OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

2026 Clean Fuels' Technical Workshop

Impact of fuel-borne impurities on close-coupled SCR catalysts for off-road engines

SCR: Selective Catalytic Reduction

Todd J. Toops

Oak Ridge National Laboratory

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The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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- Dave Montgomery, Lynsie Delp, Austin Moore, Josh Ratts, Dave Ginter

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- Steve Howell, Scott Fenwick, and Courtney Videchak

DOE: Department of Energy; TTO: Transportation Technologies Office; ORMA: Off-Road, Marine, and Aviation

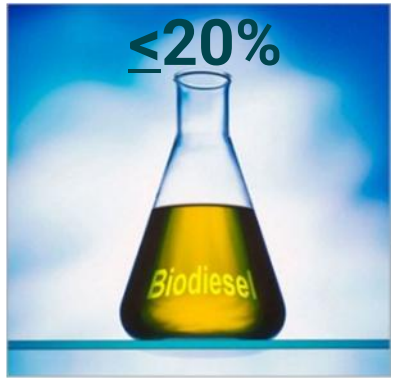
Fundamental studies of biodiesel (B100) impact on emissions control devices can advance energy addition to the market

B100 standards do not exist

B100 usage adds energy to market

Industry is interested in using biodiesel blends above B20

ASTM standard, D7467-23, is only for biodiesel blended up to 20%



Emissions more stringent

Proposed Offroad Tier 5 emissions control reduces NOx 50-90%

Advanced emission control approaches needed

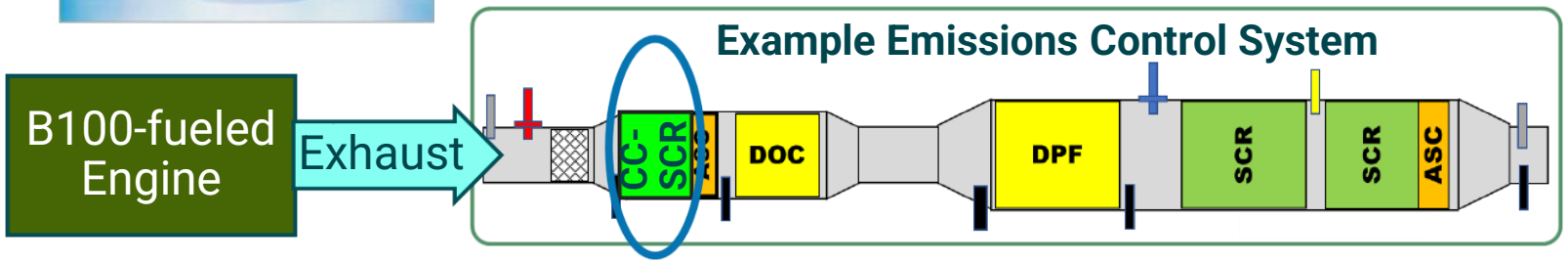
	NO (g/kWh)	Durability
Tier 3 (2006-08)	9.2	8,000 h
Tier 4 (2012-14)	0.4	8,000 h
Tier 5 (TBD)	*0.04*	*8,000 – 12,000 h*

CC-SCR adoption to increase

Close-Coupled SCR (CC-SCR) is relevant to **off-road applications** today and will likely increase

Benefits: Faster light-off, lower cold-start emissions

Vulnerabilities: More susceptible to chemical poisoning



References:
https://www.astm.org/d6751-23a.html
https://dieselnet.com/standards/us/nonroad.php
https://dieselnet.com/newsletter/2021/11.php
SAE 2021-01-0589

ASTM: American Society for Testing and Materials; DOC: Diesel Oxidation Catalyst; DPF: Diesel Particulate filter; ASC: Ammonia Slip Catalyst

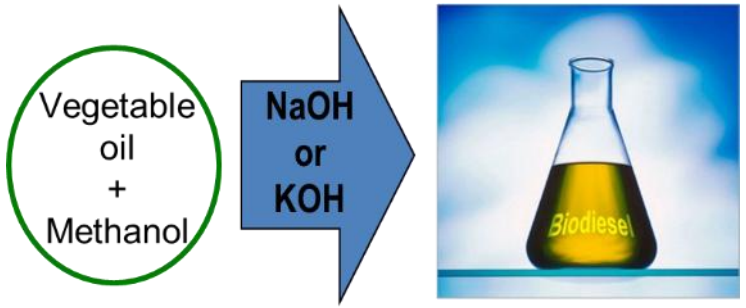
Metal impurities in biodiesel are a significant concern hindering widespread usage

Metals in B100 from production process

Total metal for B6-B20 blendstock (ASTM D6751-23a):

Ca+Mg+Na+K: 4 ppm (combined)

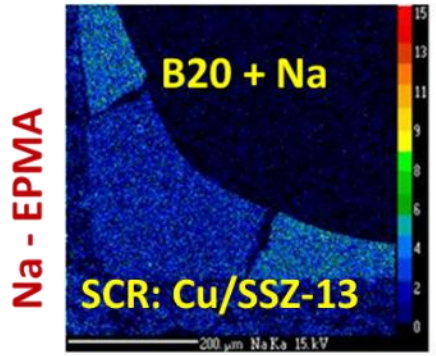
Updated in 2023 from 10 ppm

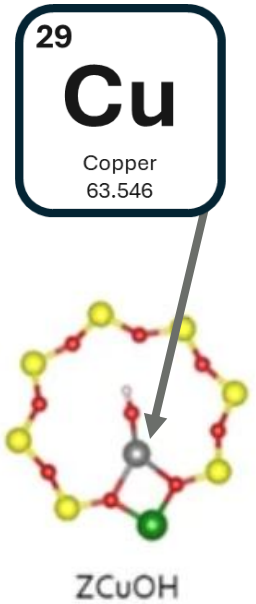


Metals can impact emissions control systems

Prior studies show impact on Cu-SCR

Known issues on DPF/ash also





Project Goal: Understand impact on V-based CC-SCR reactivity

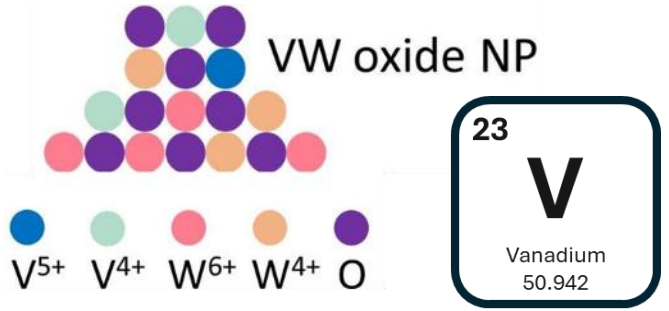
Systematic investigation of V-SCR

5x accelerated aging factor

Identify metal location on catalyst

Correlate local metal content on local catalyst functions

V-SCR: V_2O_5 -WO_3/TiO_2



Brookshear et al. Catalysis Today 184:1 (2012) 205.
Lance et al. SAE 2016-01-2322.
L.N. Wilcox, et al. ACS Catalysis 14:5 (2024) 3647-3663.
M.J. Lee et al., Appl. Catal. B 378 (2025) 125583.

EPMA: Electron Probe Micro-Analysis

Systematic CC-SCR B100-Fueled Engine Aging Approach

Doped B100

Na: 2 ppm
K: 1 ppm
Ca: 1 ppm
Mg: 0 ppm
P: 0 ppm
S: 10 ppm

2300-gallon tank



4.4L, XQ125 B100-fueled Engine

NOx | **Urea** | **200 °C ≤ T ≤ 350 °C** | **NOx**

Commercial V-W/Ti SCR (V-SCR)

Metal additives

Na-dodecyl benzene sulfonate

K-dodecyl benzene sulfonate*

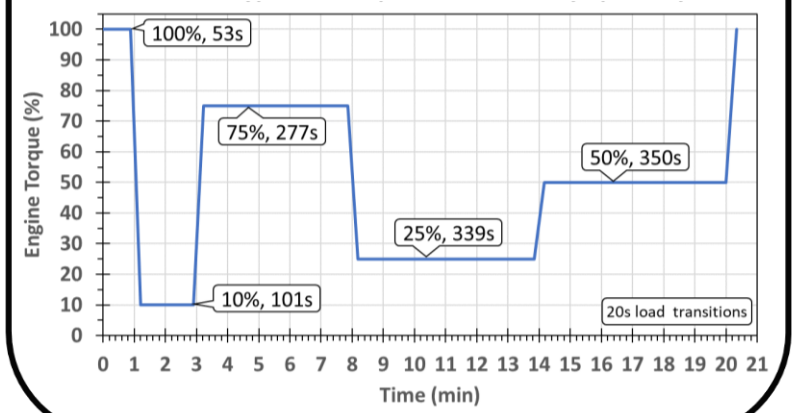
Ca-Naphthenate

S: Di-tert-butyl disulfide

** - Thanks to Jennifer Cavaleri at NLR for synthesizing*

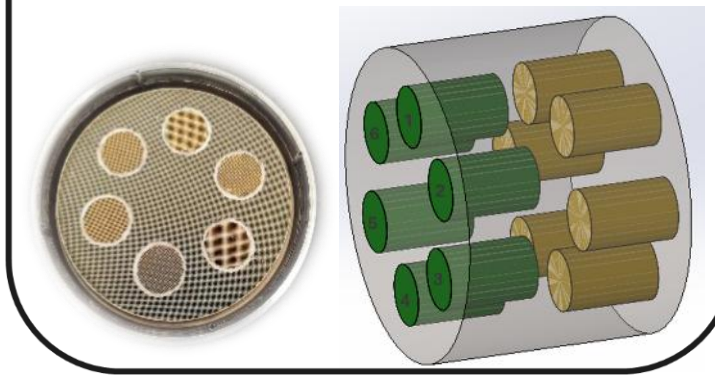
Off-Road Load Cycle

- ISO 8178 Type D2 Ramped-Modal
- Variable flowrates and Temp.



Multi-Core Housing

- 1 core/2-weeks to Analysis
- Performance & Elemental
- Metals gradient along catalyst



NLR: National Lab of the Rockies; ISO: International Organization for Standards

Installation at ORNL



2300-gallon fuel tank inside

Heated and insulated fuel lines

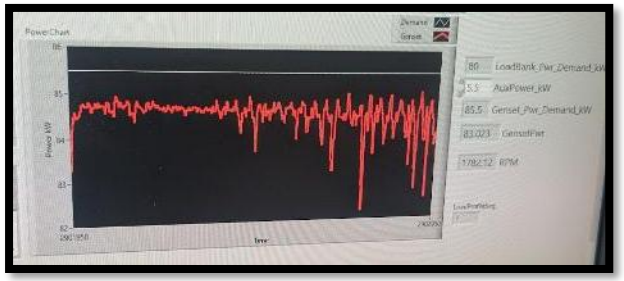
Programmable Electronic Load Bank

Caterpillar XQ125



Heated 180 gallon Diesel Exhaust Fluid (DEF) tote with auto refill

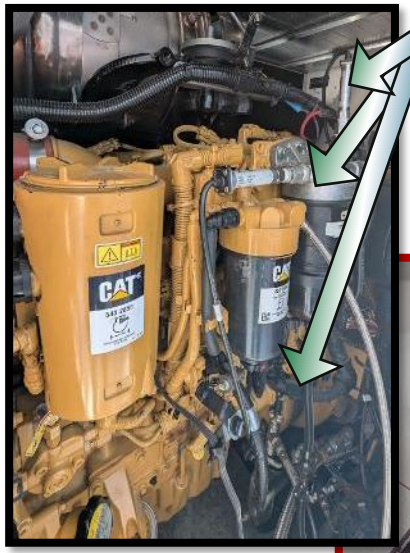
Initial progress with B100 was limited at high power; eventually determined to be a fuel filter issue



Unstable after ~2 days of operation



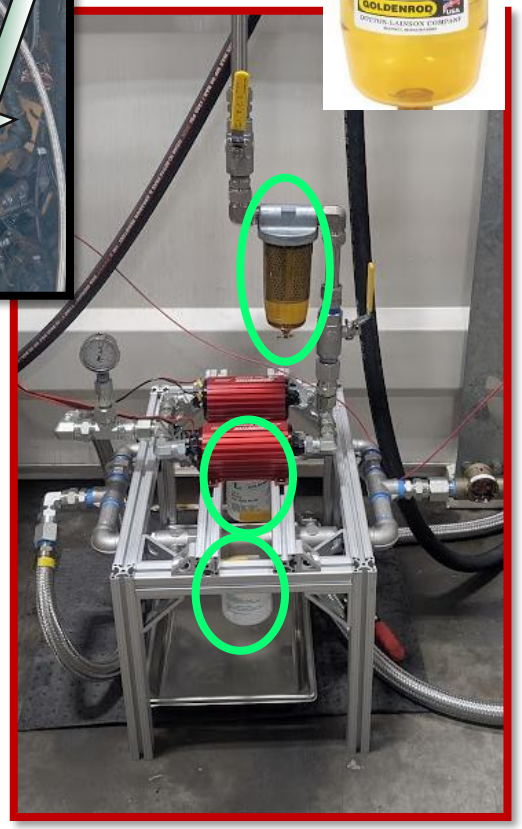
Working with Caterpillar to understand filter issue



Added P sensors to genset

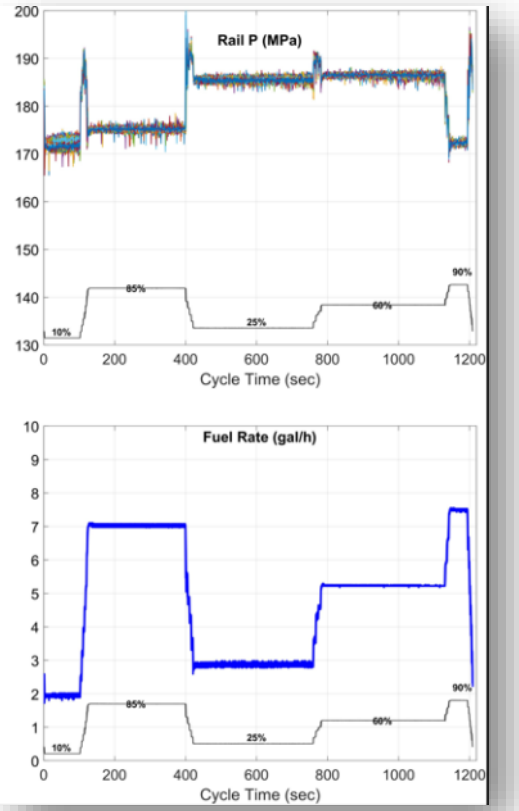


Fuel tank "kidney" loop

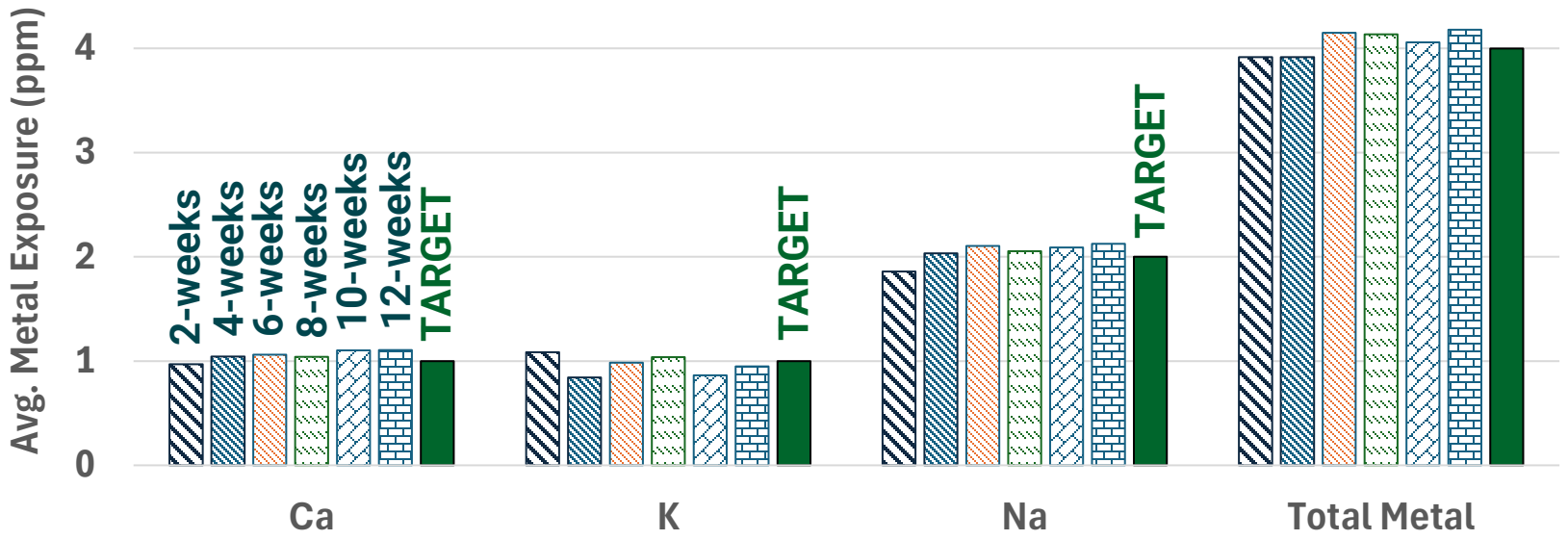


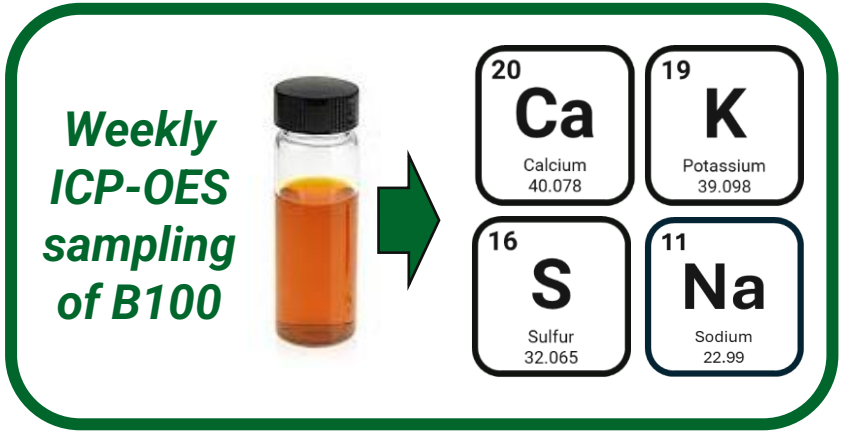


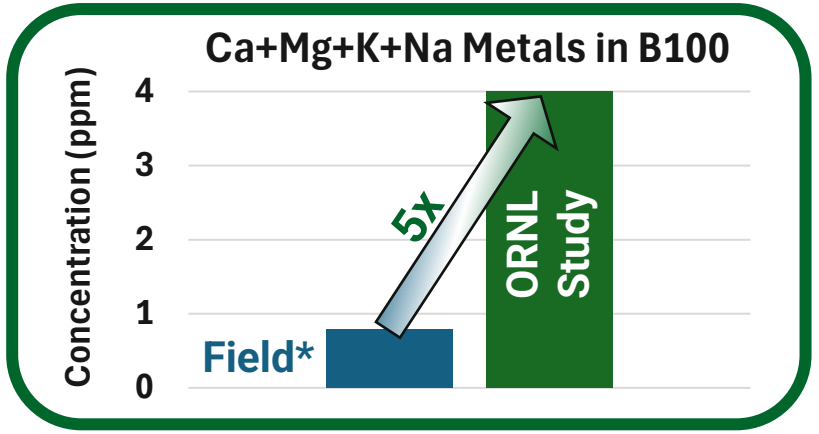
Issue solved with ~weekly "kidney" loop filter changes; *increased filter changes with new fuel*

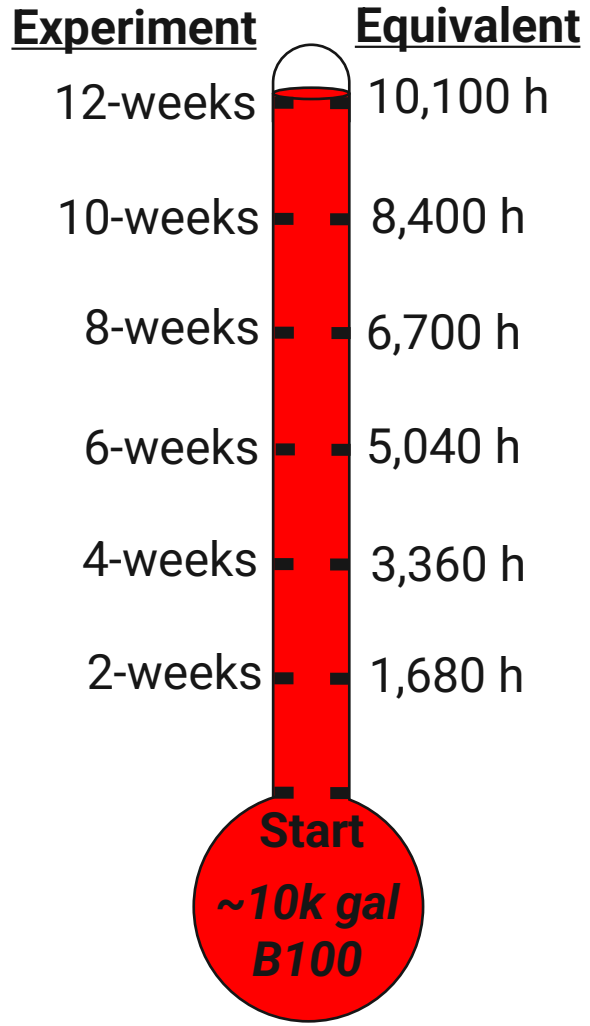


Completed 12-week/full useful life equivalent washcoated Vanadium-SCR exposure with target 4 ppm total metal in B100





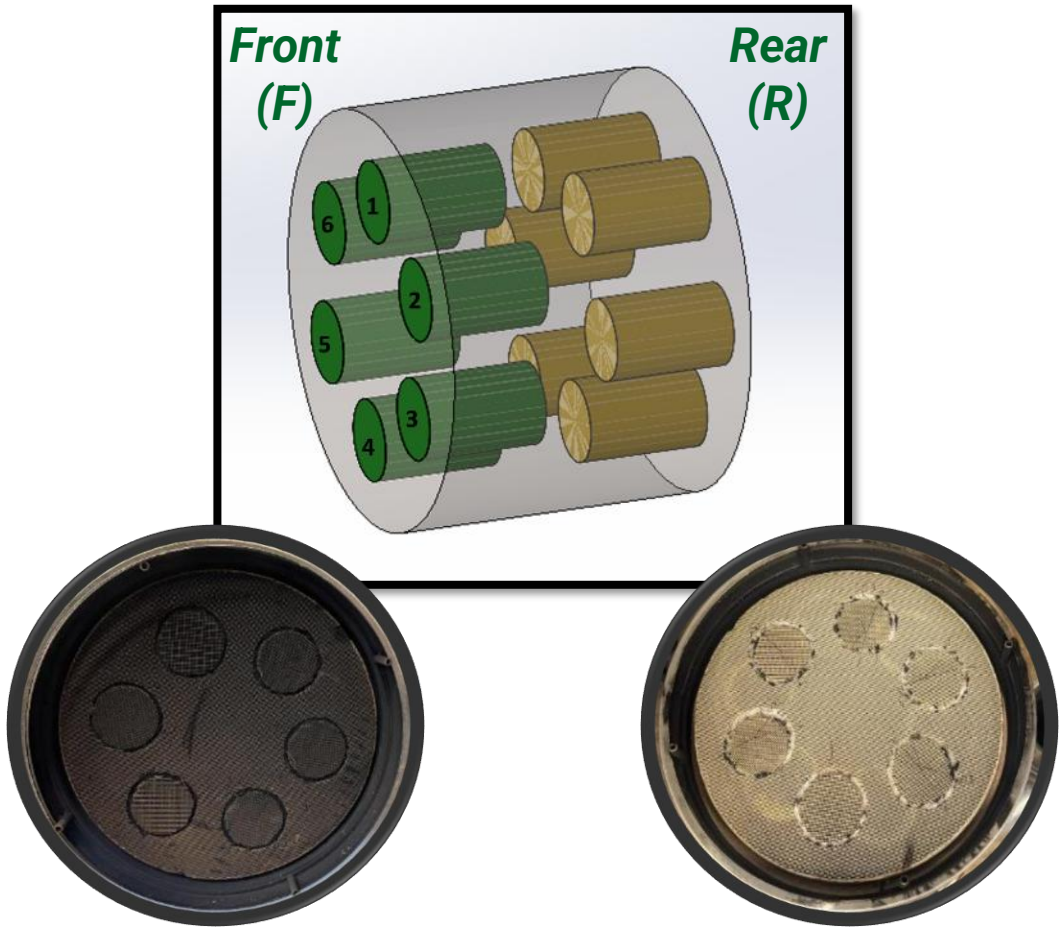


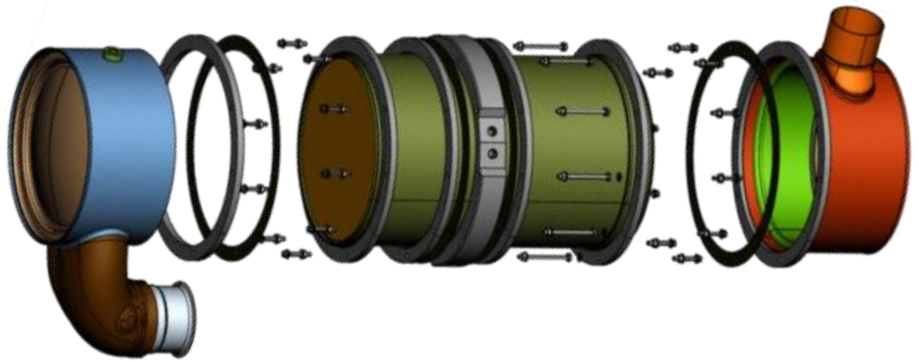


ICP-OES: Inductively coupled plasma optical emission spectroscopy

* - R. McCormick, "Assessment of BQ-9000 Biodiesel Properties for 2024," NREL/TP-2A00-95754.

