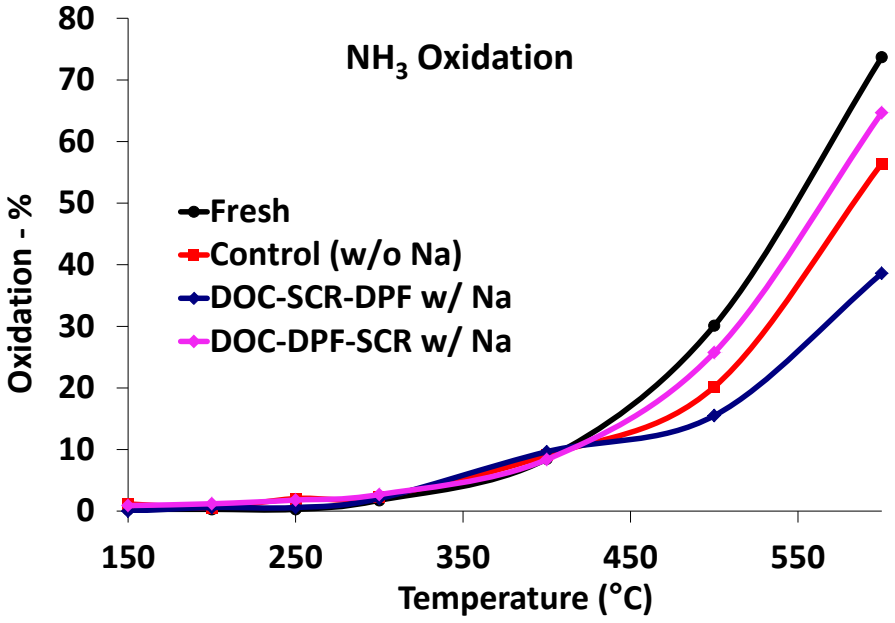
# $NH_3$ storage similar to that of fresh SCR

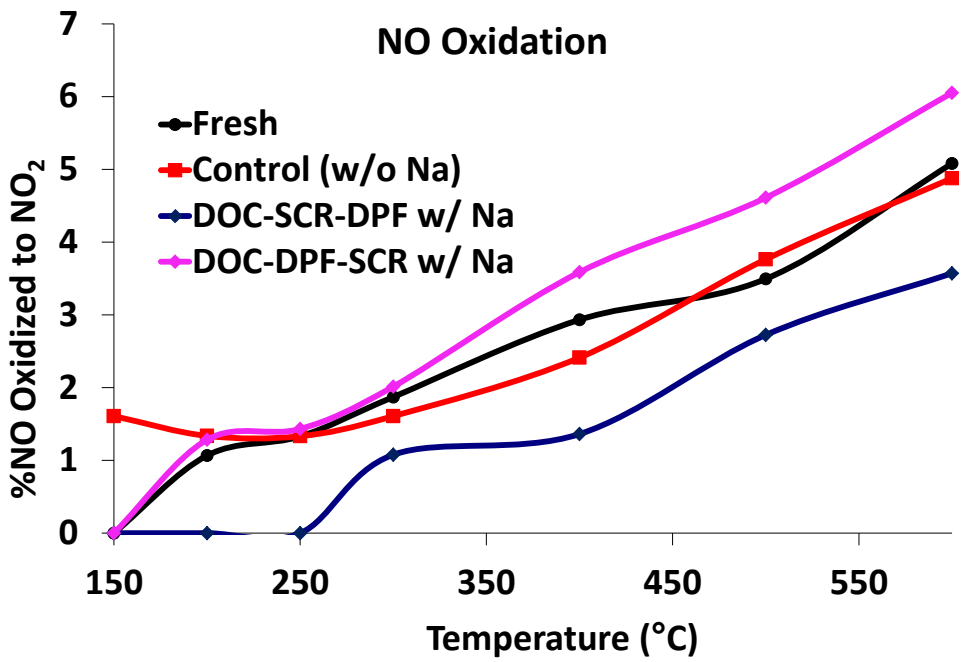
- No aging or Na contamination impact on $NH_3$ storage capability of catalyst
  - DPF upstream of SCR preserves storage capability of catalyst



# NO and $NH_3$ oxidation were similarly less affected

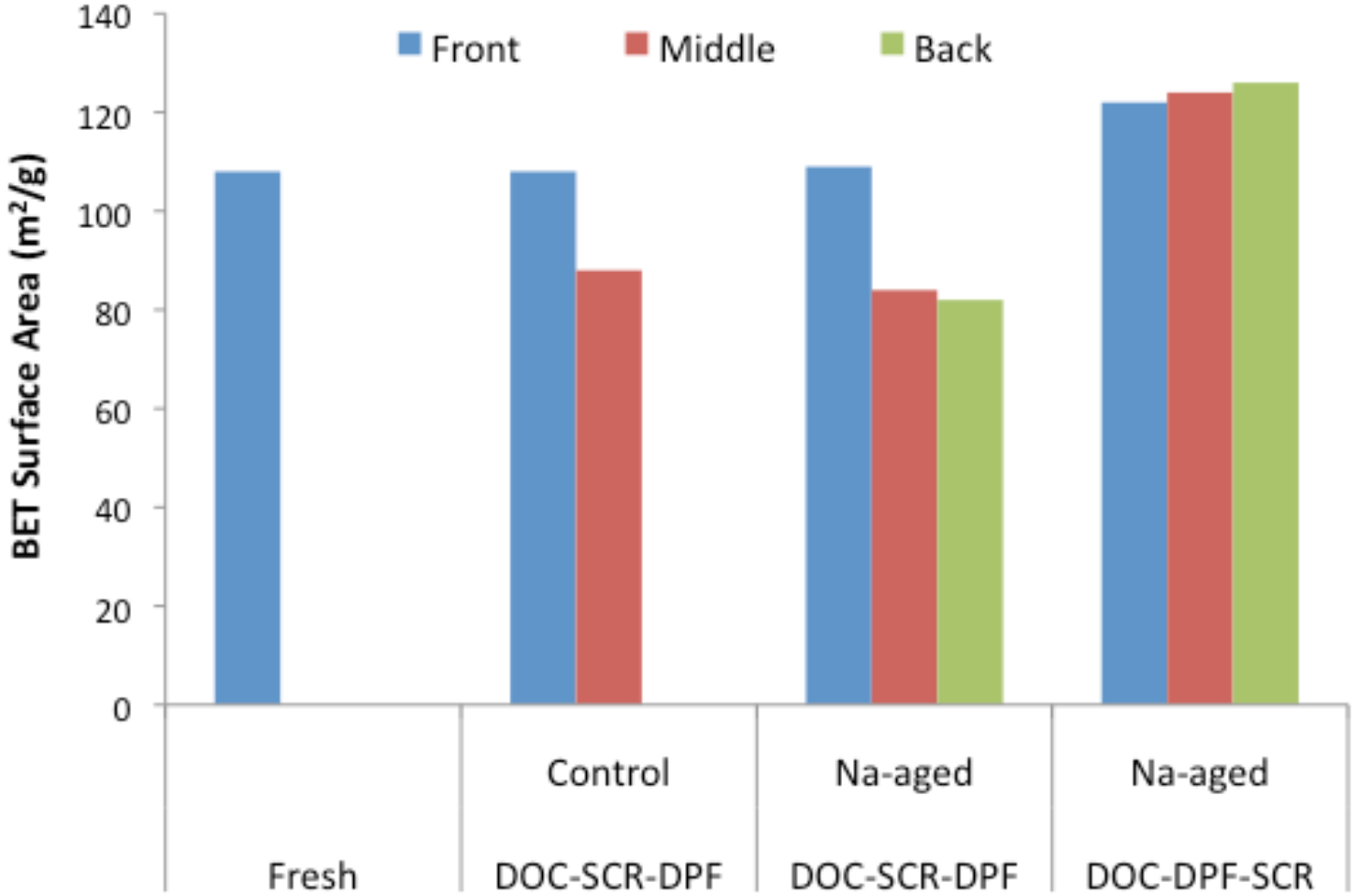
- $NH_3$ oxidation only slightly lower than that of fresh SCR
- NO to $NO_2$ oxidation shows moderately higher oxidation activity