V-SCR cores removed throughout exposure and provide a wide range of samples to characterize including several repeats









FRONT	
2-weeks	4 samples
4-weeks	2 samples
6-weeks	2 samples
8-weeks	2 samples
10-weeks	1 sample
12-weeks	1 sample

REAR	
2-weeks	4 samples
4-weeks	2 samples
6-weeks	2 samples
8-weeks	2 samples
10-weeks	1 sample
12-weeks	1 sample

Initial characterization aimed at identifying metal distribution and evaluating full-core reactivity

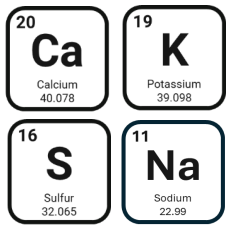
ICP-OES for bulk elemental analysis



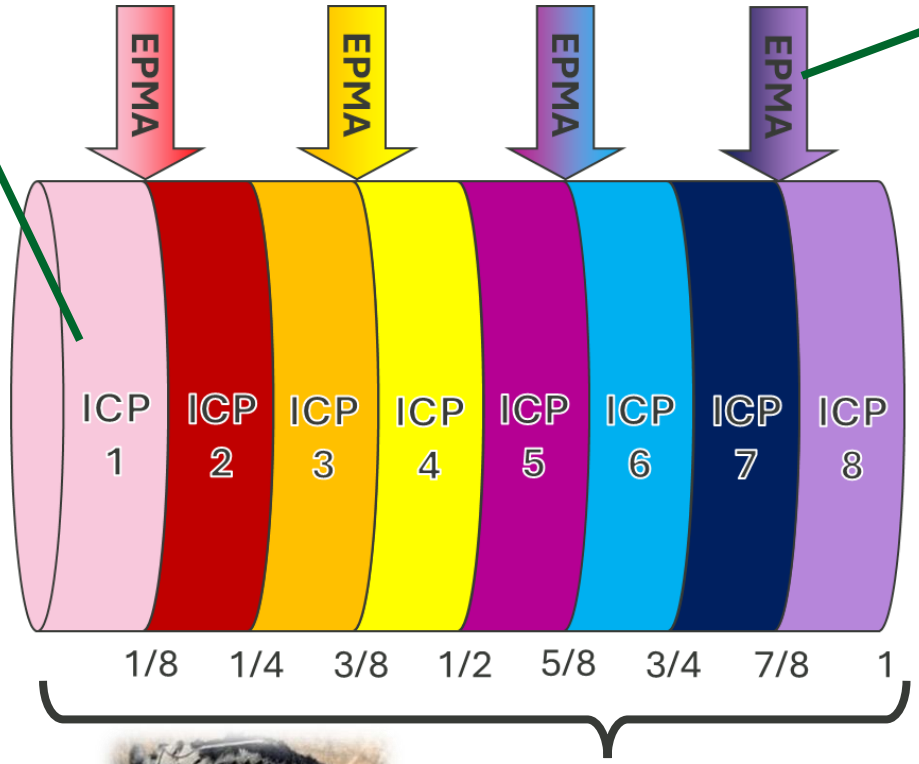
Crush



Dissolve



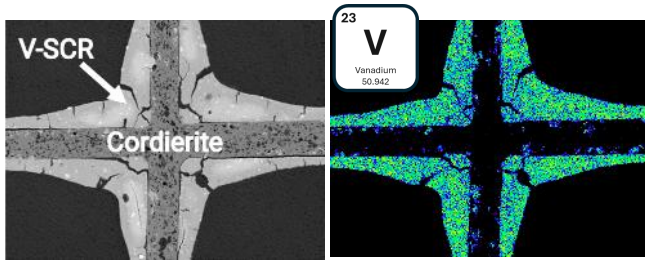
Analyze





50x75 mm core from FRONT section

EPMA: Elemental mapping

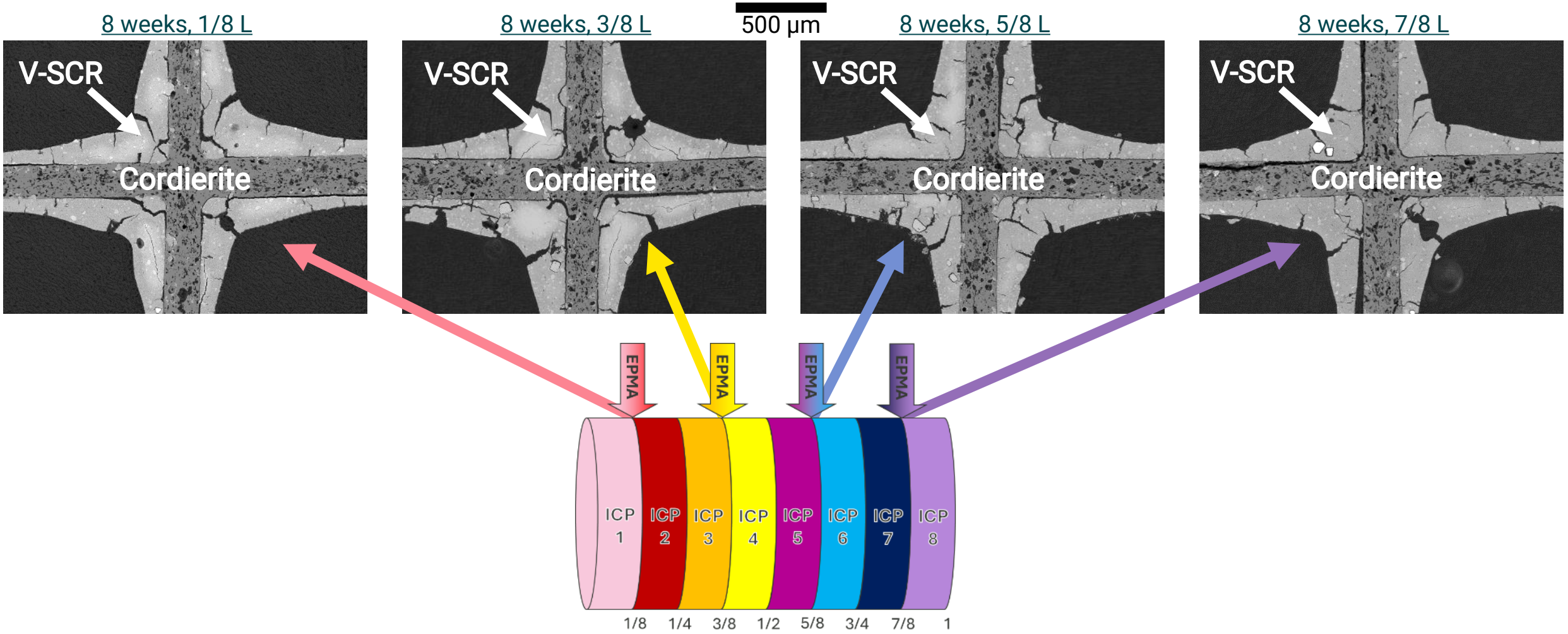


Initial flow reactor evaluation of full core

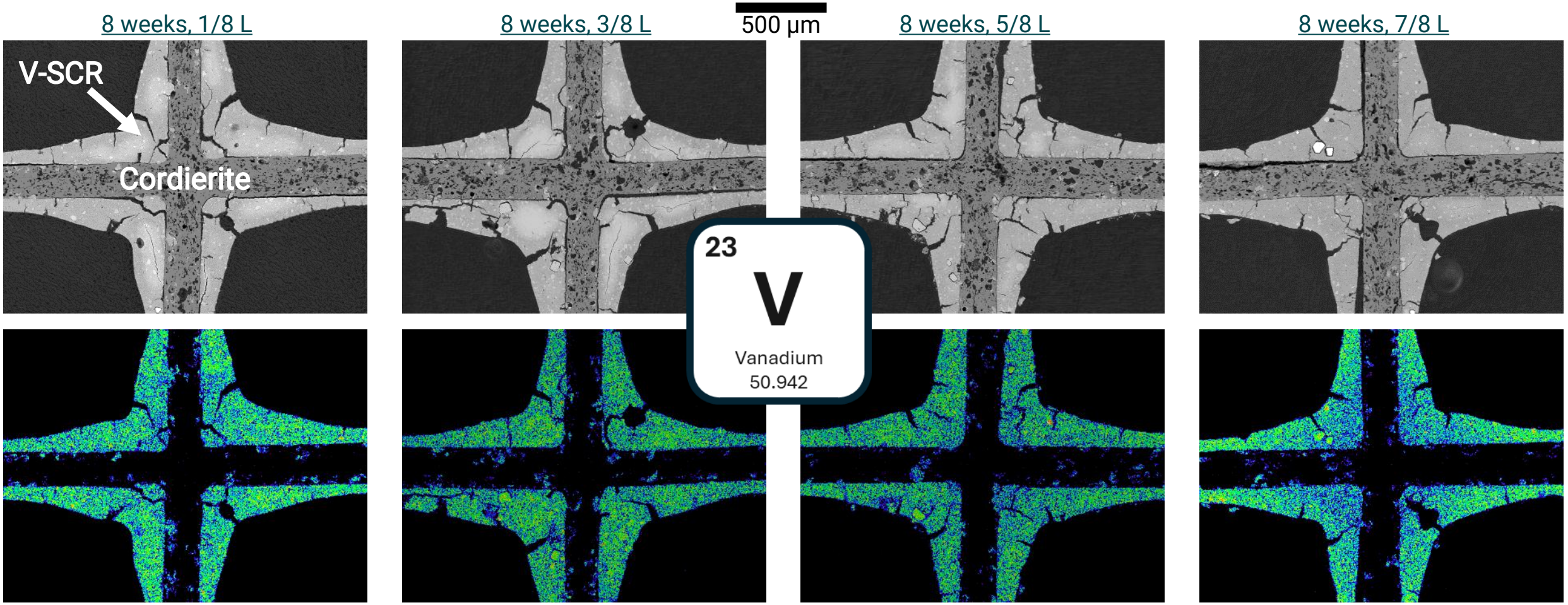


ICP-OES: inductively coupled plasma optical emission spectroscopy; EPMA: electron probe microanalysis

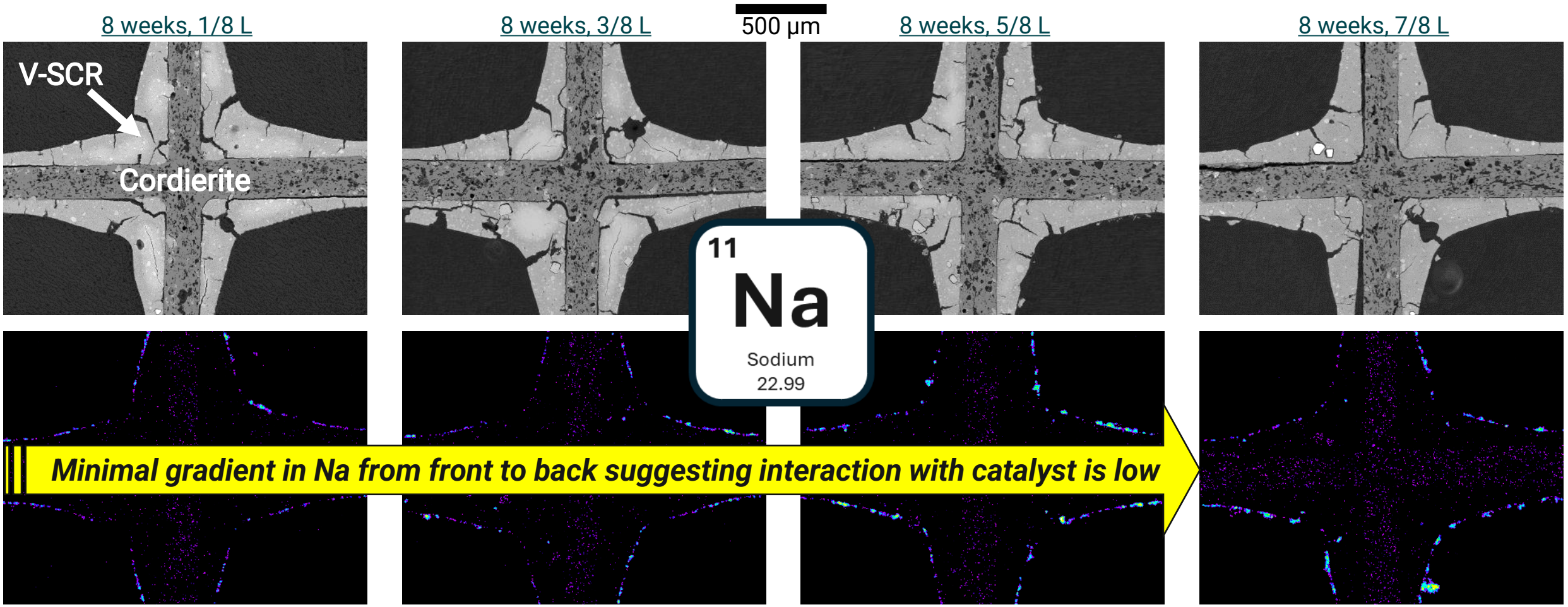
Elemental mapping performed on V-SCR cross-section after 8 weeks of B100 exposure



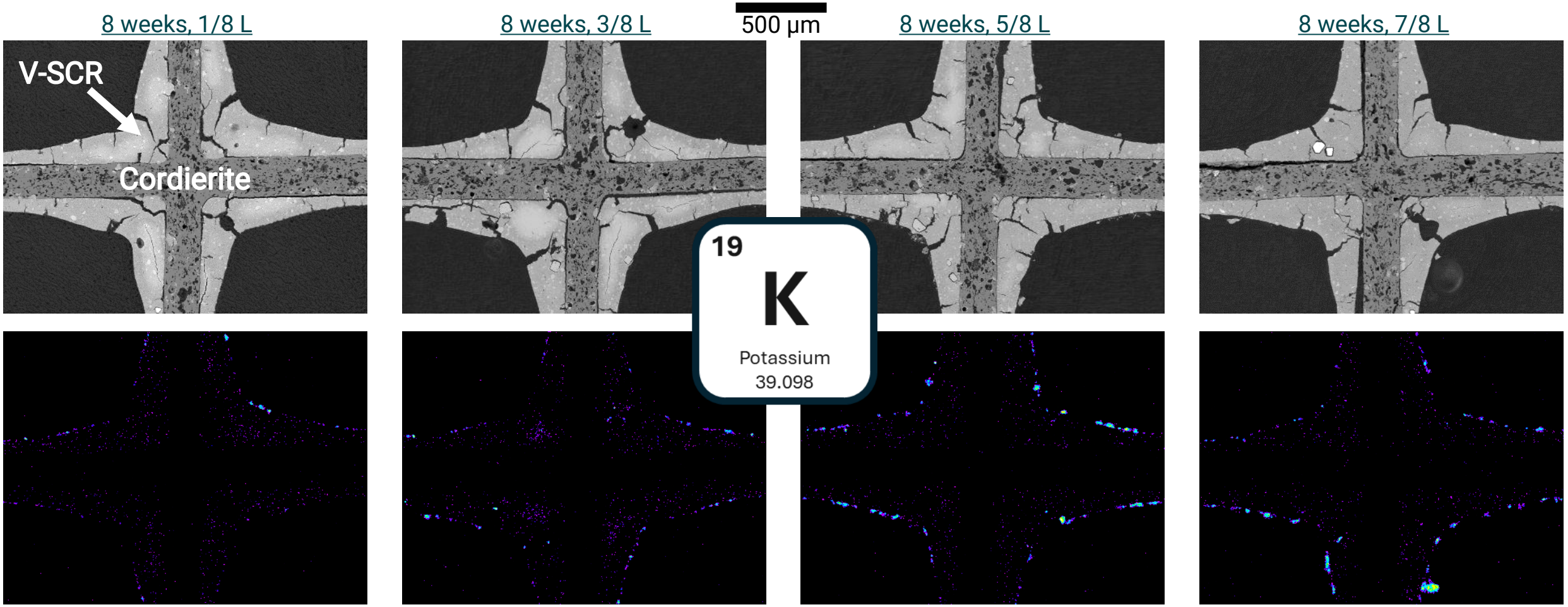
Elemental mapping performed on V-SCR cross-section after 8 weeks of B100 exposure



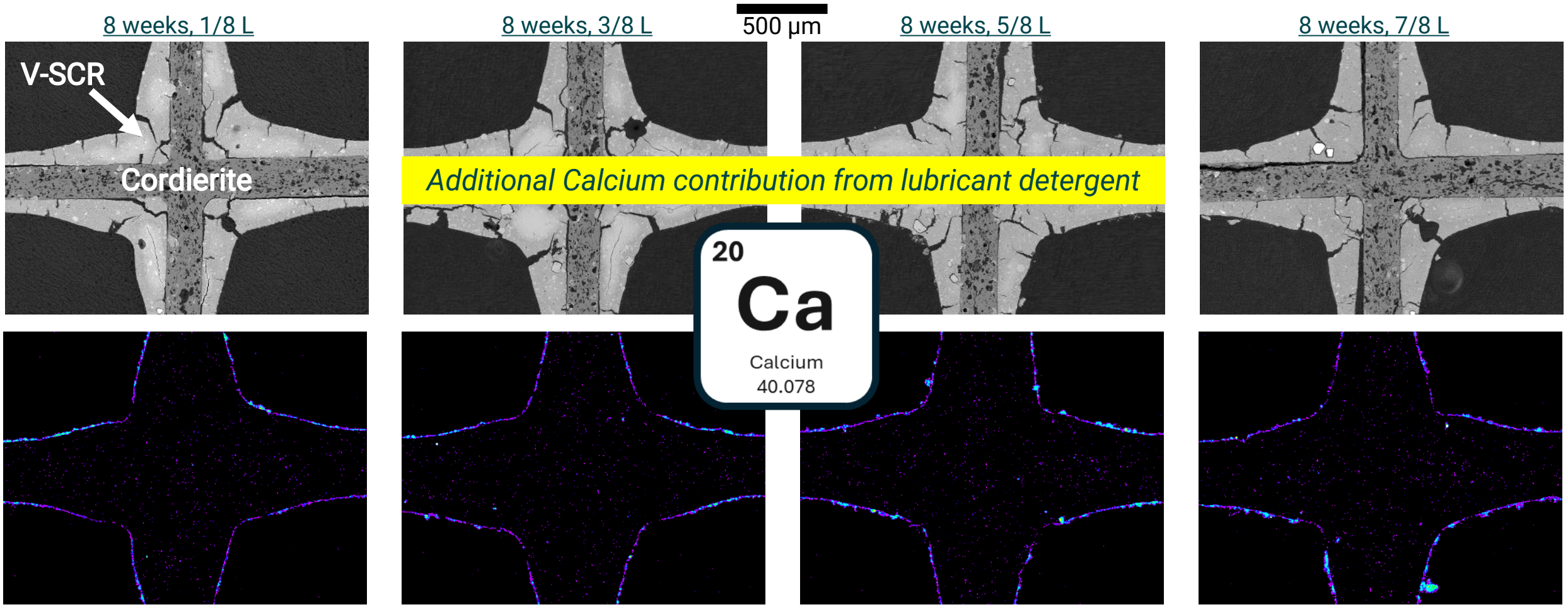
Minimal interaction with catalyst and metal/ash deposition increasing along length



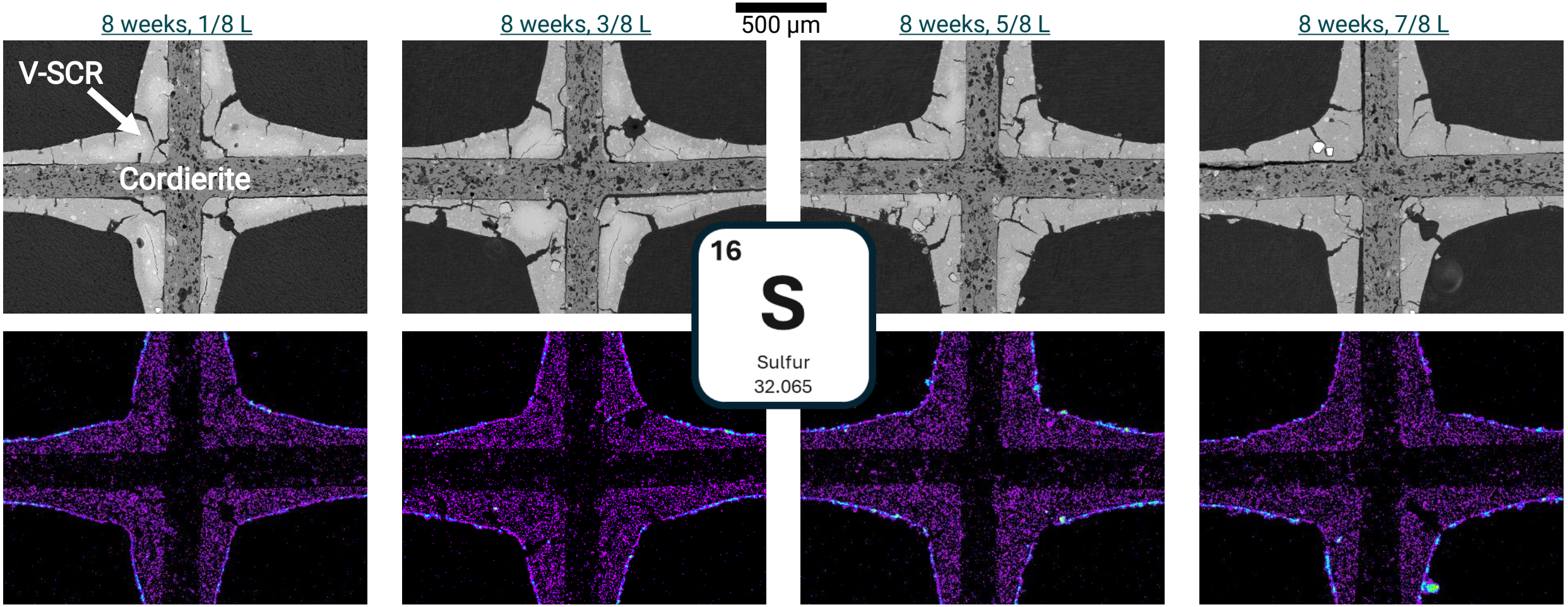
Minimal interaction with catalyst and metal/ash deposition increasing along length