# BET Surface Area Analysis of SCRs

- SCR from DOC-SCR-DPF configuration shows highest surface area reduction, while SCR from DOC-DPF-SCR configuration is unaffected



# Future Directions

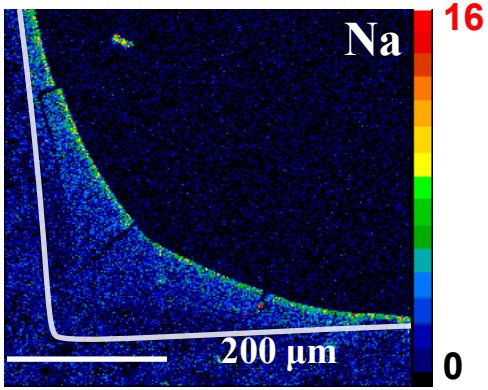
- Does ASTM specification need to be lowered? If so what level?
  - NREL lead collaboration
    - Focus of NREL/MECA/Ford/ORNL/NBB collaboration
  - Ford F250 with full emissions control system
  - 150,00 mile equivalent with ULSD, Na, K, and Ca
  - Light Duty (DOC-SCR-DPF) results forthcoming

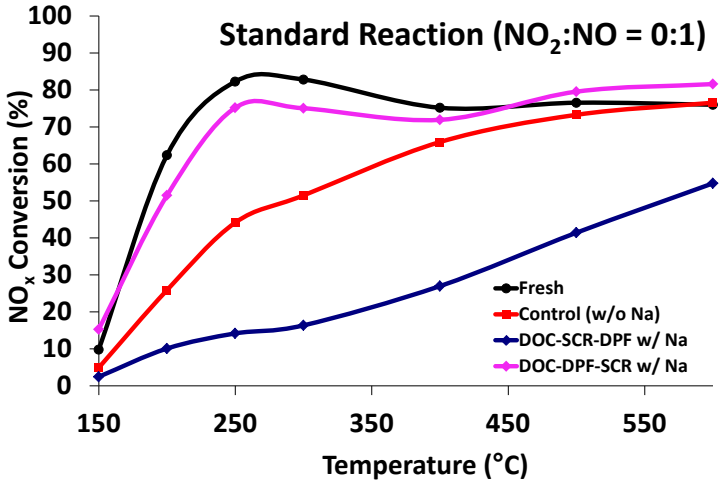


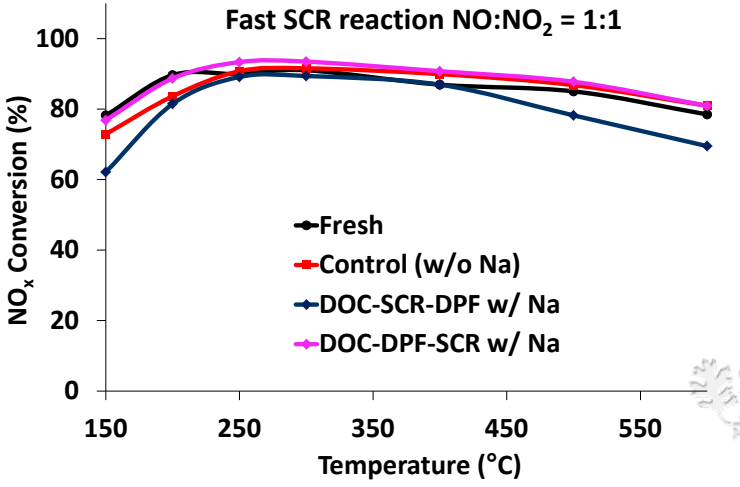

- Systematic study of Na impact on mechanical strength of DPF walls
  - Funded through the Advanced Propulsions Materials Program (Jerry Gibbs)
  - Collaboration with Michael Lance and Andy Wereszczak
    - ORNL – Materials Science and Technology Division
    - Strength testing technique discussed at poster Tuesday night (P-15)
  - Long term aging approach with overnight operation

# 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 contamination less severe when feeding equimolar amounts of NO and $NO_2$
- Results discussed in bonus slides
  - Na contamination in accelerated aged samples mimics that seen in long-term engine aged catalysts
  - Na penetrates cordierite walls of DPF
- Manuscript submitted to Catalysis Today (under review)



# 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

# COMPARISON OF ACCELERATED APPROACH TO LONG-TERM AGING

# Long-term engine-aged systems used for comparison when possible

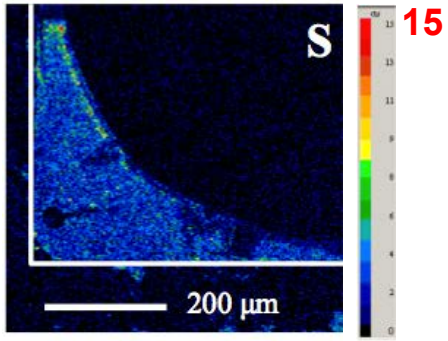
*B20 → DOC → DPF*

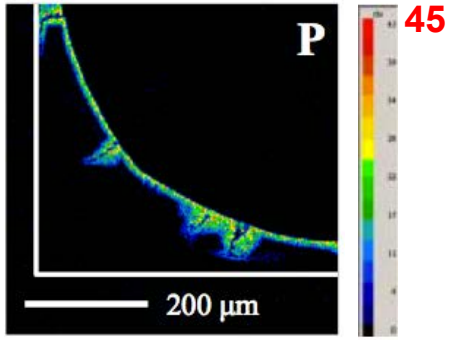
- Obtained from GM
  - Pt/$Al_2O_3$-based DOC
  - SiC-based DPF
- Field-aged system with B20
  - 120,000 mile equivalent
- Minimal knowledge about aging details
  - Na content was below specification
    - Exact value unknown
  - Temperature history unknown

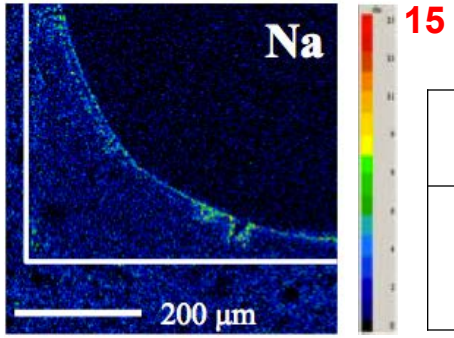
- Unfortunately unable to secure any B20-aged SCR catalysts