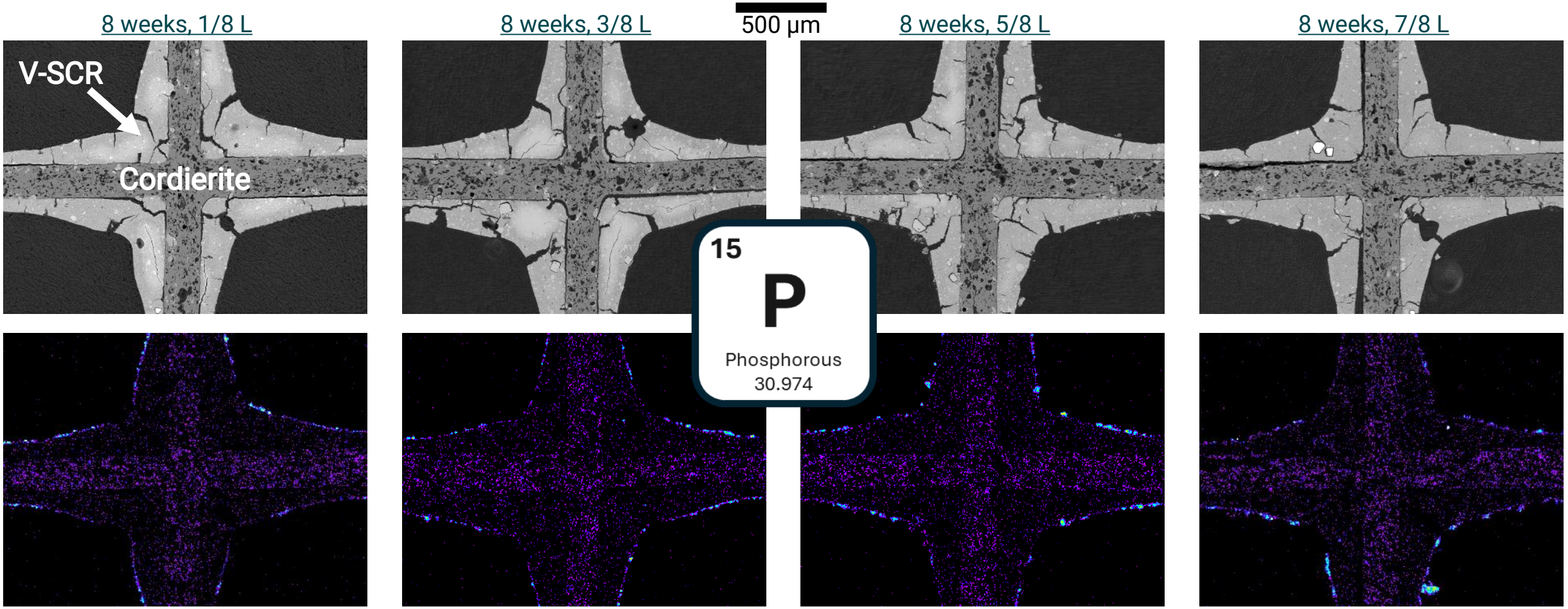
Minimal interaction with catalyst and metal/ash deposition increasing along length



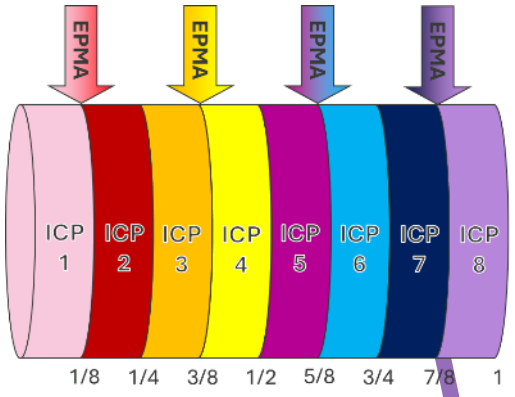
Minimal interaction with catalyst and metal/ash deposition increasing along length



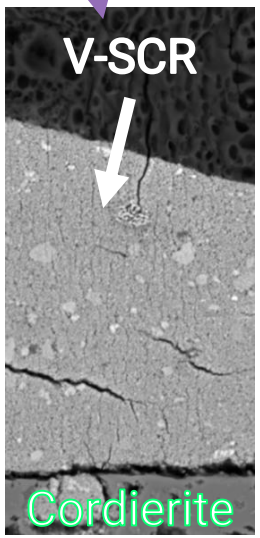
Minimal interaction with catalyst and metal/ash deposition increasing along length

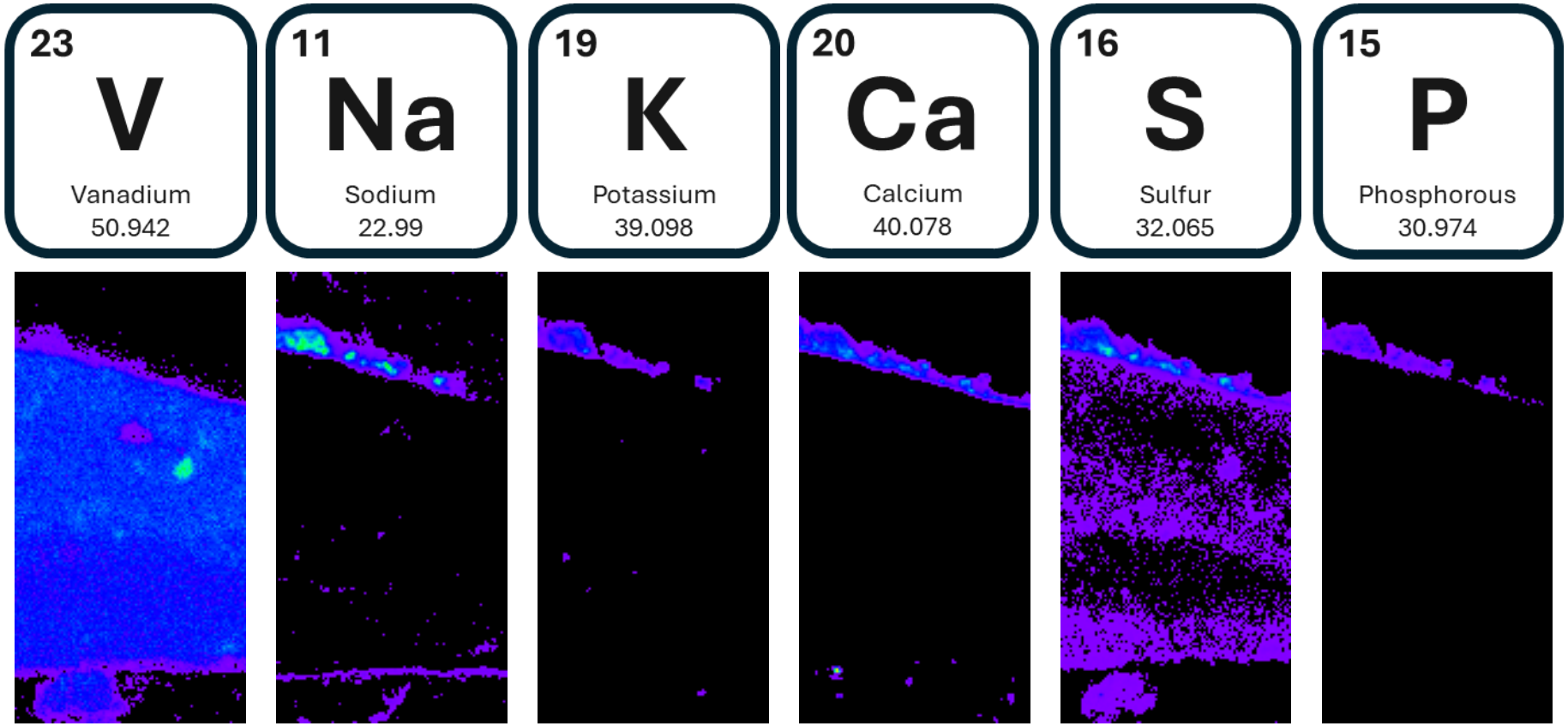


Focused analysis continues to show primarily surface interactions, with S interactions in washcoat of V-SCR



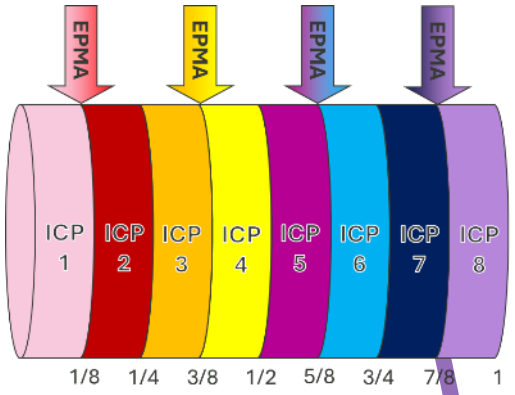
8 weeks
7/8 L



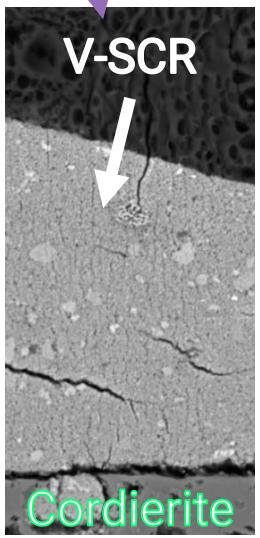


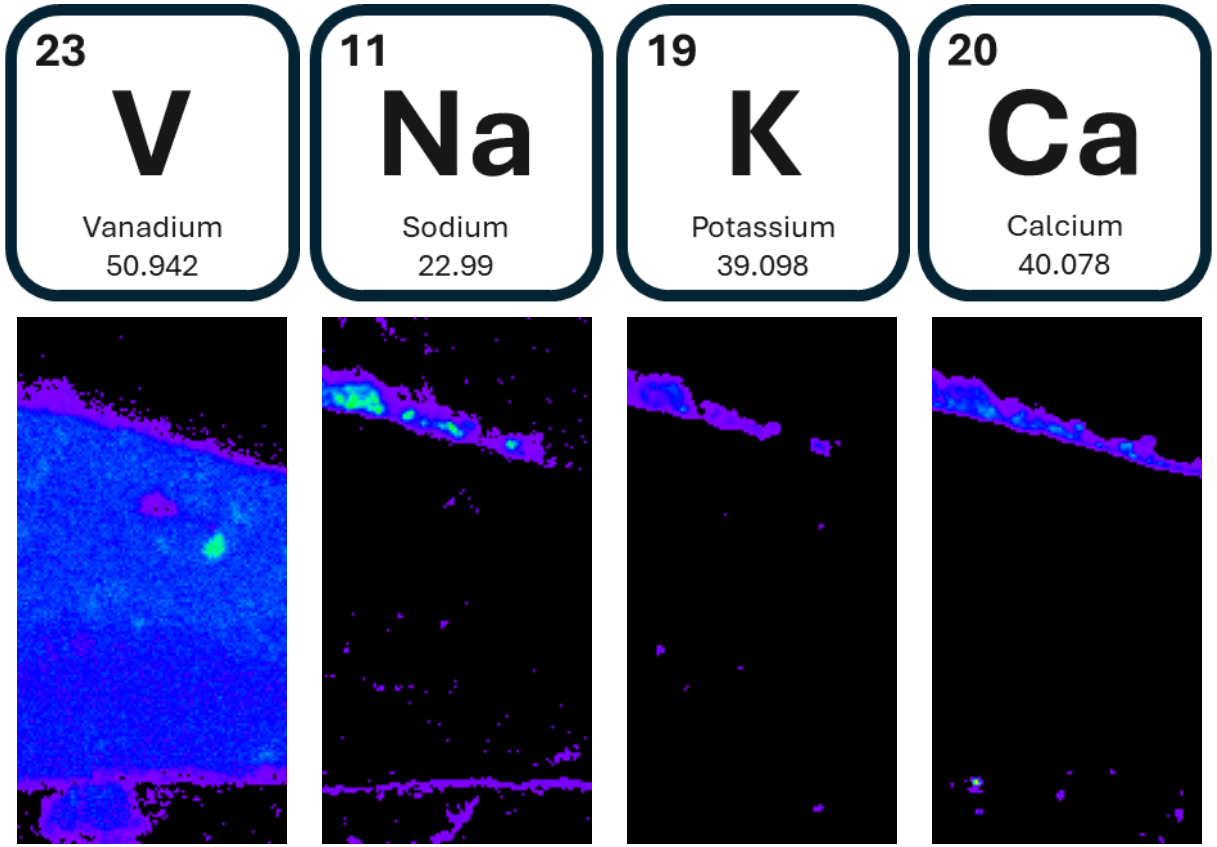
0 8%wt

Na and K interactions with V-SCR are very different compared to Cu/Zeolite SCR, but Ca effect is similar

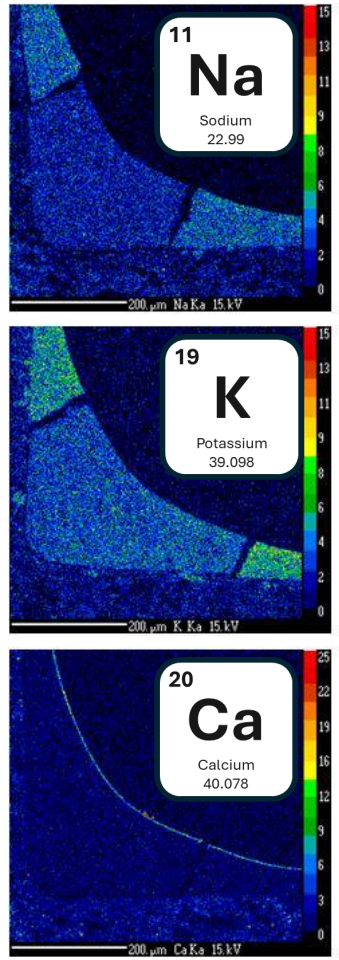


8 weeks
7/8 L





0 8%wt



Cu/Zeolite SCR

Bulk elemental analysis shows increasing metal content with operation

ICP-OES for bulk elemental analysis

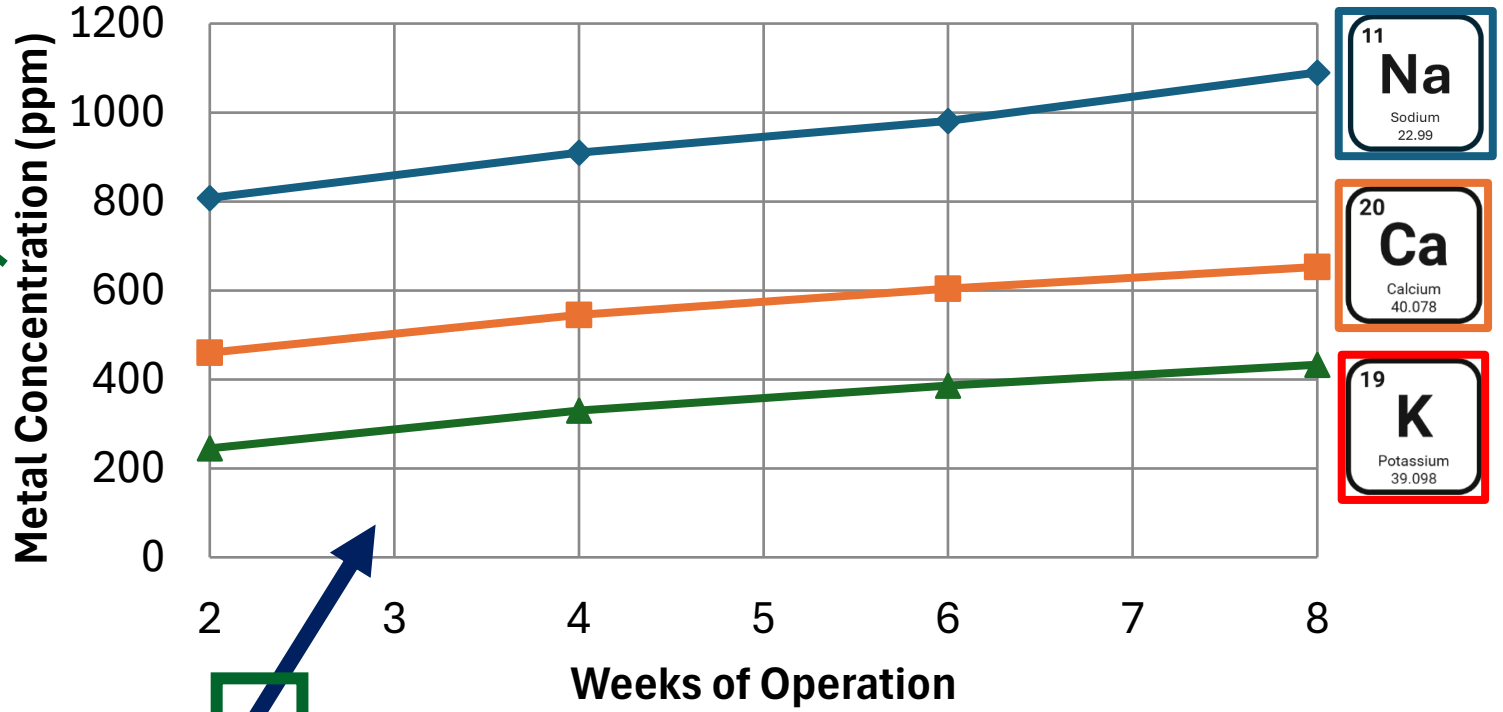


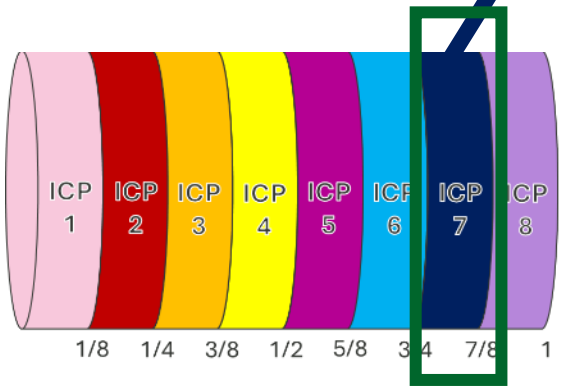
Crush

Dissolve

Analyze

20 Ca Calcium 40.078 | 19 K Potassium 39.098 | 16 S Sulfur 32.065 | 11 Na Sodium 22.99





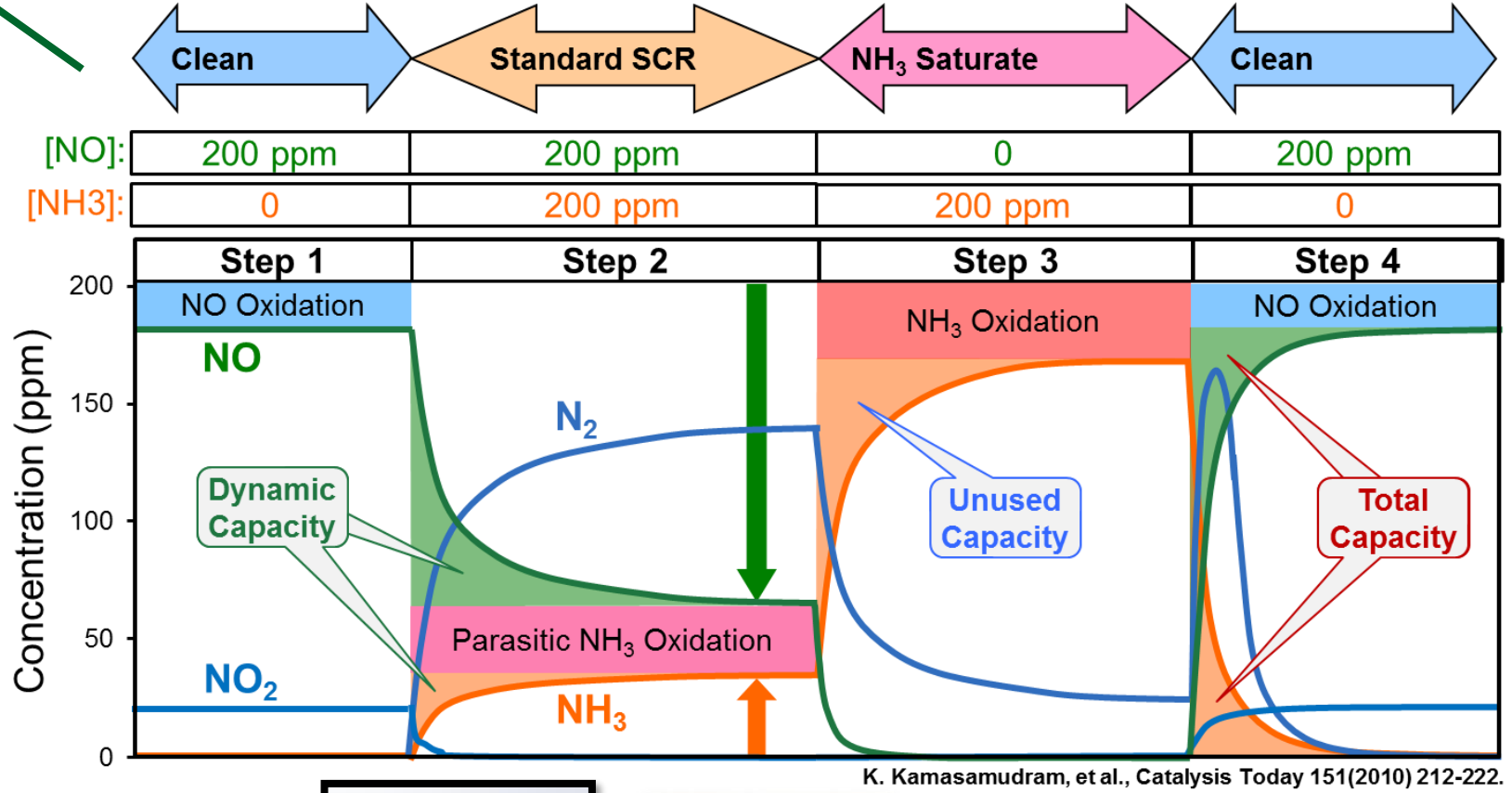
- At the 7/8 position, the bulk elemental analysis shows the increasing metal content
- General trends from ICP confirmed

Flow reactor evaluation of full-length core after 2- and 8-weeks

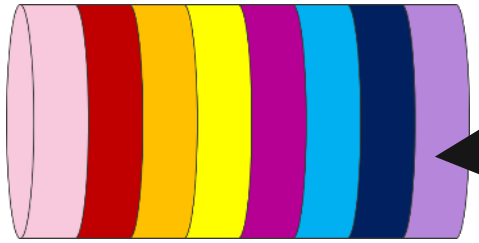
Initial flow reactor evaluation of full core