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

*Long-term aged DOC*



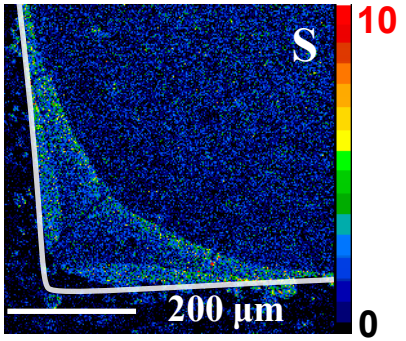



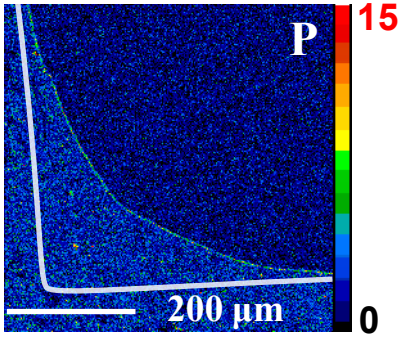



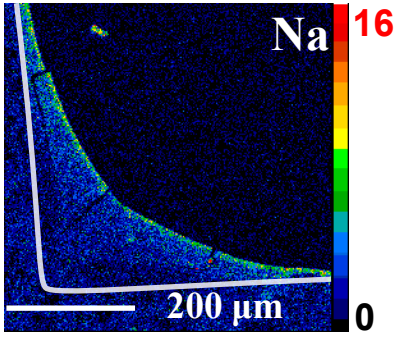

- Na, S and P observed in DOC
  - Inlet cross-sections shown with EPMA
- Long–term aged
  - S throughout washcoat
  - P at surface of washcoat
  - Na observed at surface
    - Primarily at inlet of DOC
- Accelerated aged
  - S throughout washcoat
  - Minimal lube oil phosphorous detected
  - Na observed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