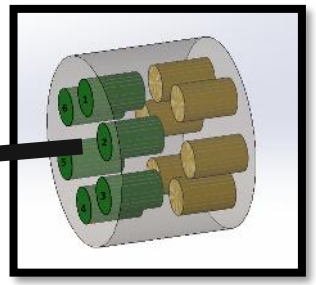






K. Kamasamudram, et al., Catalysis Today 151(2010) 212-222.



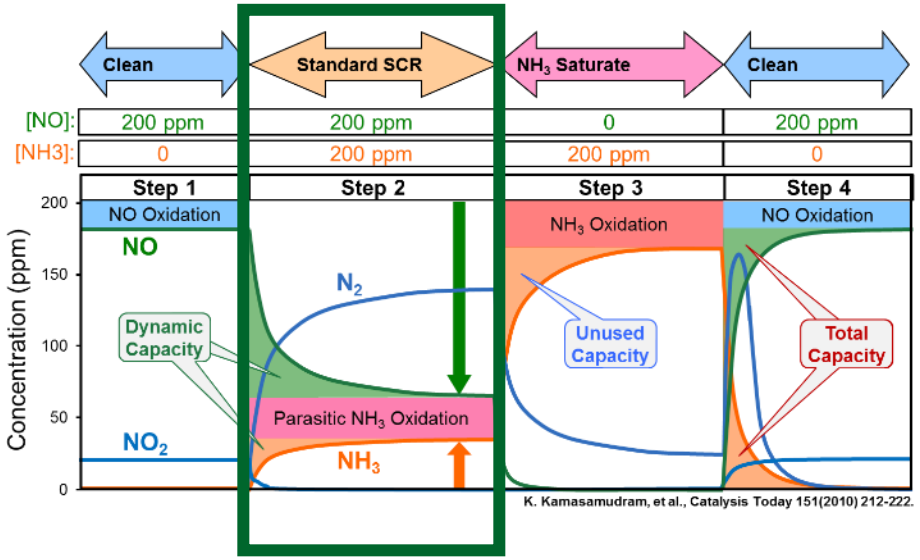




20x75 mm core from FRONT section evaluated at 40,000 h^{-1} GHSV

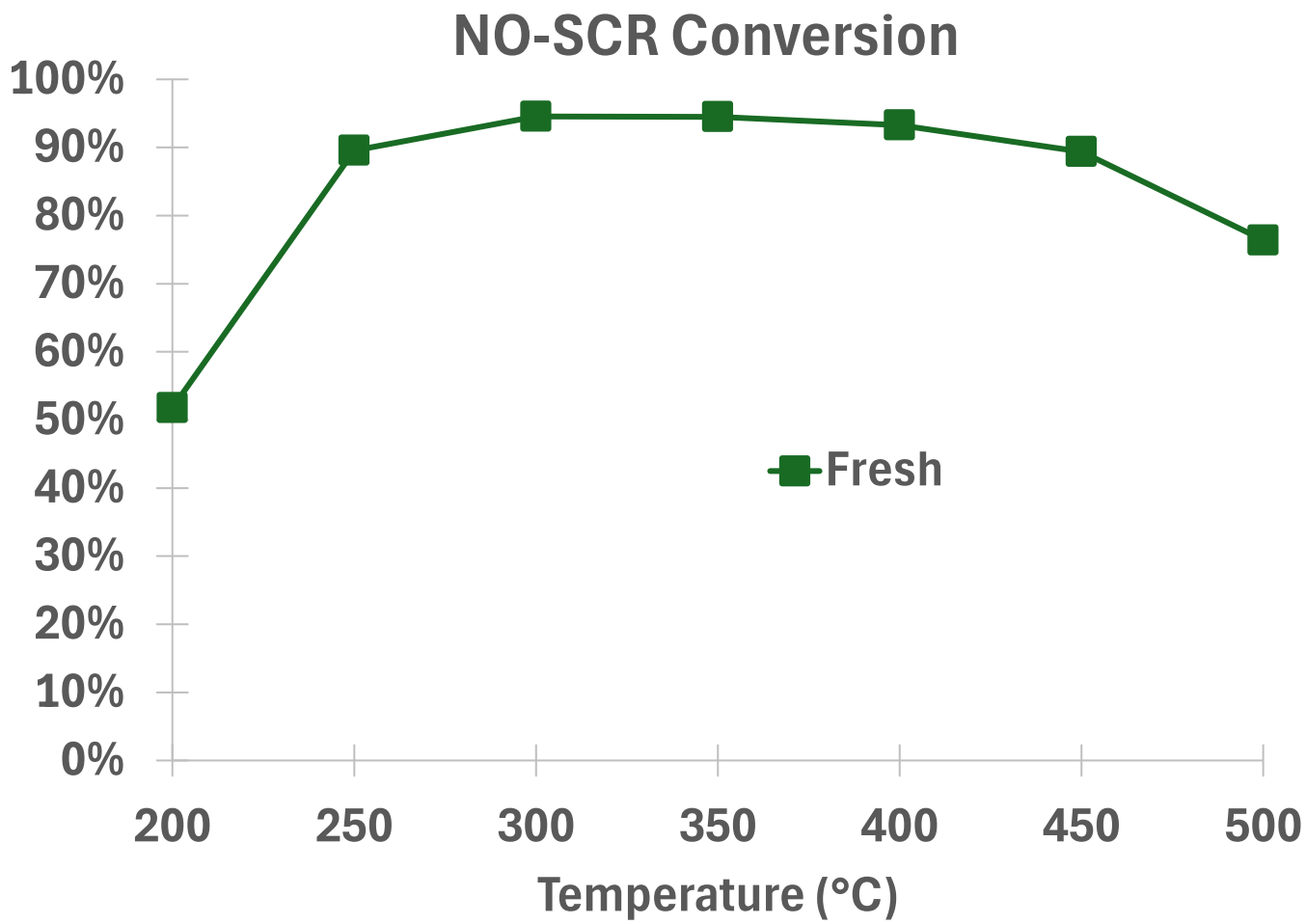
GHSV: Gas Hourly Space Velocity

NO reduction during Standard SCR on Fresh V-SCR sample

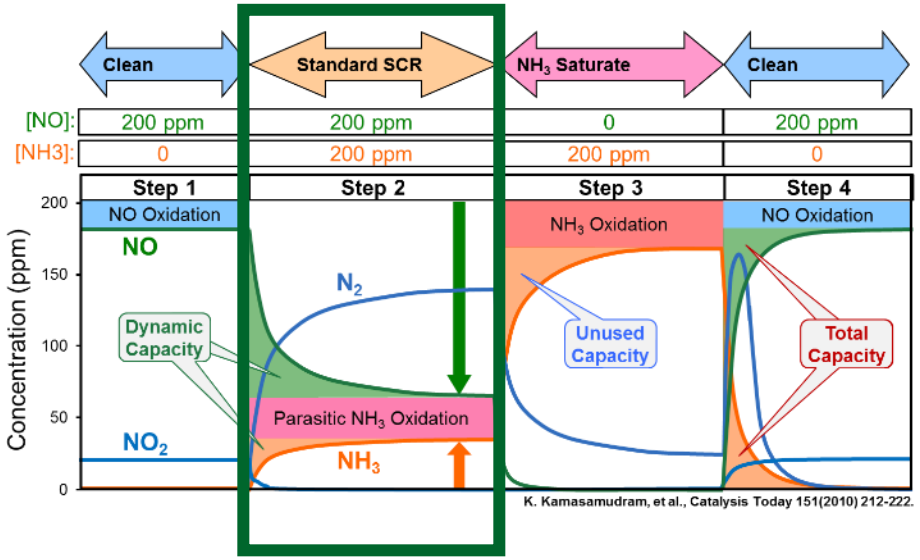


- **Catalysts in genset were loaded Fresh and were not Degreened***

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

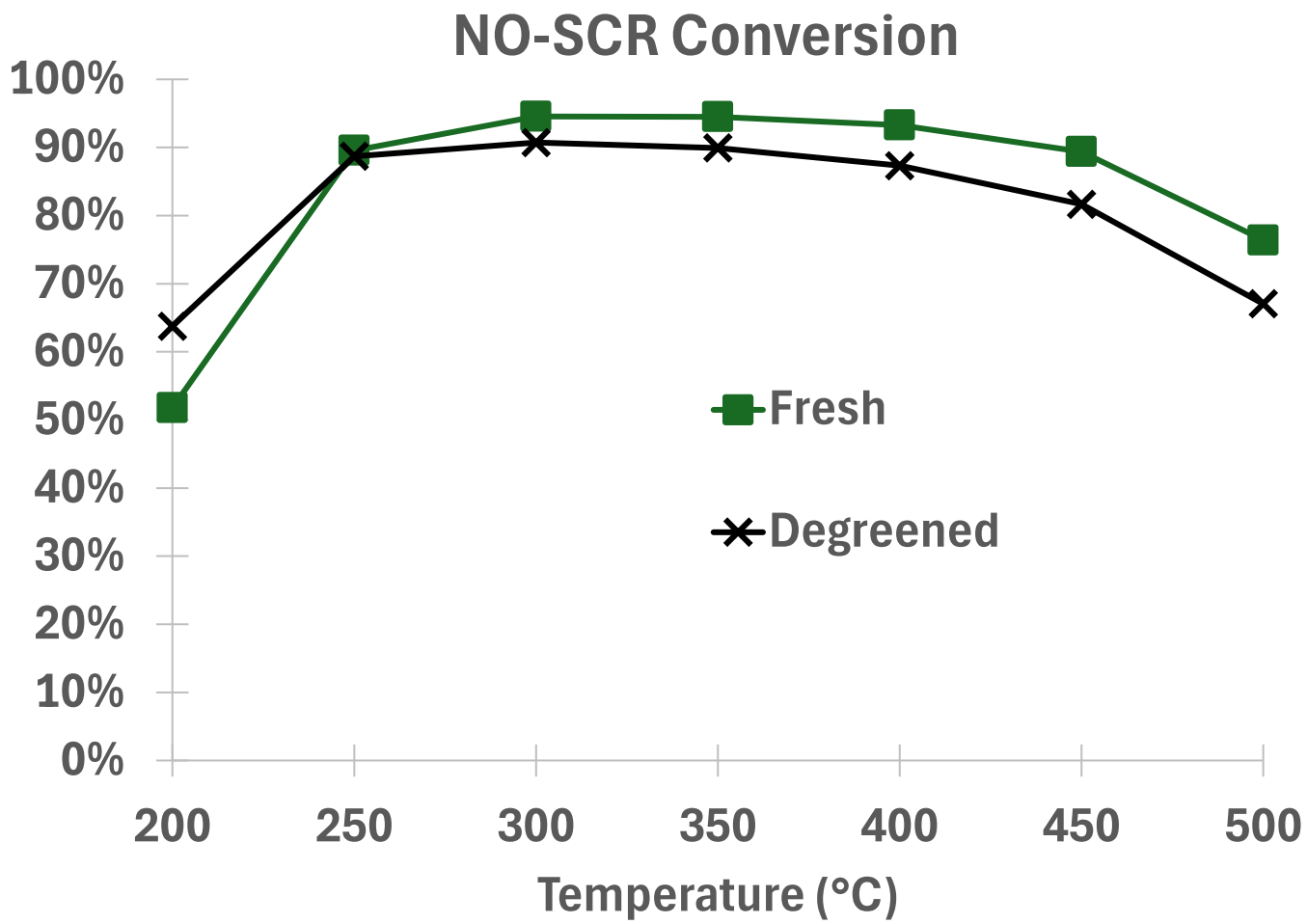


In flow reactor experiments, a hydrothermal “de-greening” is typically performed to stabilize reactivity

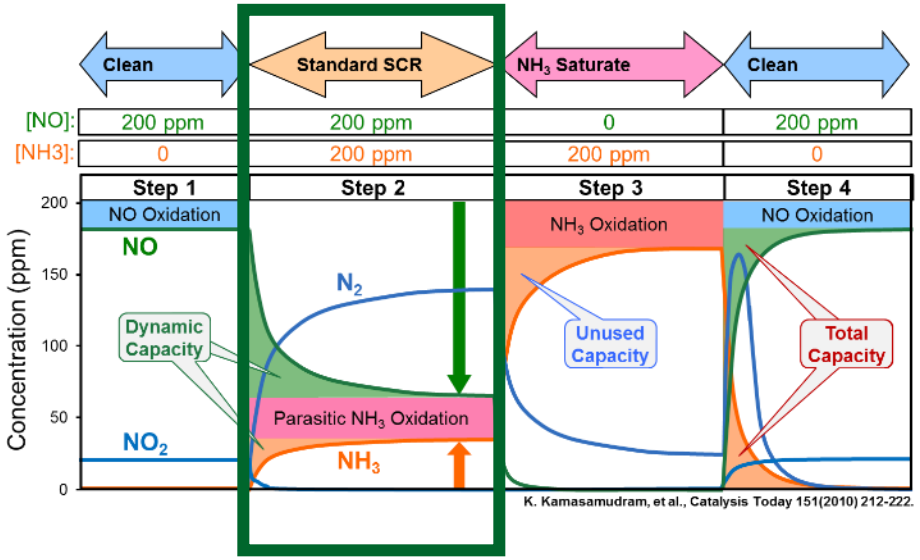


- **Catalysts in genset were loaded Fresh and were not Degreened***
- **Degreened* sample has lower performance above 250 °C**

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

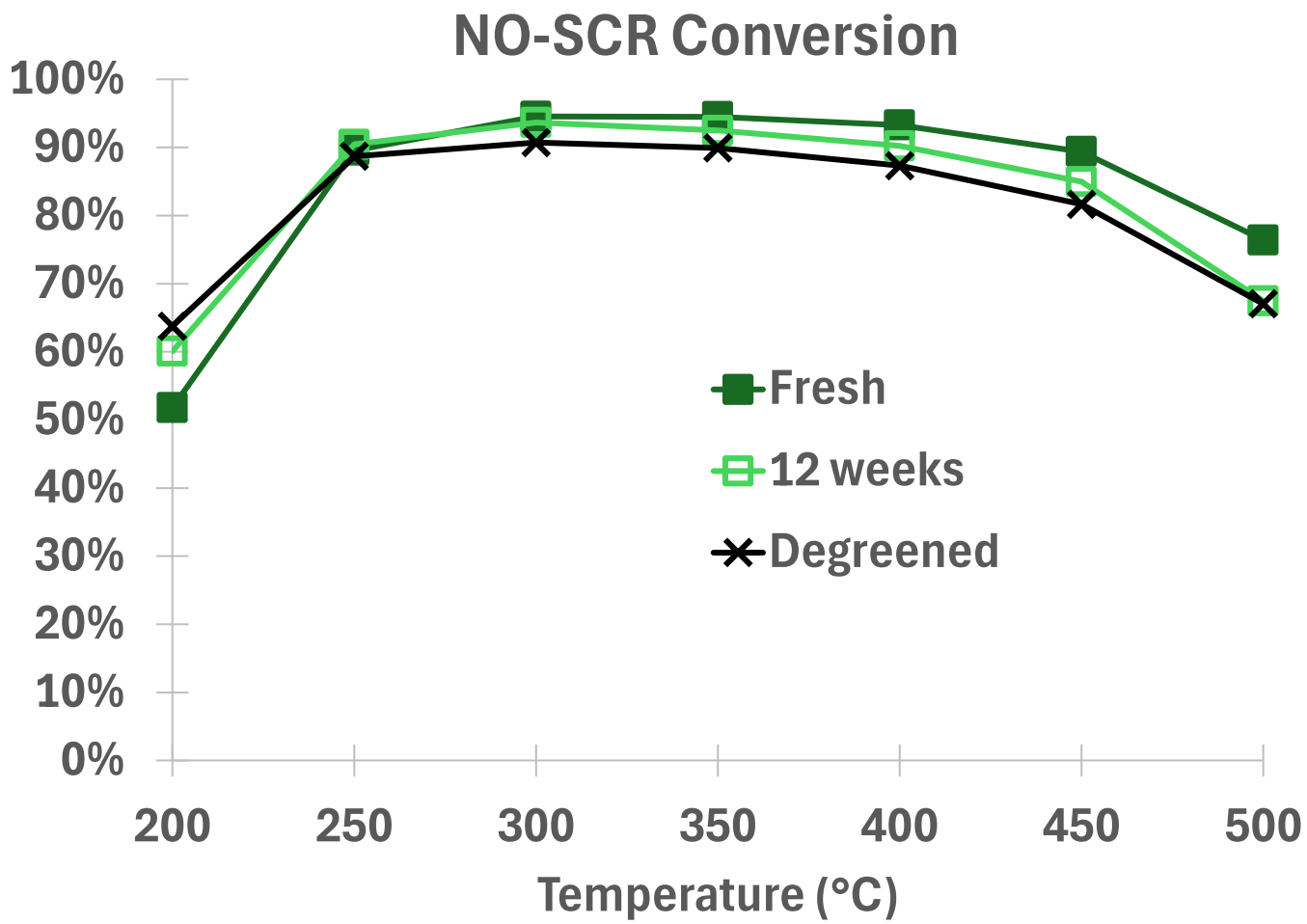


Overall, NO reduction shows minimal degradation during SCR

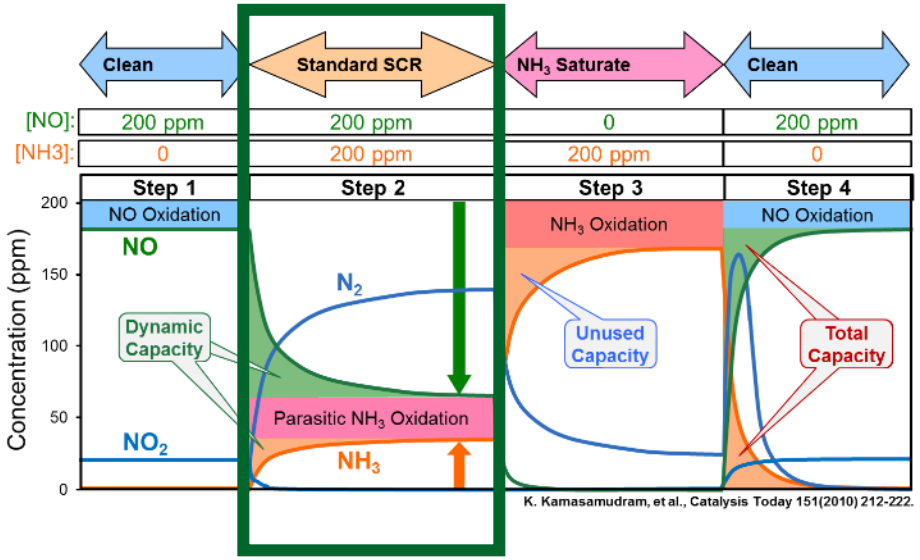


- 12-week aged sample has reactivity in between Fresh and Degreened*
- Overall, degreened sample shows lowest reactivity

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

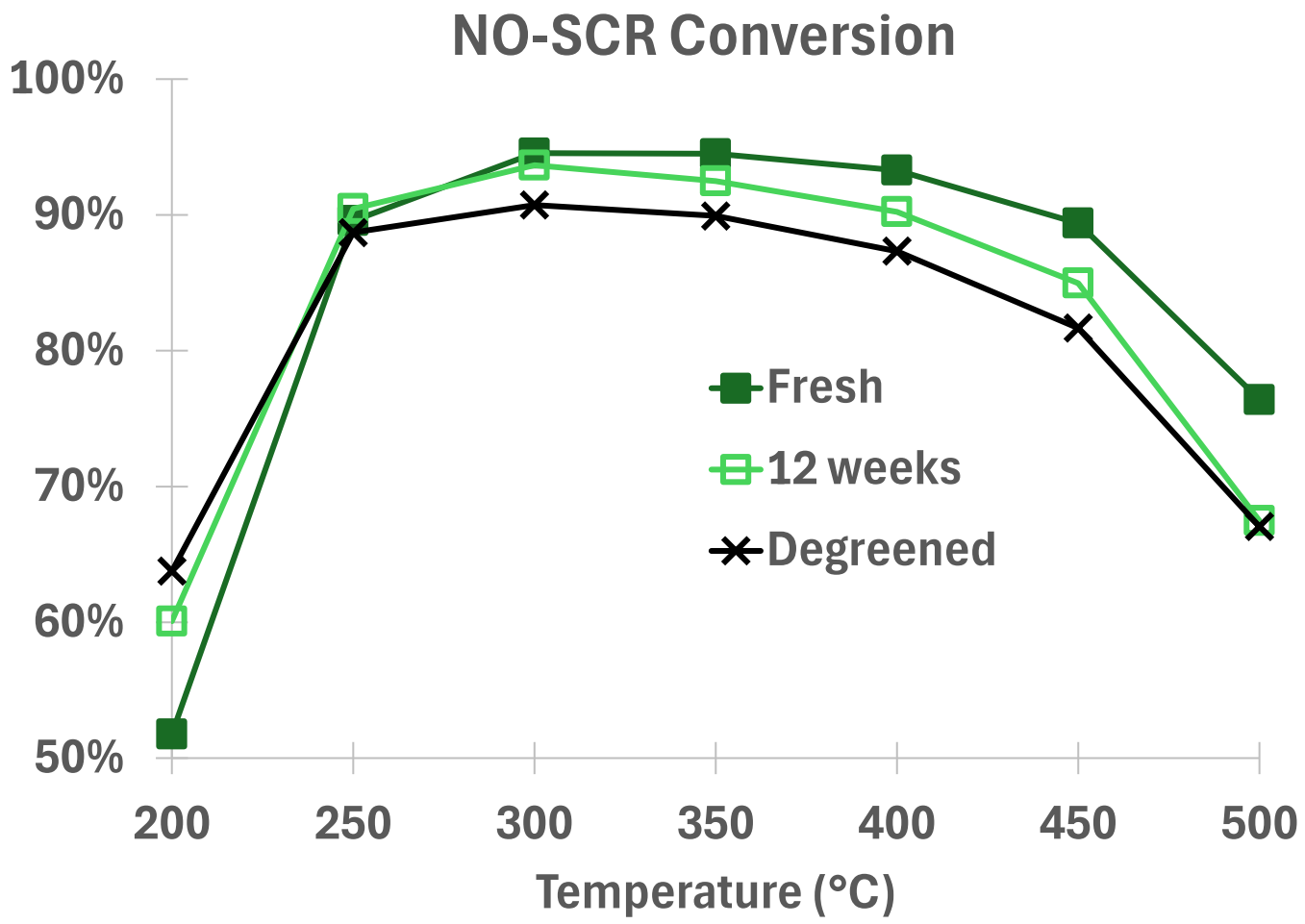


Overall, NO reduction shows minimal degradation during SCR

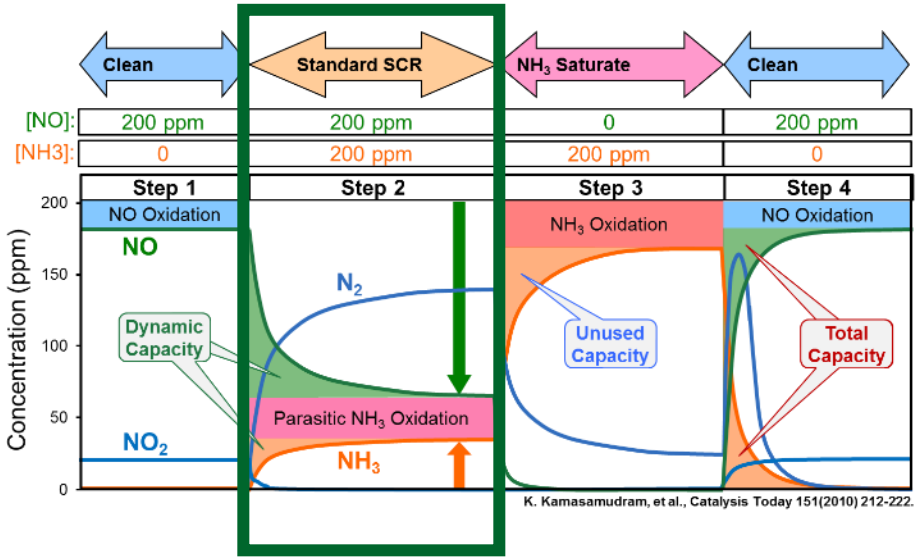


- 12-week aged sample has reactivity in between Fresh and Degreened*
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** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