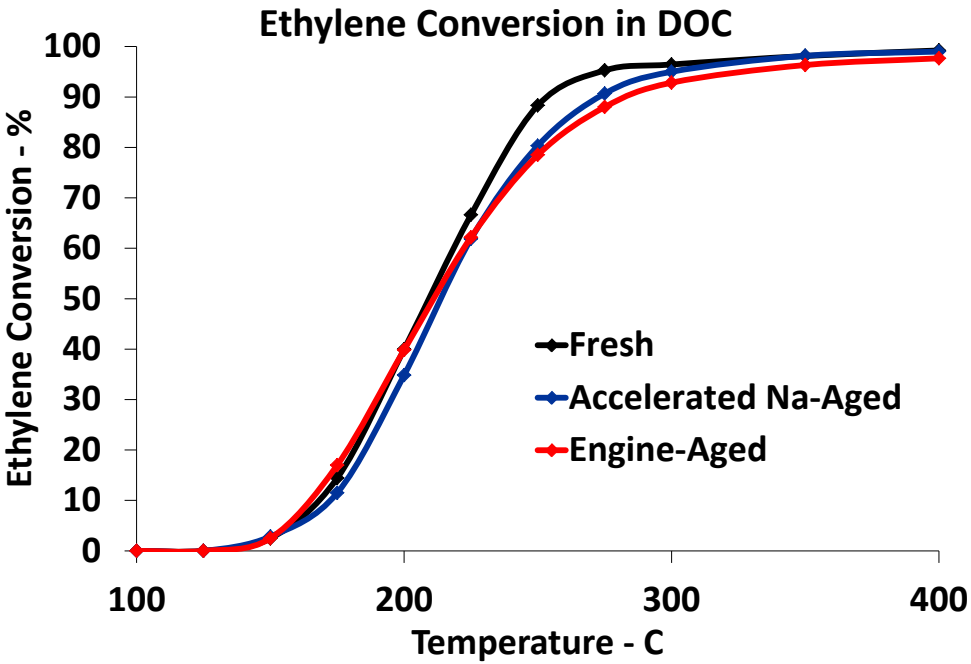


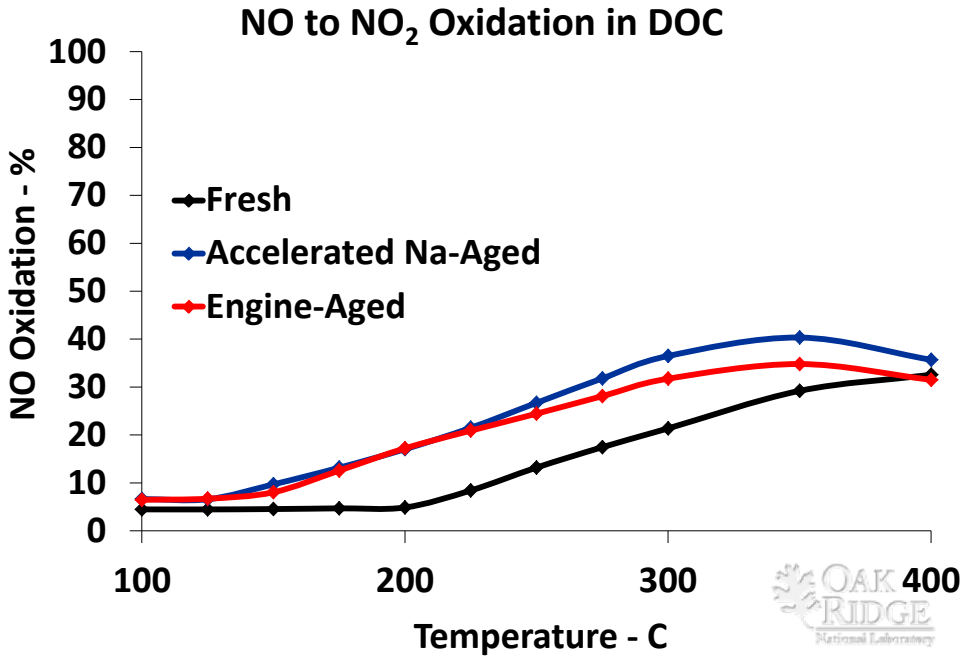



# DOC minimally affected; similar effects shown for both accelerated- and engine-aged devices

- Both aged samples show slight decrease between 225°C and 300°C
  - Conversion decreases by <12%