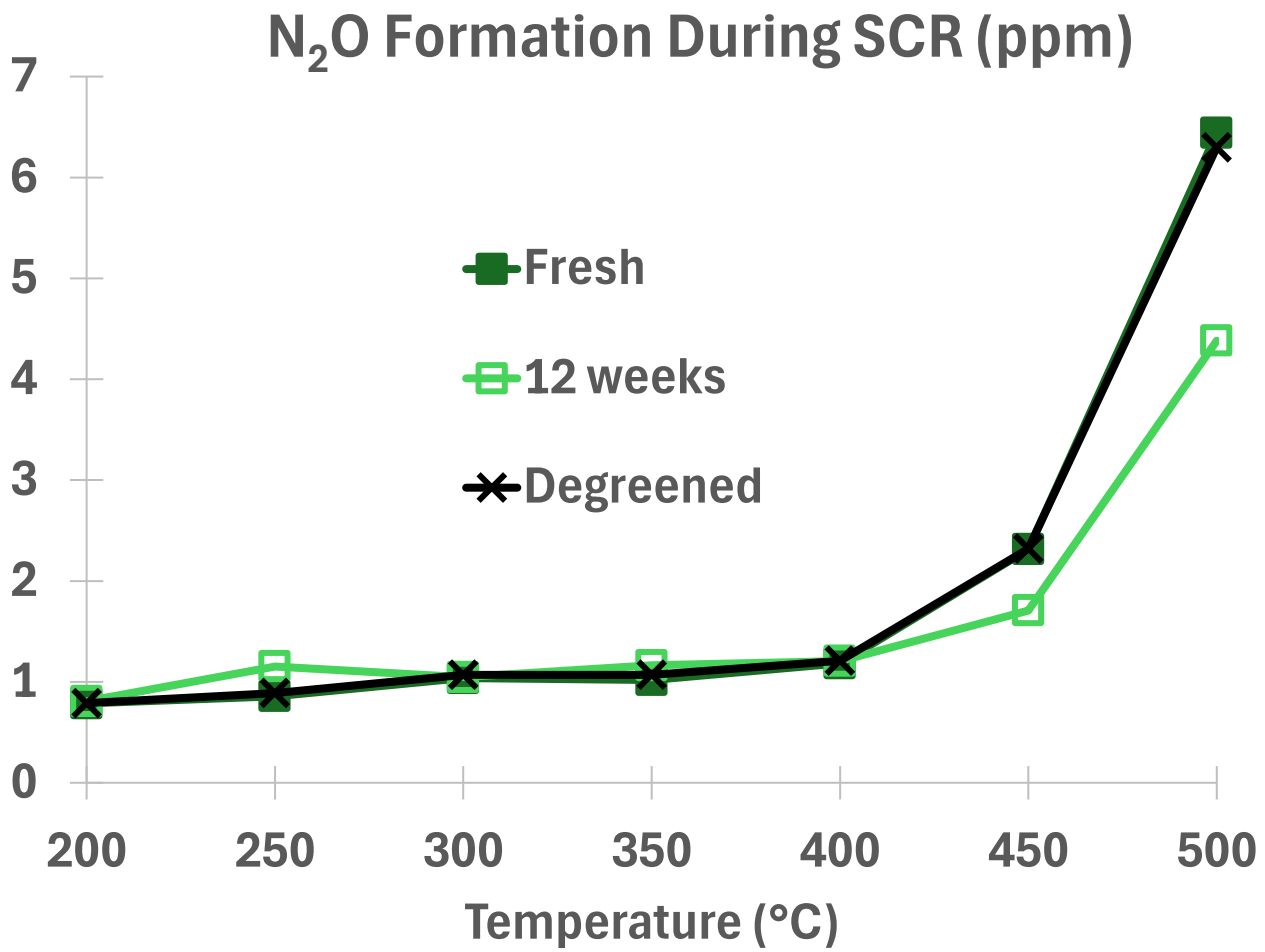


No change in N_2O formation

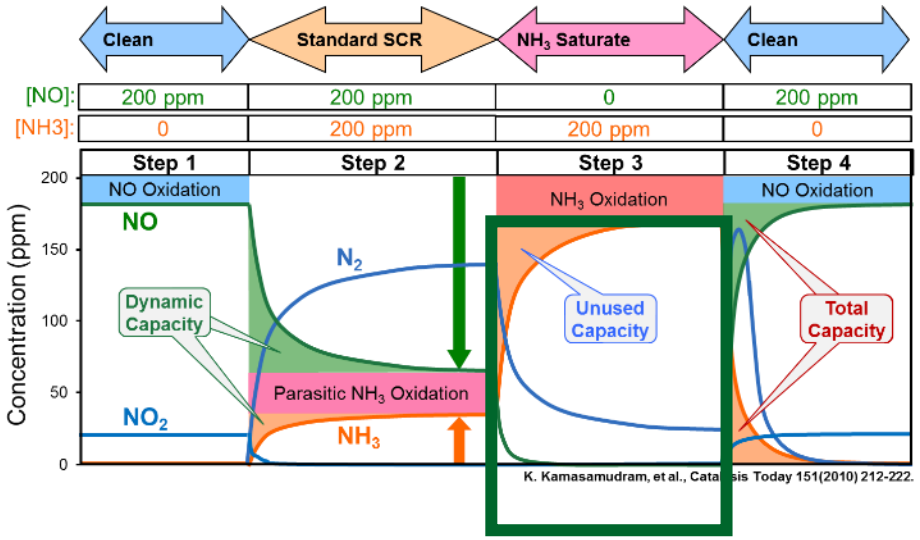


- **No difference between Fresh and Degreened* sample**
- **Slightly lower N_2O formation in 12-week aged sample**

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

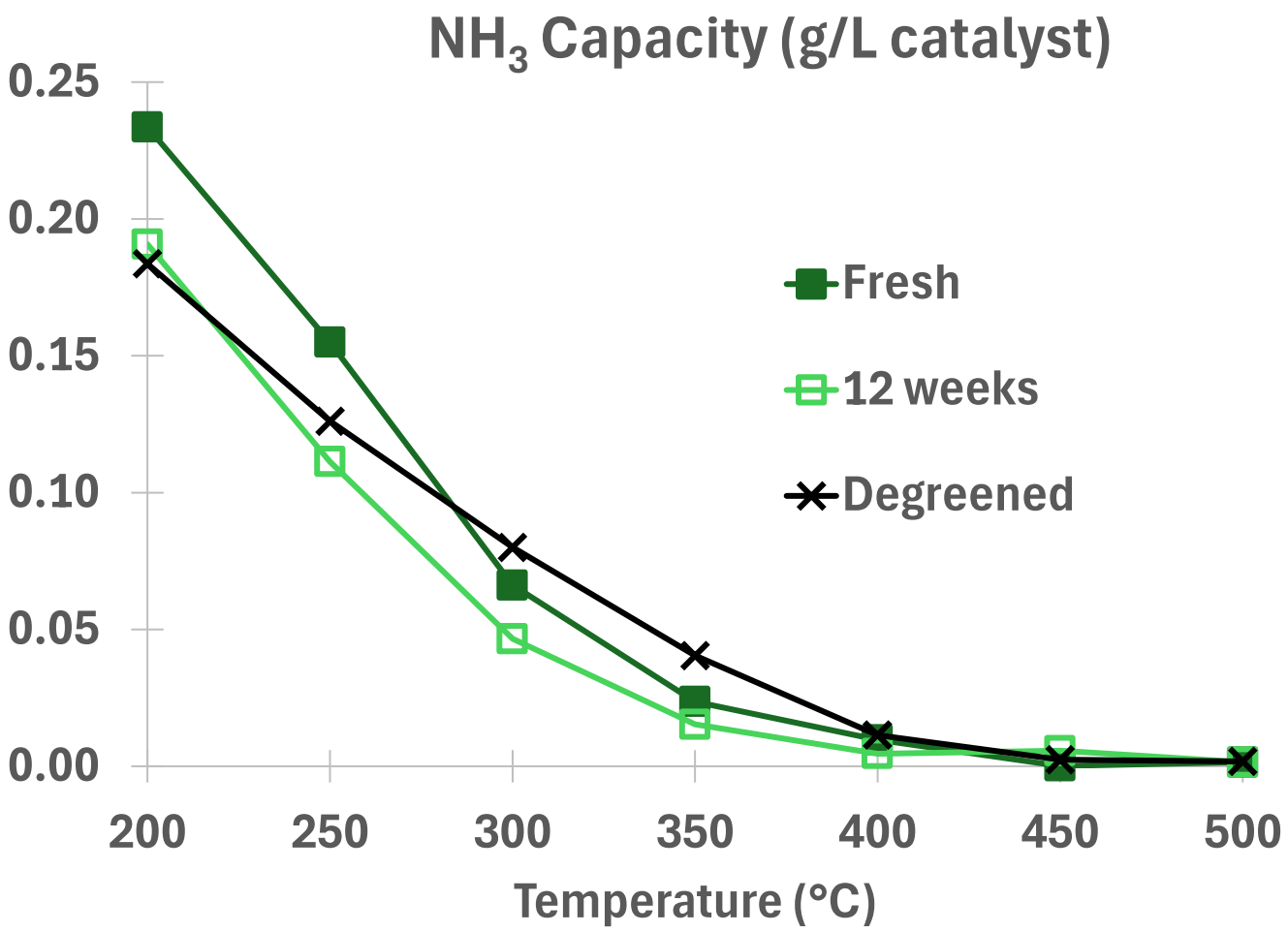


NH_3 capacity shows minimal degradation

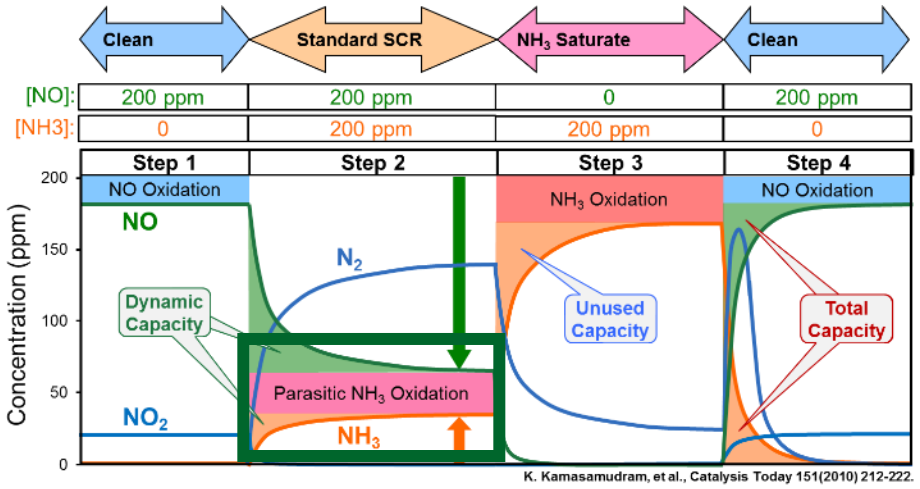


- Slight decrease in 12-week aged sample
- Overall, all samples have similar NH_3 storage capacity

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

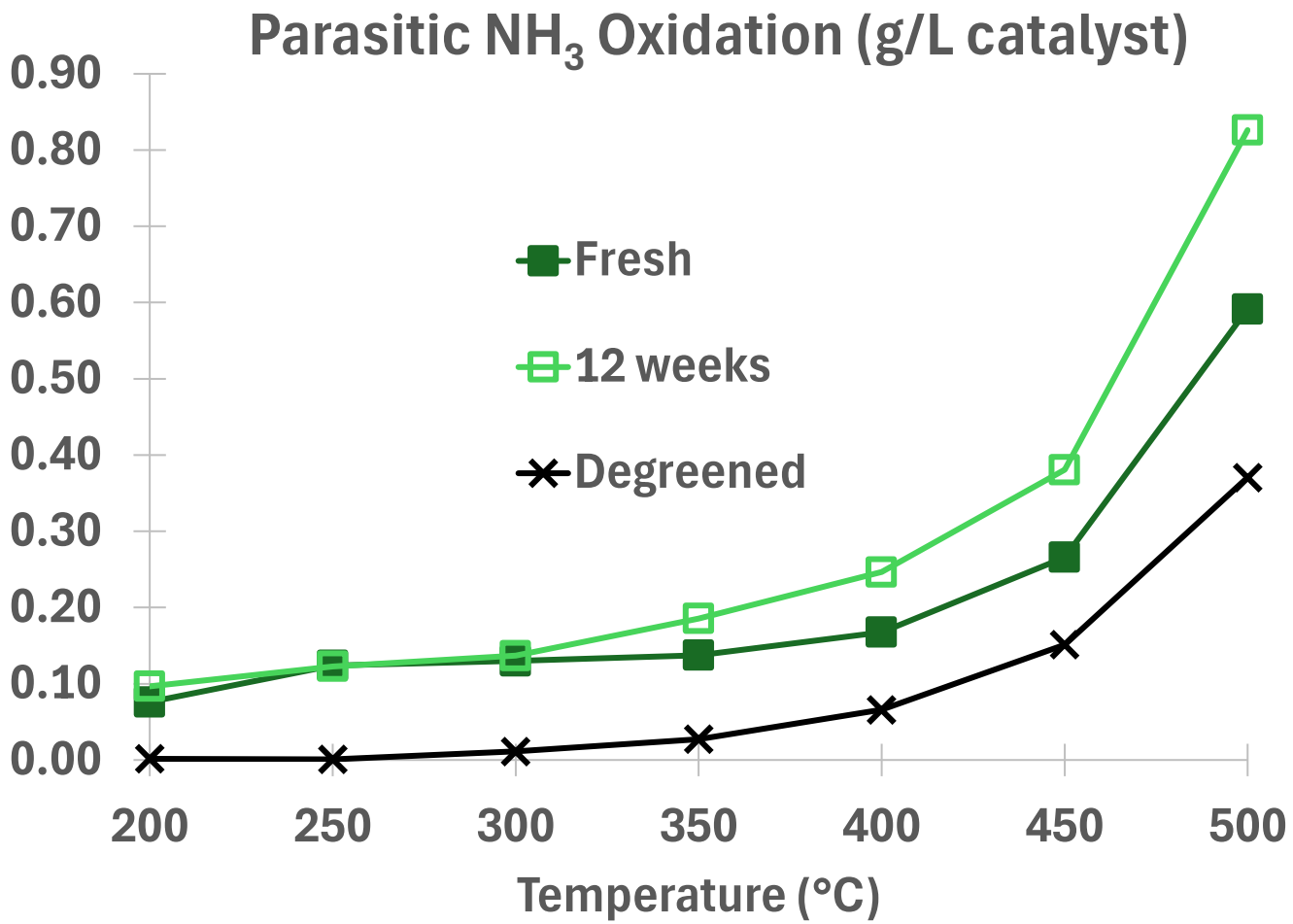


Parasitic NH_3 oxidation shows some indication of impact

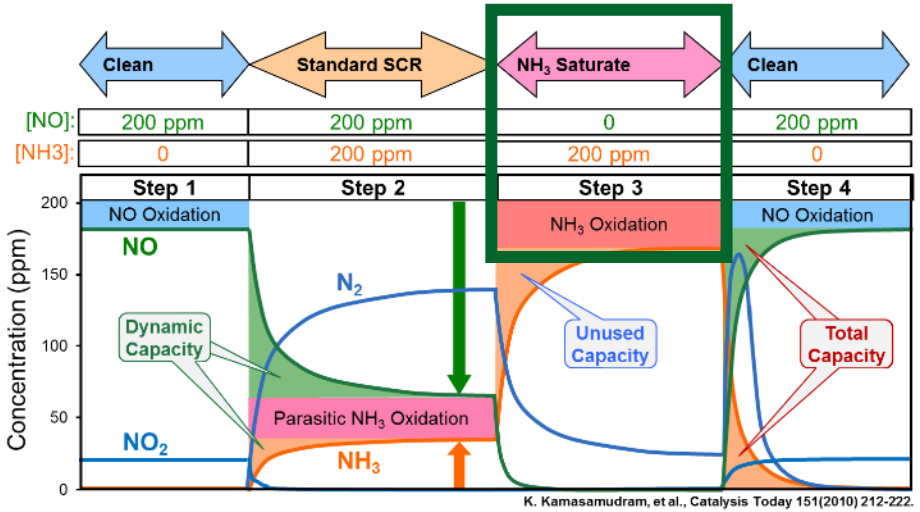


- Step change for Degreened* sample compared to others
- 12-week aged sample does she increase above 300 ℃

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

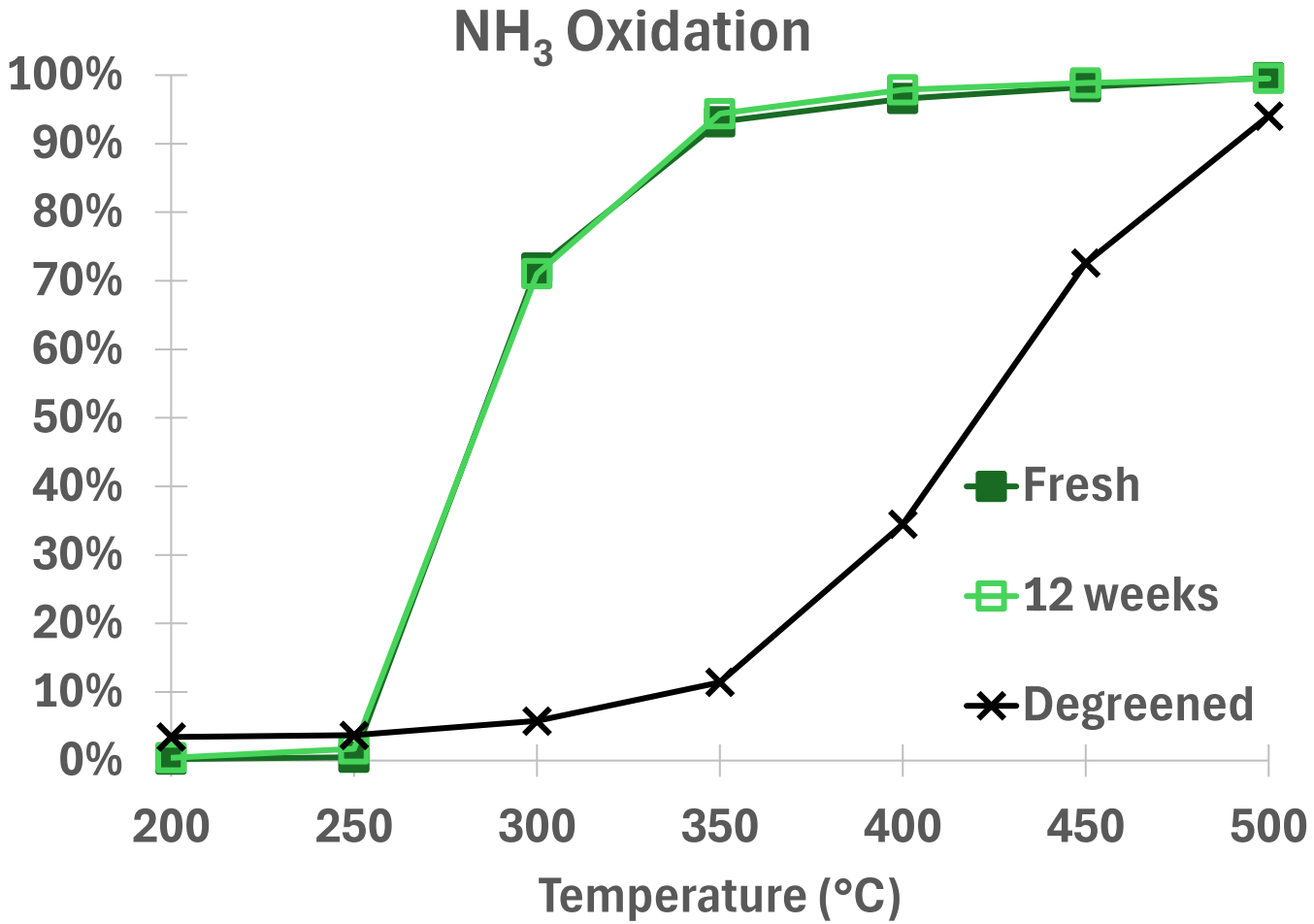


NH_3 oxidation in the absence of NO is significantly higher, but progression not observed



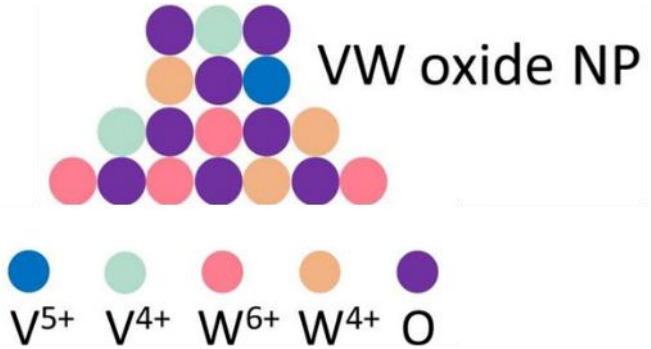
- Degreened* sample very different
- 12-week & Fresh samples identical
- Further investigation to understand differences caused by degreening

** - Degreened catalyst heated to 550°C for 4h in 10% O_2 and 6% H_2O (balance N_2)*

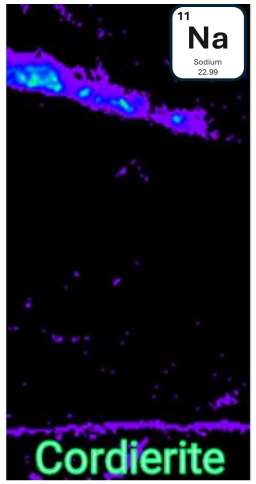


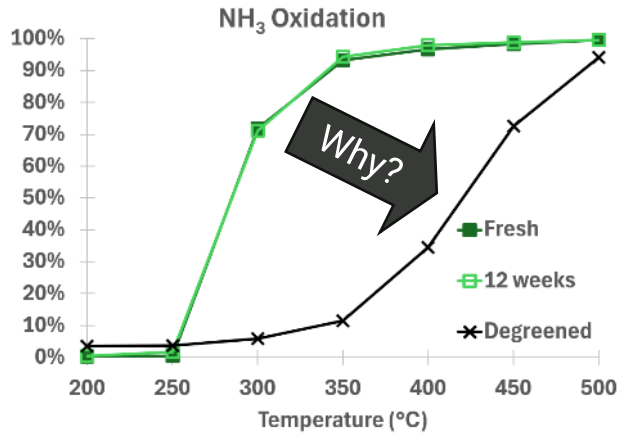
Remaining challenges are focused on understanding V-SCR NH_3 oxidation and determining fuel filter issues

V-SCR: V_2O_5 -WO_3/TiO_2



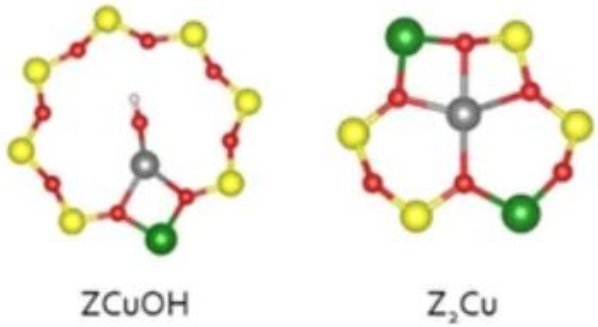
M.J. Lee et al., Appl. Catal. B 378 (2025) 125583.

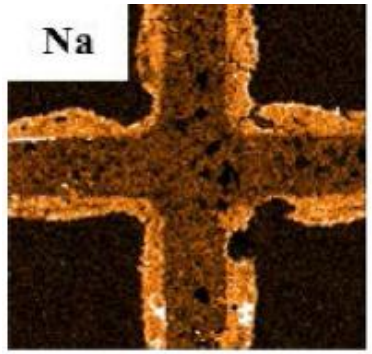




Cu/Zeolite

Does ion exchange of single Cu atom, make it more susceptible to alkali metal contaminants?

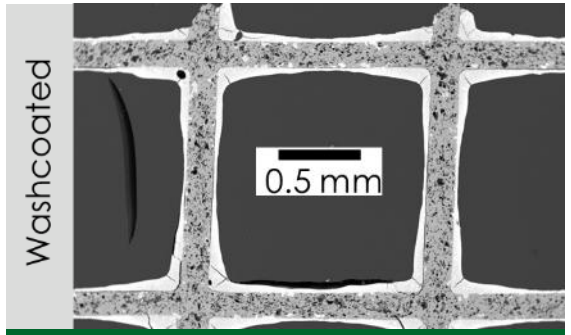




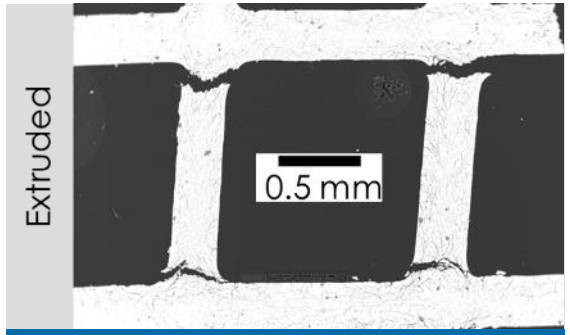
L.N. Wilcox, et al. ACS Catalysis 14:5 (2024) 3647-3663.