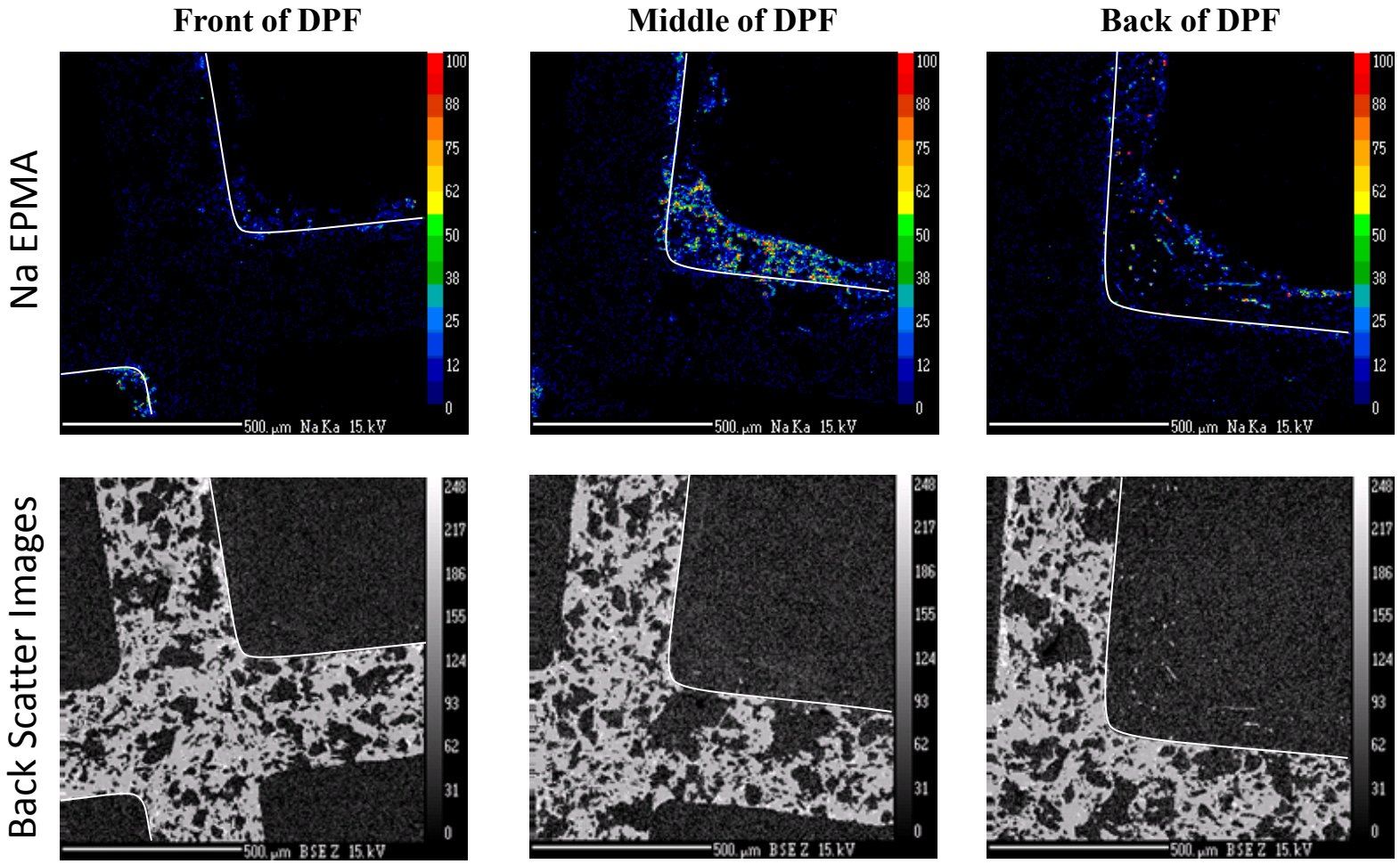

- Oxidation of NO to $NO_2$ is as much as 12% higher in engine-aged DOC samples than in fresh
  - This effect is possibly due to increased Pt particle size from thermal aging, which can improve NO to $NO_2$ oxidation