- **Why is interaction with V_2O_5 -WO_3/TiO_2 so minimal?**
- **Is it oxidation state incompatibility? →Na^+ & K^+ vs. V^{5+}**
- **Can interaction increase at higher temperatures?**
- **What if the DOC is in front of V-SCR?**

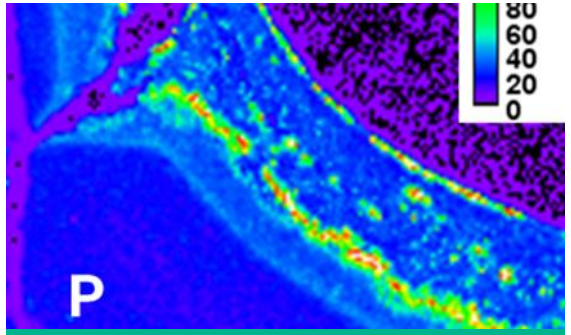
Proposed Future Research



Complete characterization of washcoated distributive effects aged samples



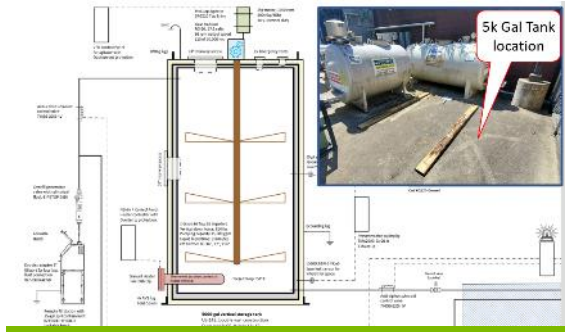
Complete extruded Na+K+Ca exposure



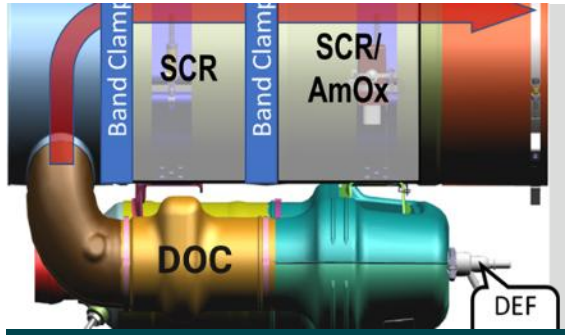
Implement fuel-borne P-study to highlight differences with lubricant P in V-SCR & Cu-SCR



Fuel filter analysis and characterization to identify key plugging components



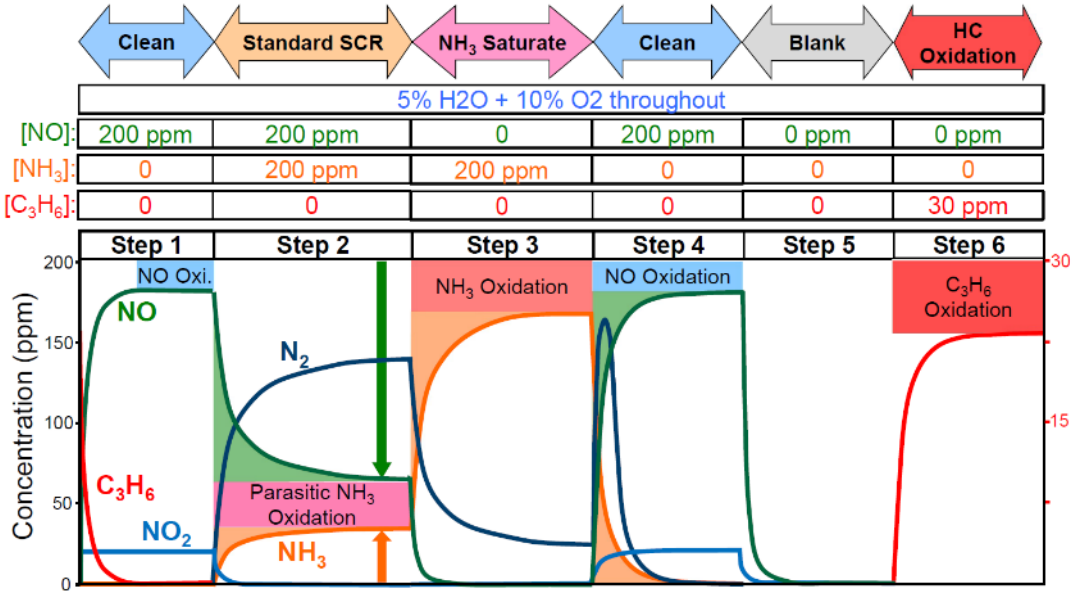
Install insulated, heated, agitated, and recirculating B100 tank (raising funds now)



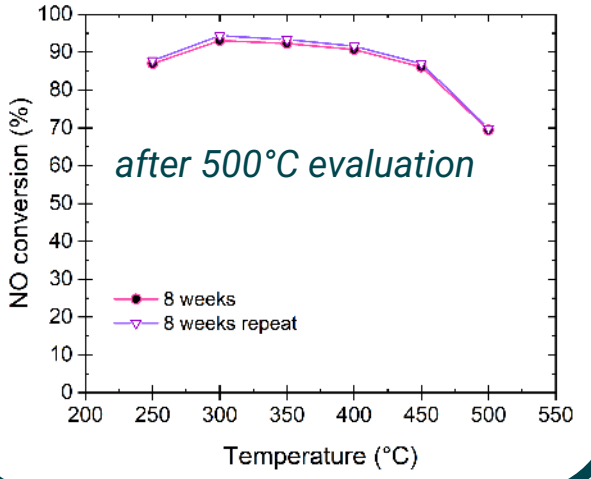
Work with industry to identify different catalyst configurations to study

Technical back-up slides

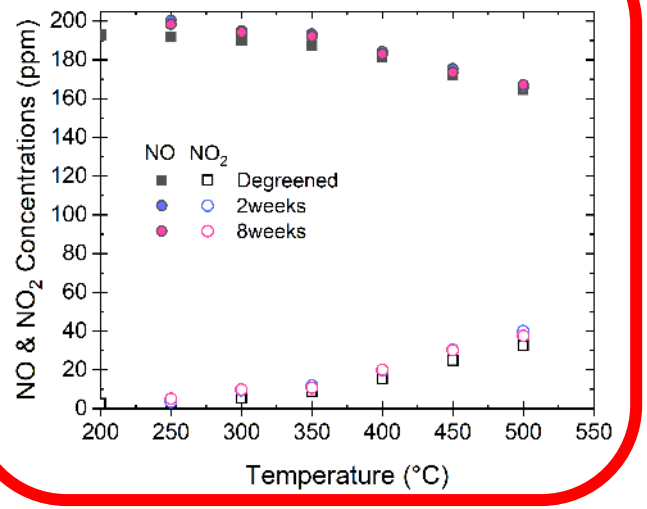
Other observations from the performance characterizations



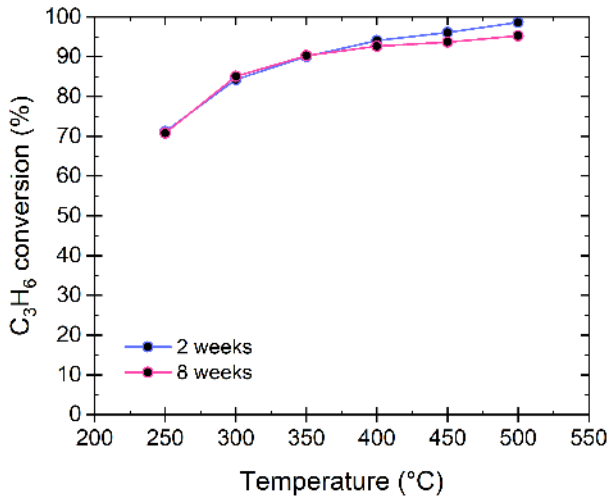
Repeat of 8-week



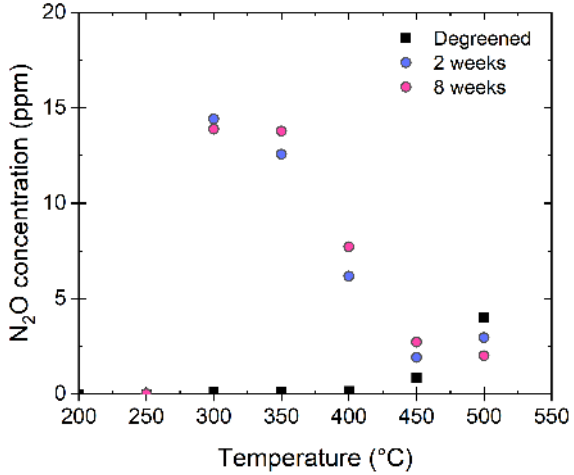
NO oxidation

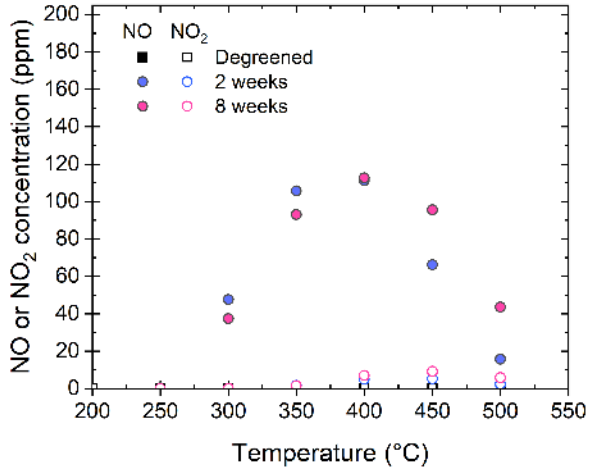


Propylene (C_3H_6) oxidation over V-SCR on B100-aged samples

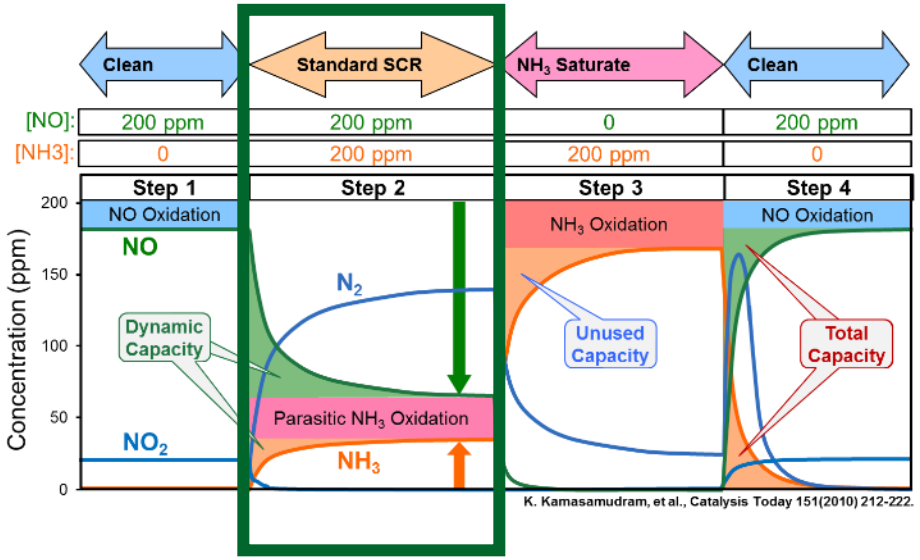


N-based products during NH_3 oxidation



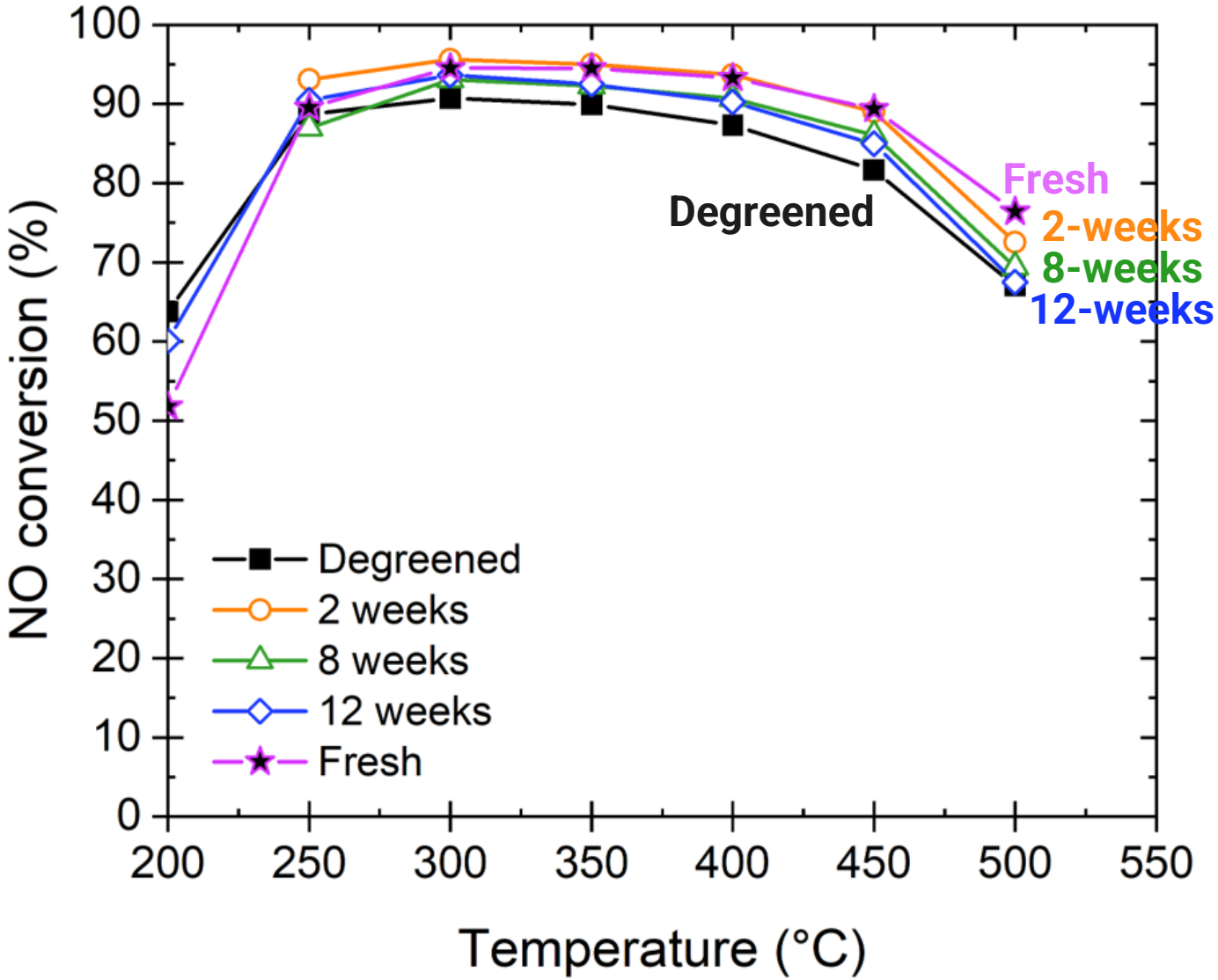


Overall, NO reduction shows minimal degradation during SCR

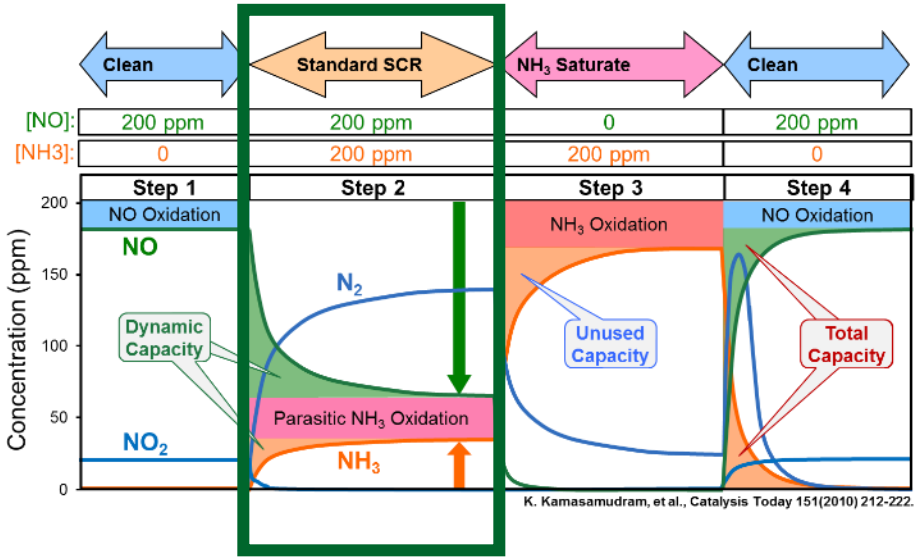


- **Progression observed from 2- to 8-weeks of aging; especially at 250 °C**
- **Overall, aged samples have reactivity on par with degreened* sample**

** - Degreened catalyst heated to 550°C for 4h*

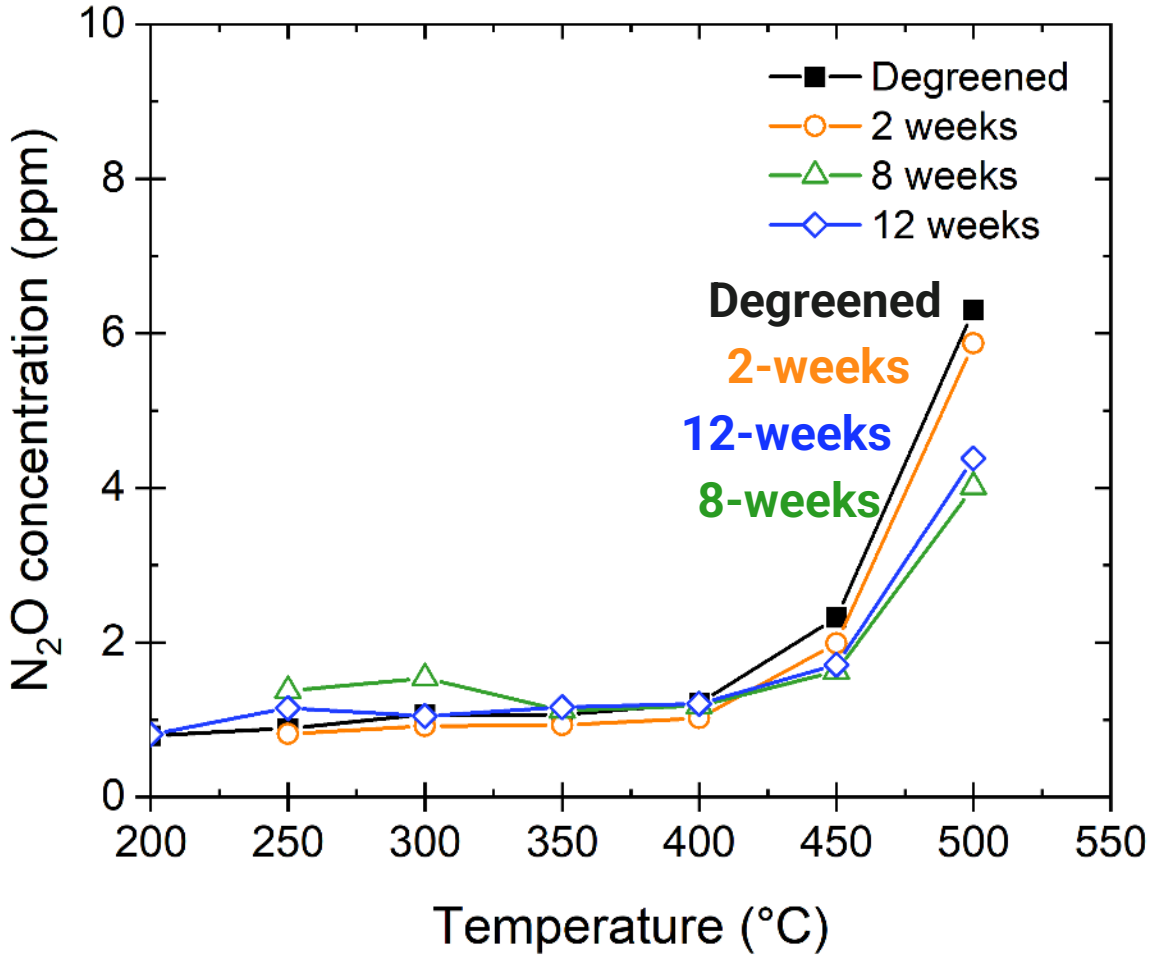


No change in N_2O formation

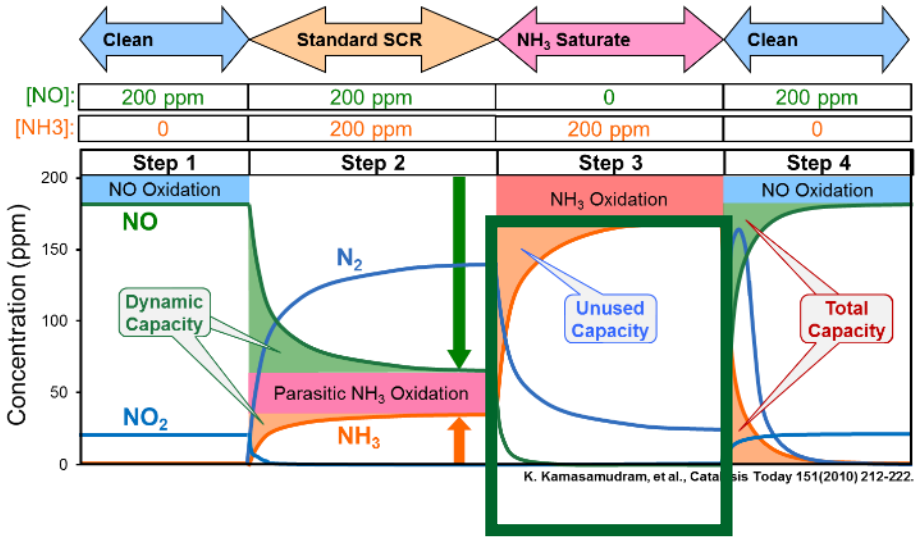


- **No difference compared to degreened sample**

** - Degreened catalyst heated to 550°C for 4h*

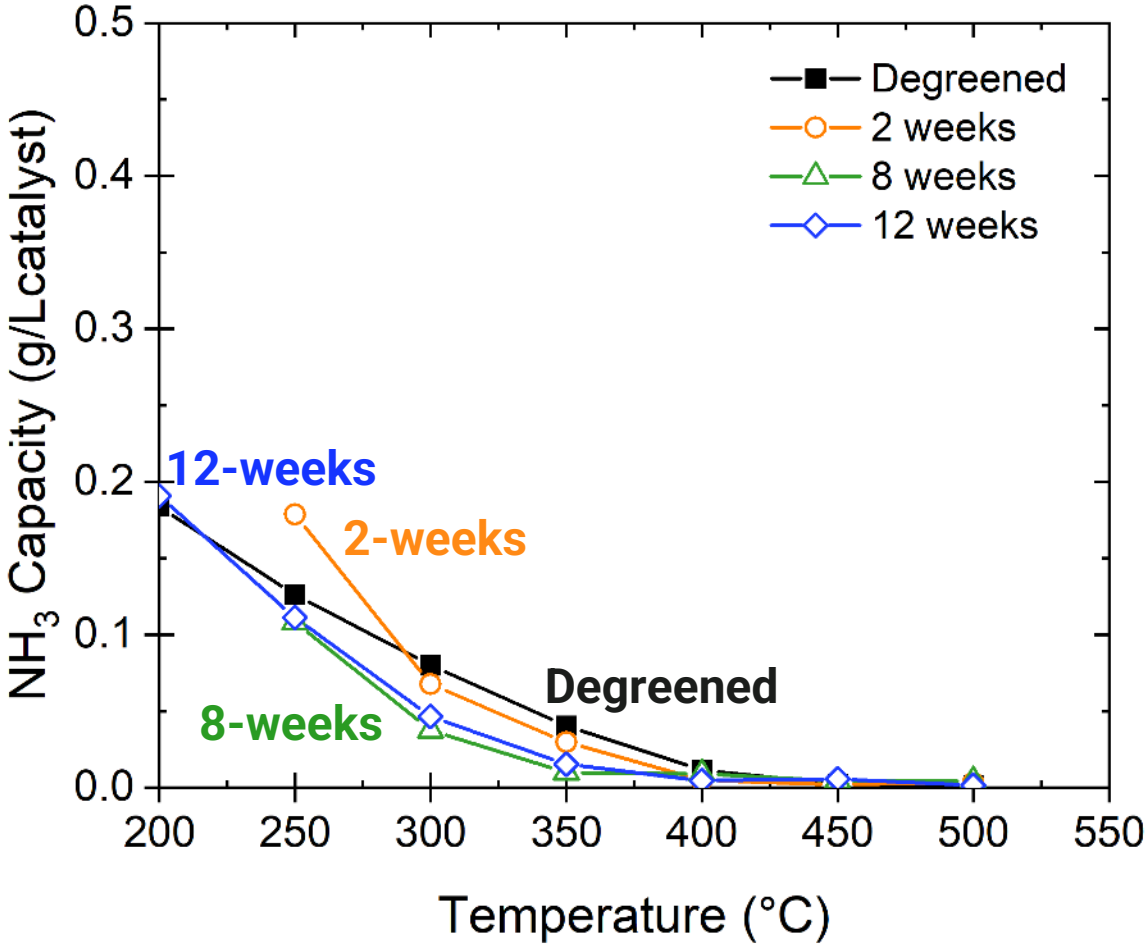


NH_3 capacity shows minimal degradation

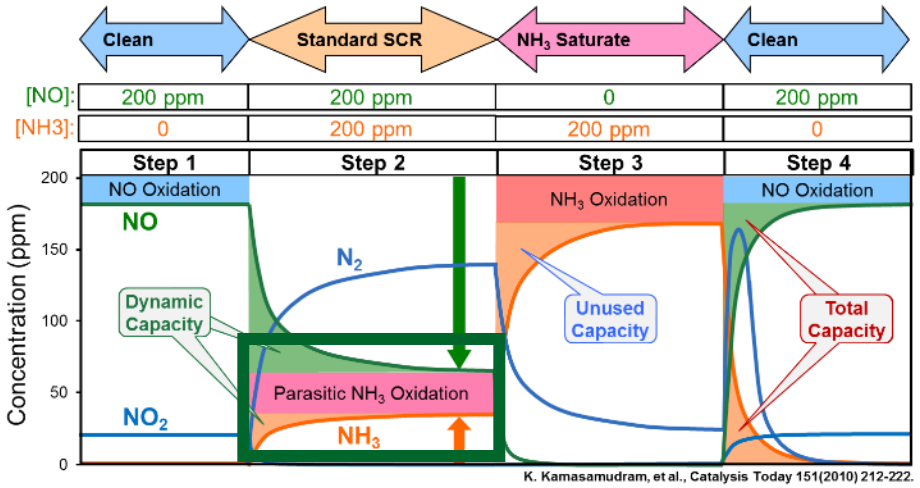


- **Progression of potential deactivation observed from 2- to 8-weeks**
- **Overall, aged samples have reactivity on par with degreened* sample**

** - Degreened catalyst heated to 550°C for 4h*

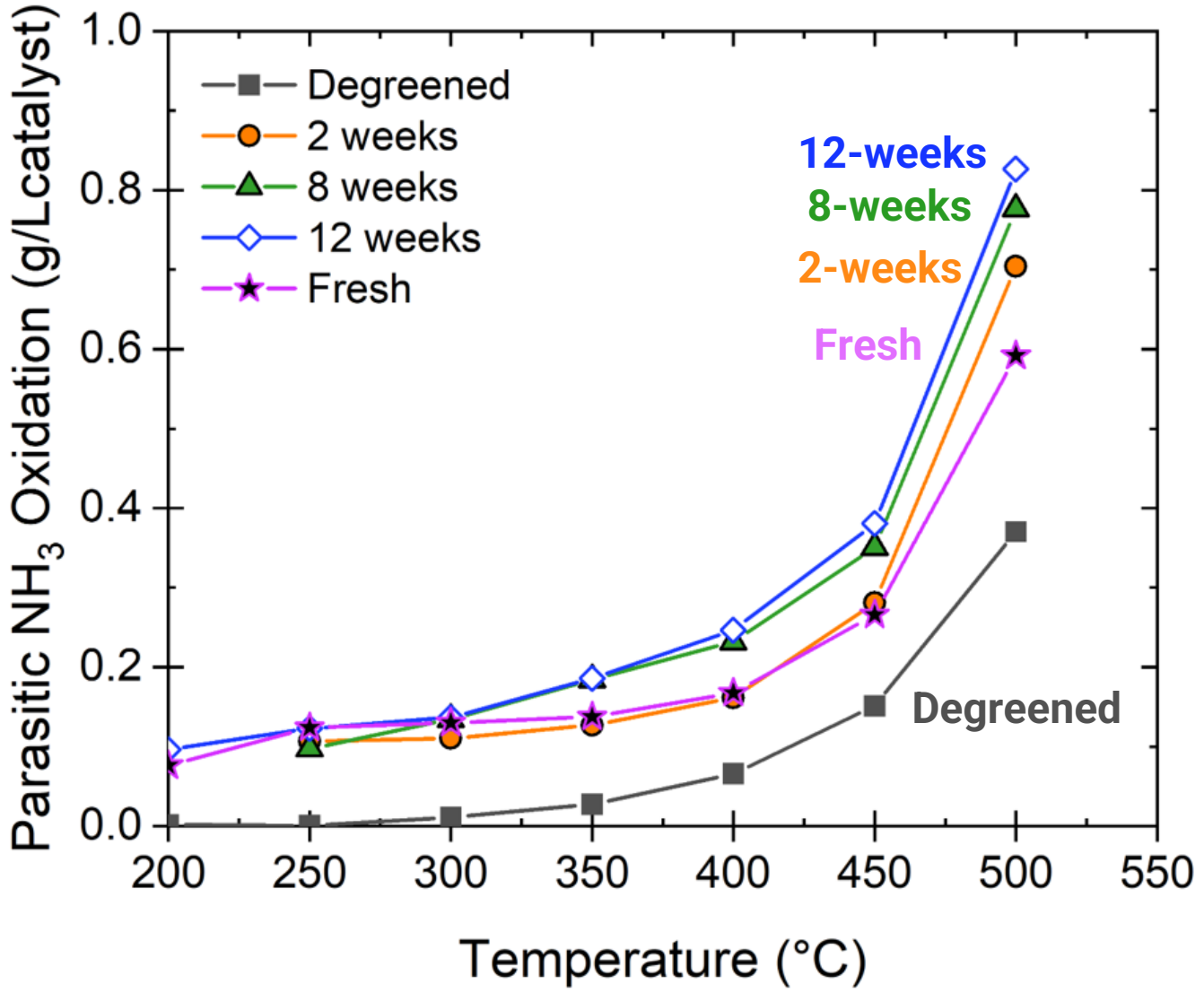


Parasitic NH_3 oxidation shows some indication of impact



- More of a step change for the B100 samples compared to degreened
- Worth further investigation

** - Degreened catalyst heated to 550°C for 4h*



Summary

- **Relevance:**
  - Understanding biodiesel impacts on off-road emissions control is needed to enable industry acceptance
  - Metals in biodiesel are a significant concern hindering adoption and CC-SCR could be particularly vulnerable
- **Approach:**
  - Systematic CC-SCR B100-Fueled Engine Aging with Na+Ca+K at 4 ppm (5x the field average for B100)
  - V-based CC-SCR with removal of cores in 2-week intervals followed by performance and materials characterization
- **Technical Accomplishments:**
  - Completed 12-week/full useful life equivalent exposure on washcoated V-SCR
  - Identified Na, K, and Ca interactions with V-SCR are minimal in materials characterization; more ash like behavior
  - Initial performance evaluations indicate minimal loss in SCR reactivity; indication of increased NH_3 oxidation
- **Future* Work:**
  - Complete characterization of washcoated distributive effects aged samples out to 12-weeks;
  - Evaluate interactions with extruded V-SCR, and implement study on fuel-borne P; include Cu-Zeolite cores in studies
- **Collaborations:**
  - Primary Technical Advisors: Cummins, Caterpillar, Clean Fuels Alliance America (CFAA)
    - Cummins and Caterpillar have provided funds to support work; CFAA provided biodiesel
  - Other informal communications: NLR, PNNL, SwRI

Collaborations

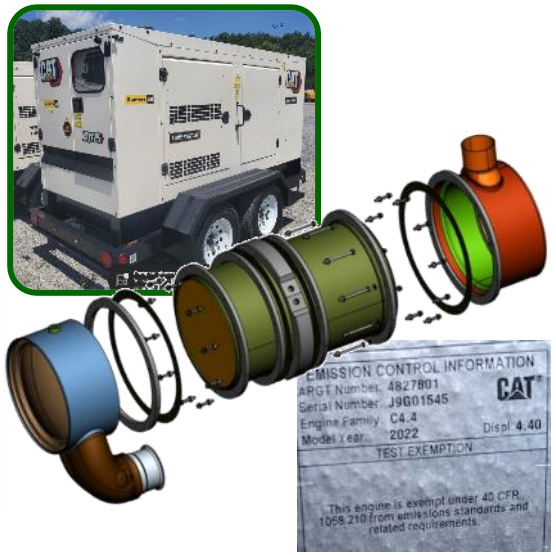
Cummins

- Bi-weekly meetings
- CC-SCR aging model
- Washcoated V-SCR
- Core holder design



Caterpillar

- Bi-weekly meetings
- DAQ & communication
- Extruded SCR samples
- EPA emissions waiver
- Oil sampling program
- Fuel filter analysis



Clean Fuels Alliance America

- Monthly meetings
- Supplied 8000 gallons of B100 biofuel
- Providing input on additives and infrastructure design



Additional

- National Lab of the Rockies (NLR): Additive prep and general discussions
- Southwest Research Institute (SwRI): Additive mixing routines
- Pacific Northwest National Laboratory (PNNL): general catalyst discussions

Summary

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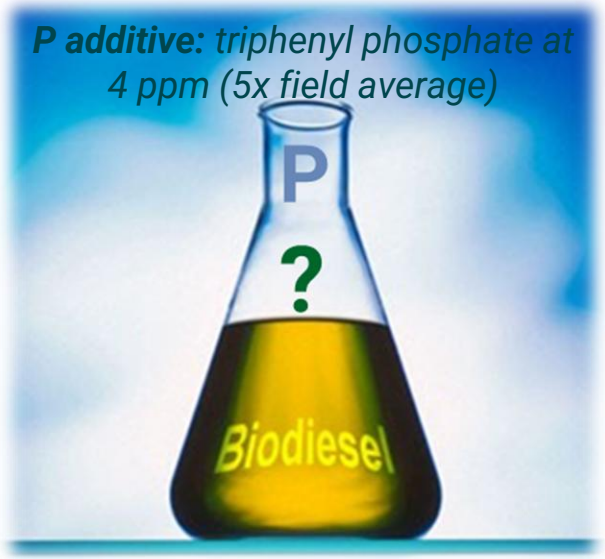
** - Any proposed future work is subject to change based on funding levels*

Milestones

9/30/2025

Develop industry supported plan to investigate biodiesel-relevant P impact on LO-SCR/CC-SCR

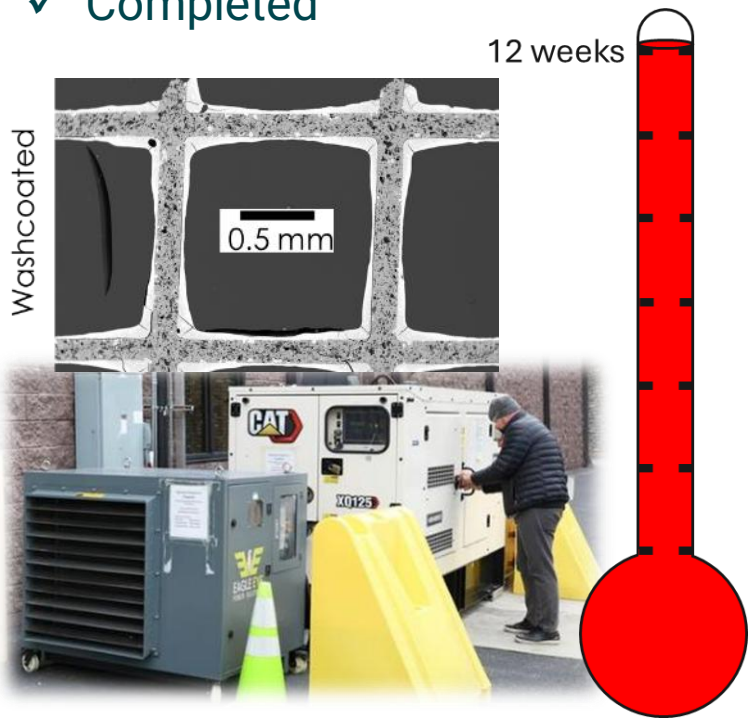
✓ Completed



3/31/2026

Complete 12-week exposure of washcoated vanadium-based LO-SCR/CC-SCR catalysts

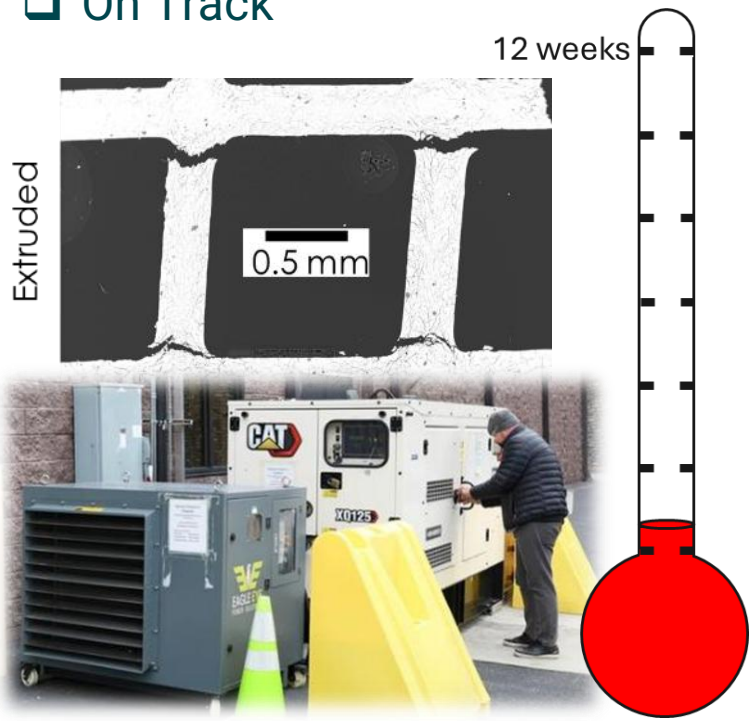
✓ Completed



9/30/2026

Complete 12-week exposure of extruded vanadium-based LO-SCR/CC-SCR catalysts

❑ On Track



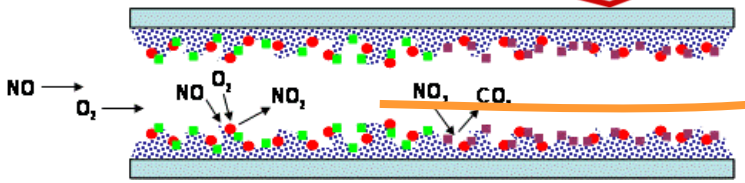
SpaciMS enables catalyst evaluations linked to metal distribution

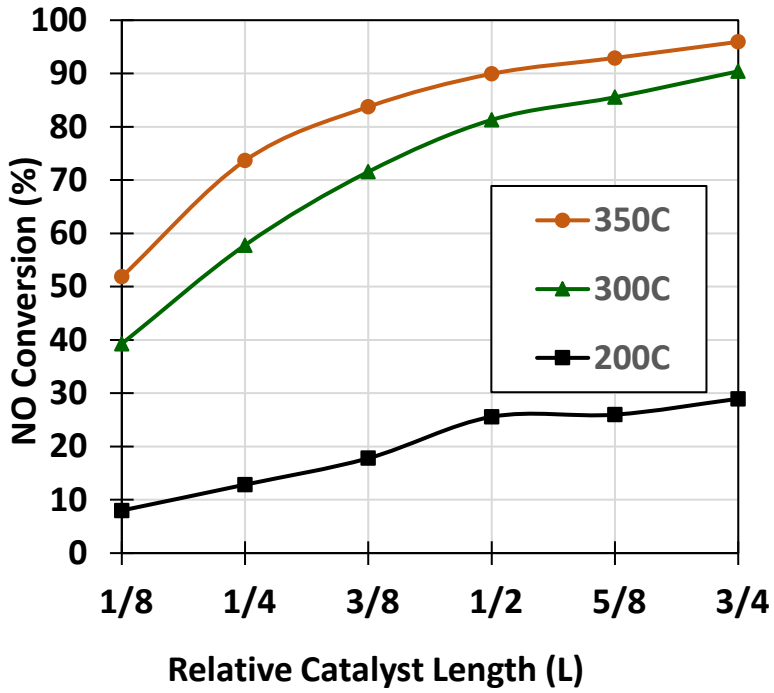
- In flow reactor, perform protocols to capture activity/capacity for modeling input
  - ➢ Multiple locations via capillary translation
- Link distributed CC-SCR performance losses/deactivation to metal distribution
  - ➢ Guide metal limits for B100 (ASTM)
  - ➢ Identify compatible catalysts/configurations

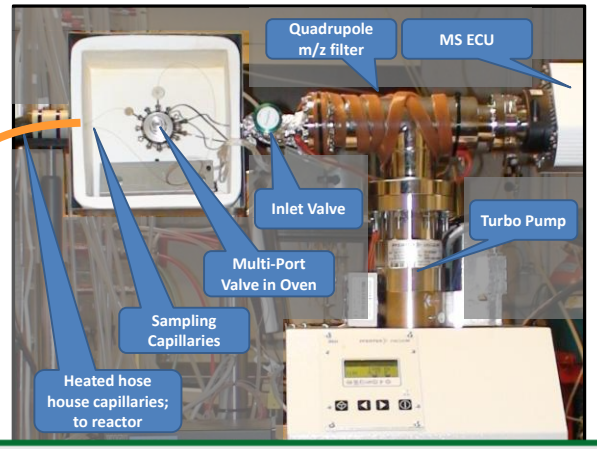
Catalyst Samples

- Single-channel schematic







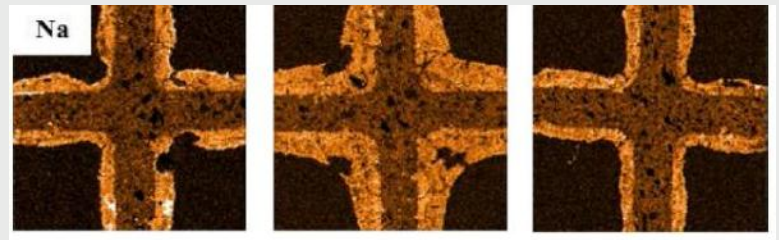


SpaciMS

- Spatial activity/storage mapping
- NO, NH_3, N_2, NO_2, N_2O, other

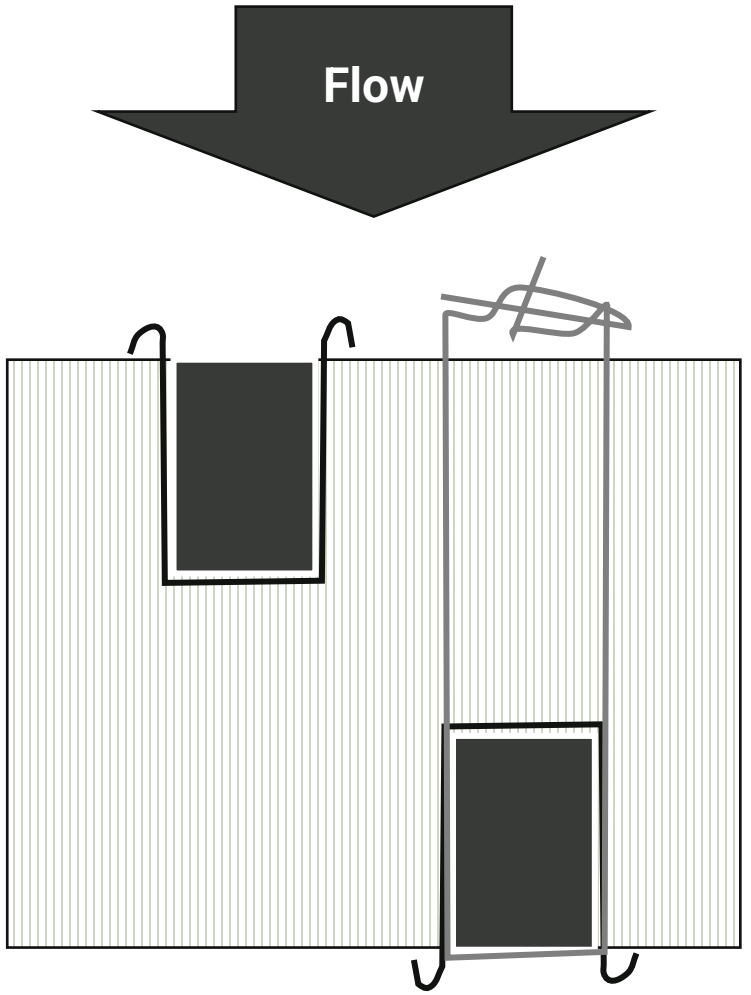
Activity linked to metal distribution

- Characterization determines metal dist.