# EPMA ANALYSIS OF DPF SAMPLES

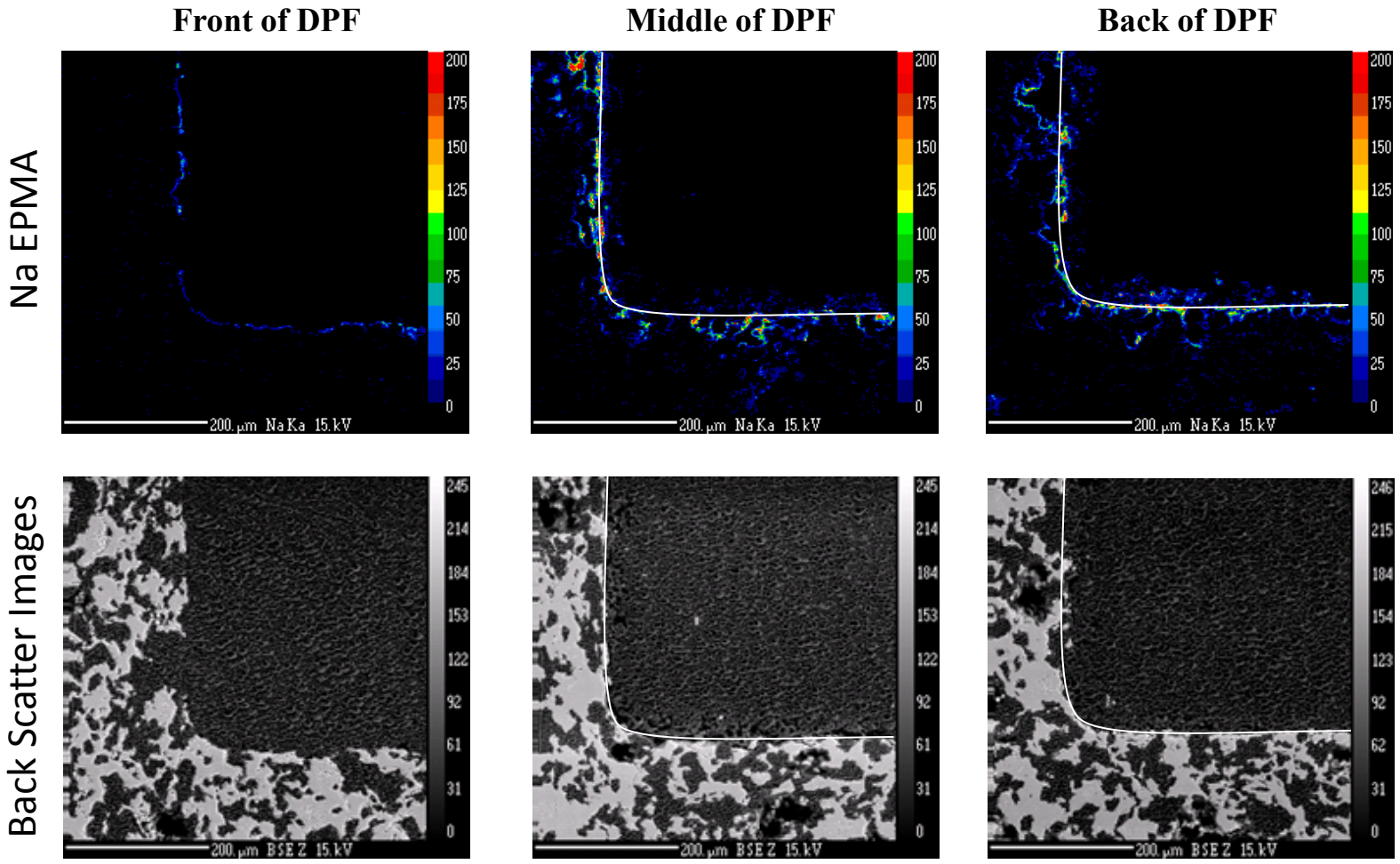
# Na found in walls of cordierite DPFs

- DOC-SCR-DPF: penetration is observed; not deep



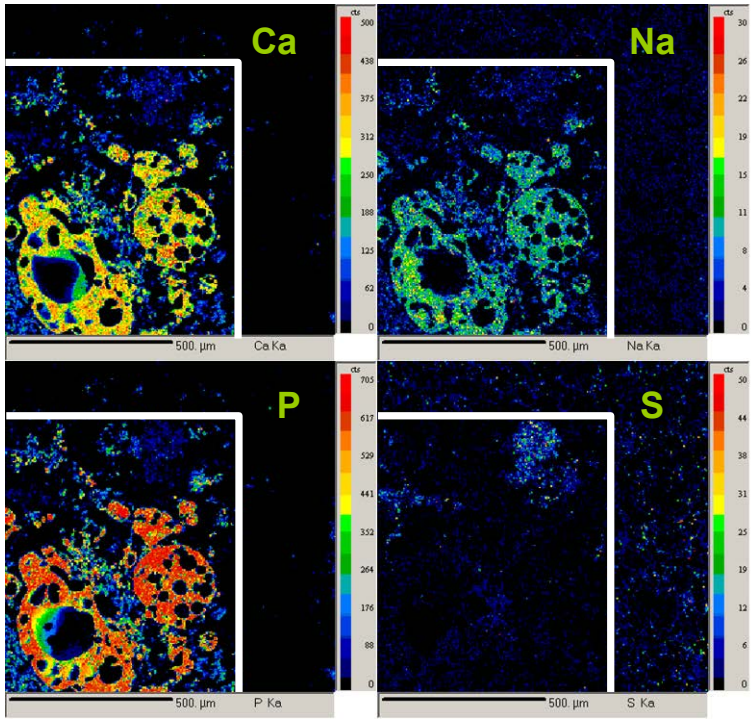
# Na found in walls of cordierite DPFs

- DOC-DPF-SCR: penetration is more severe; closer to DOC exotherm



# Ash in long-term GM-aged DPFs (SiC)

**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 <u>not</u> detected in wall of SiC DPF

**Ash plugs in exposed DPF channels**