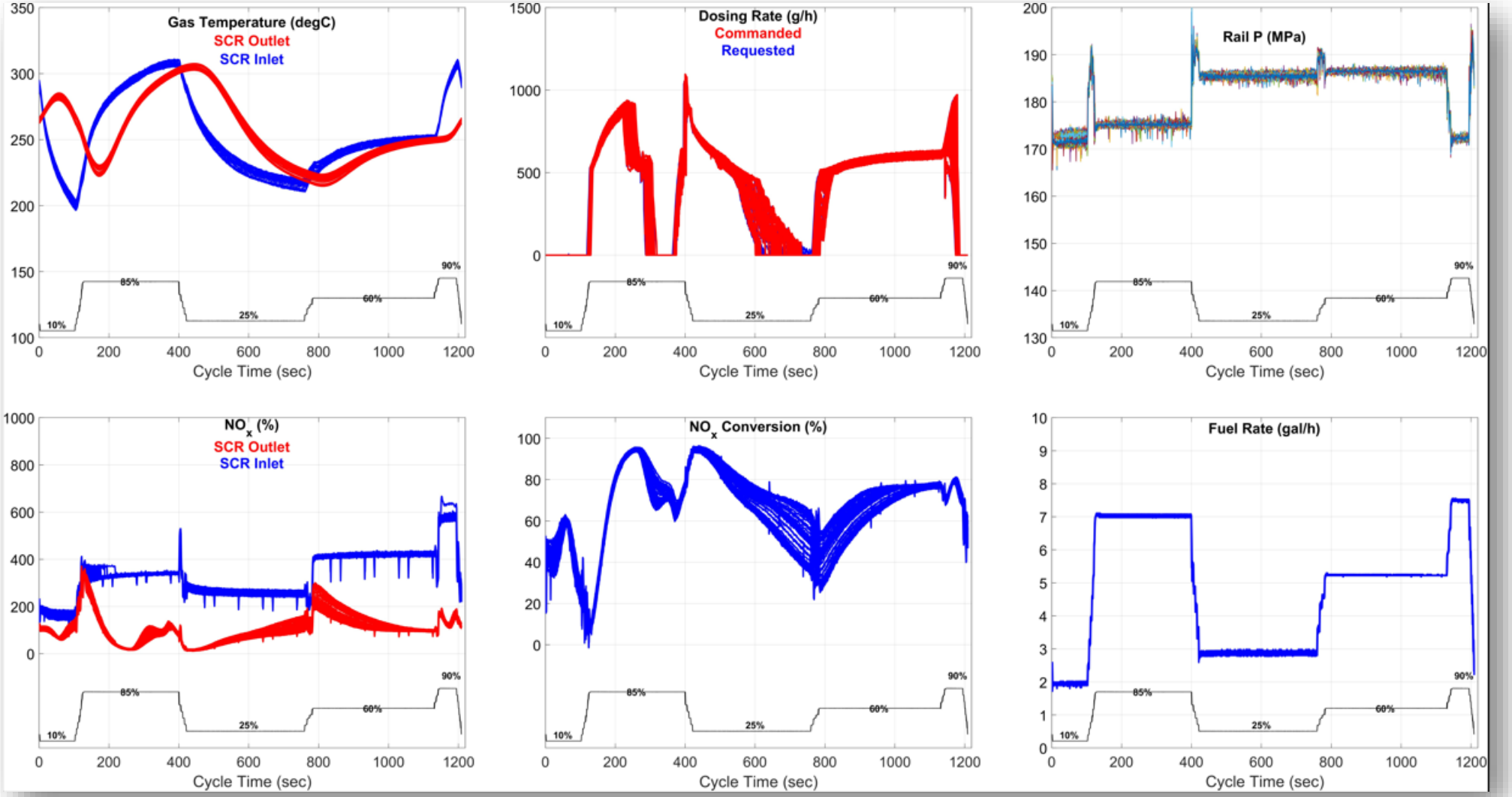


Wire system implemented to aid core removal and ensure rear cores stay in place

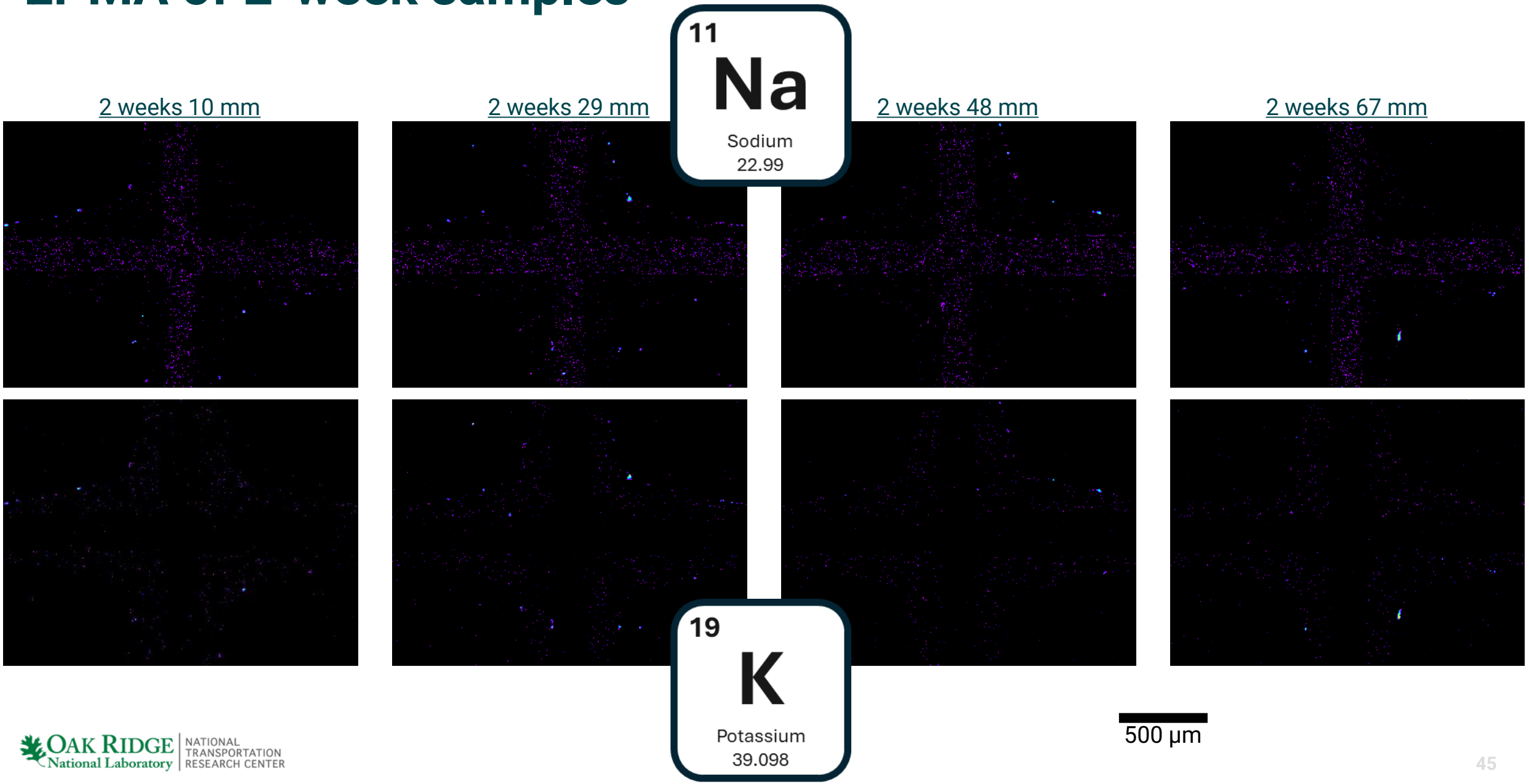




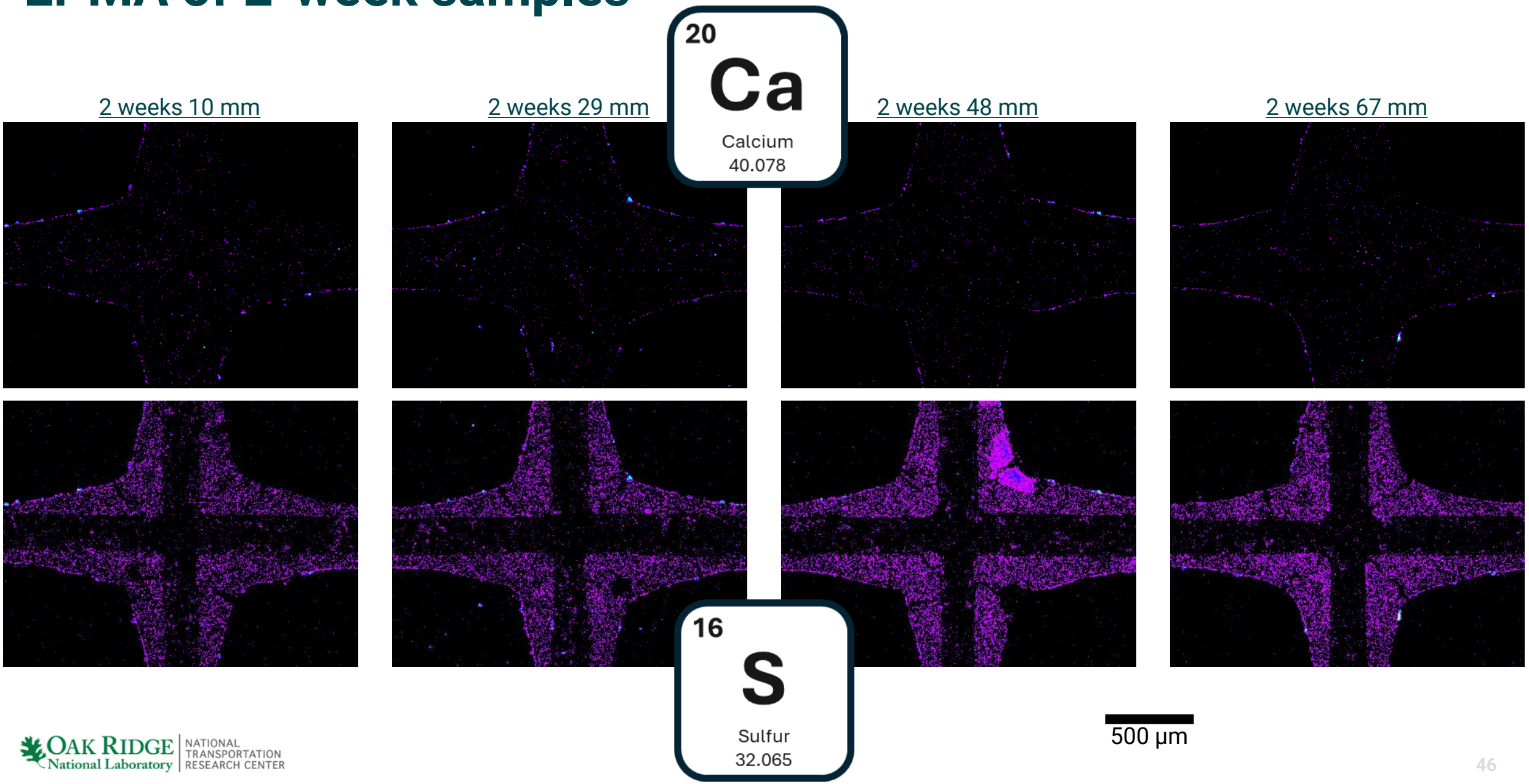
Example dataset during load cycle from genset

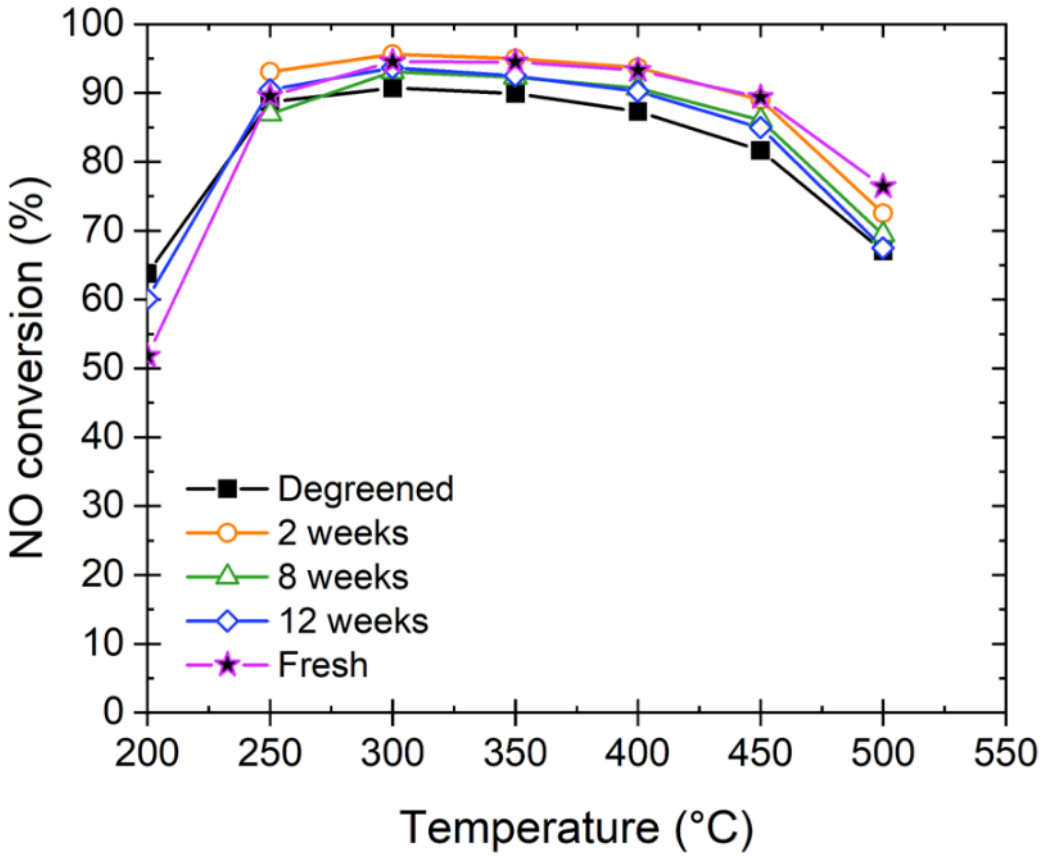


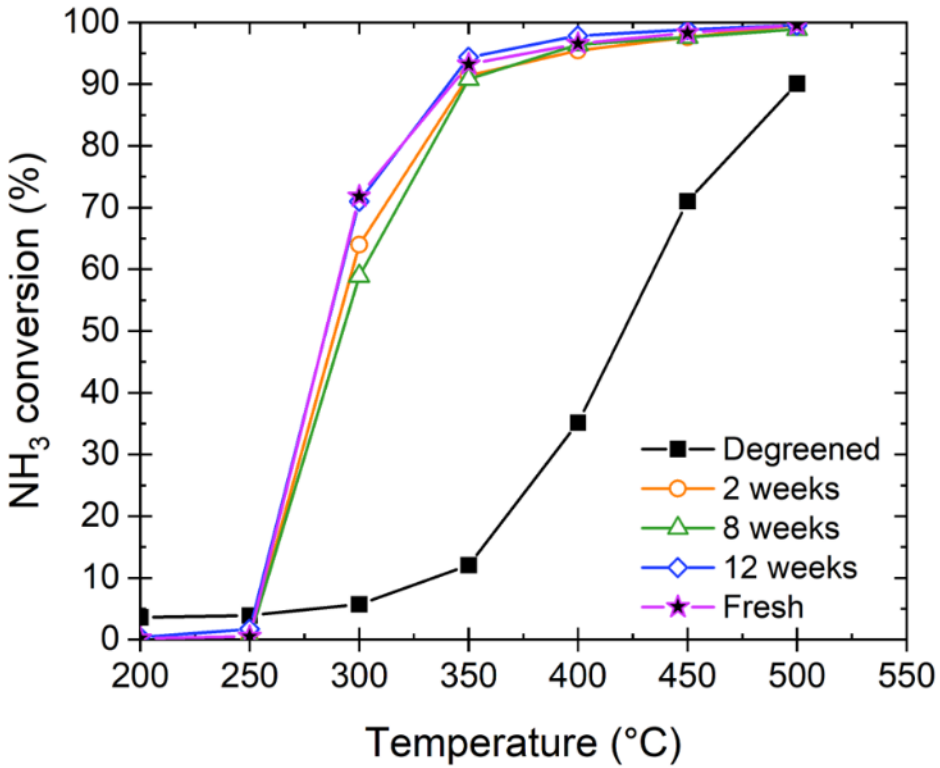
EPMA of 2-week samples



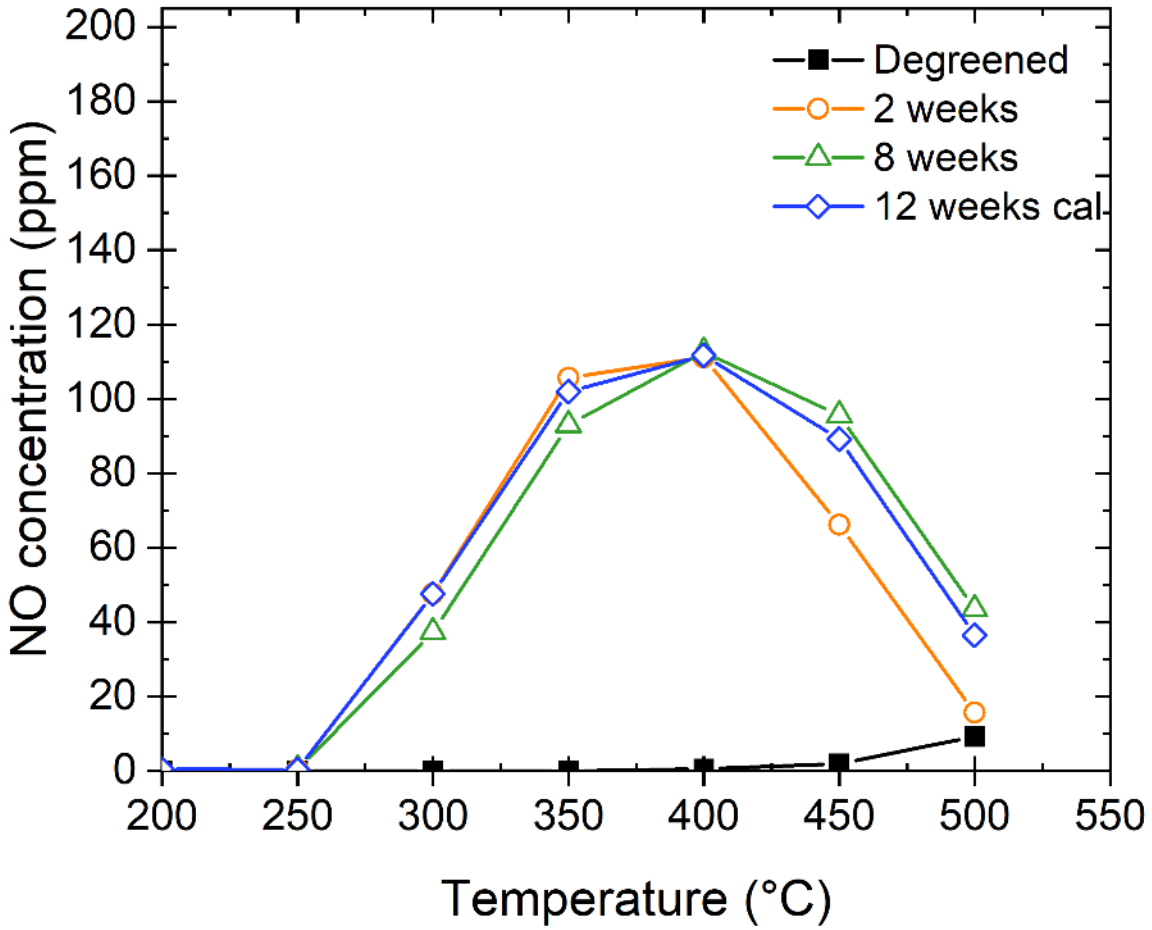
EPMA of 2-week samples



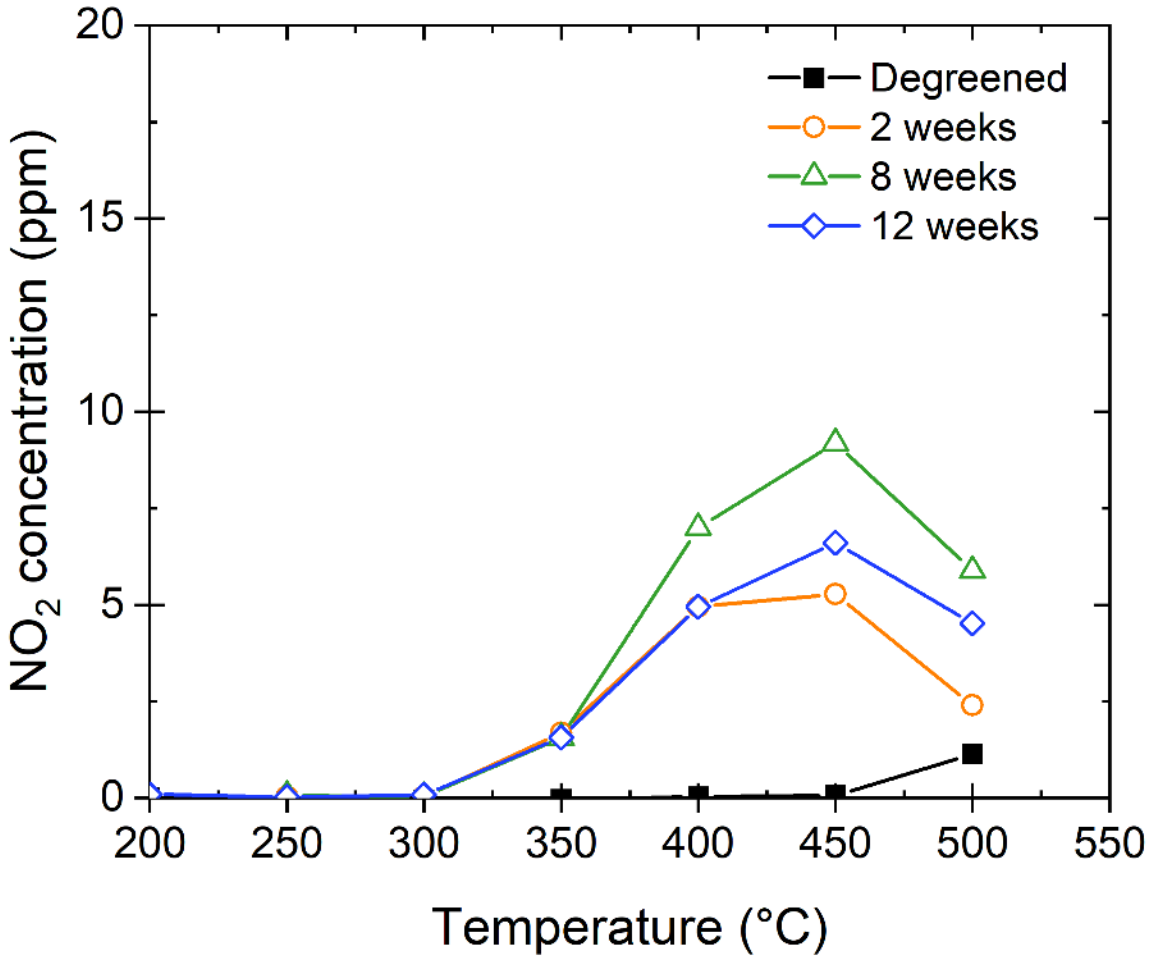

NO conversion (%)
Temperature (°C)
Degreened
2 weeks
8 weeks
12 weeks
Fresh


NH3 conversion (%)
Temperature (°C)
Degreened
2 weeks
8 weeks
12 weeks
Fresh

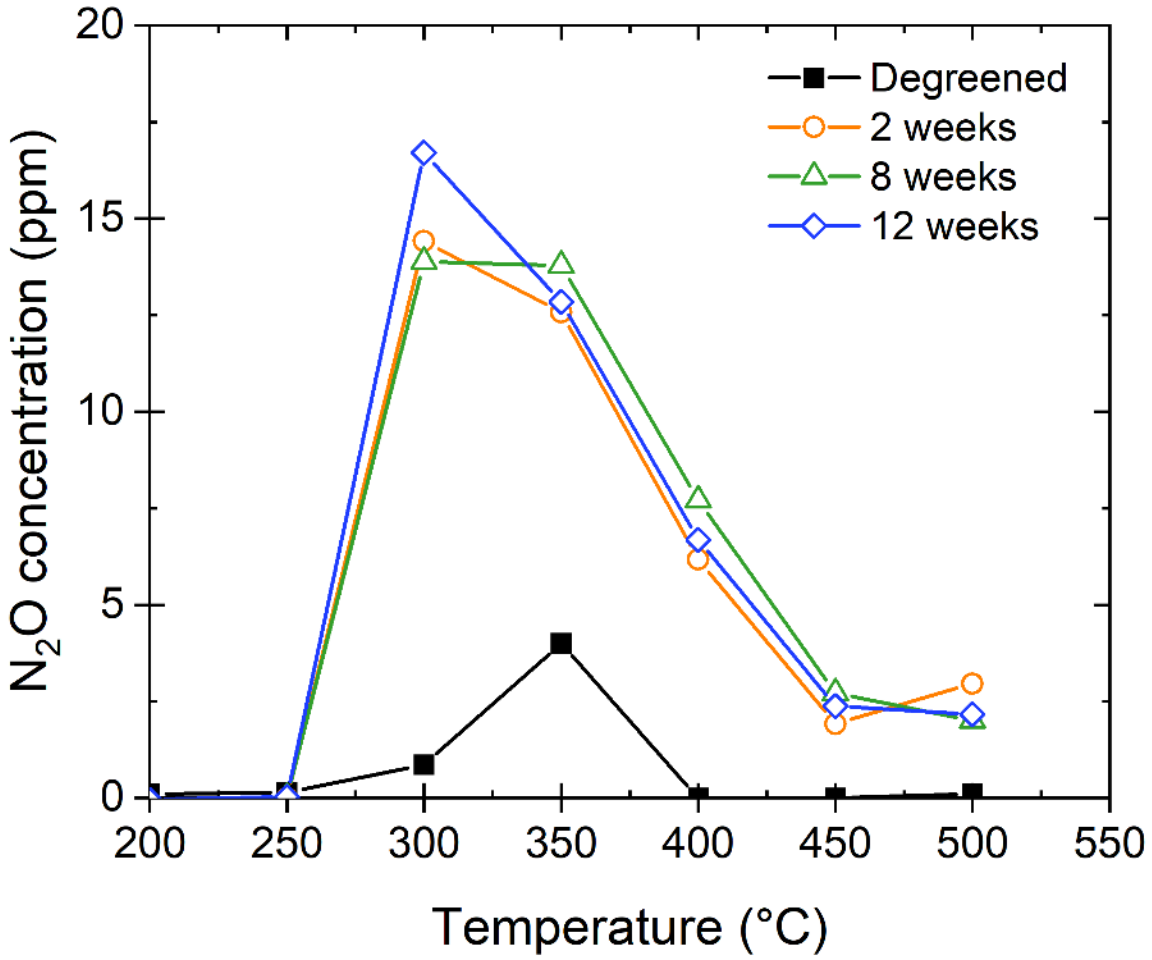
NH_3 oxidation (step 3) – NO



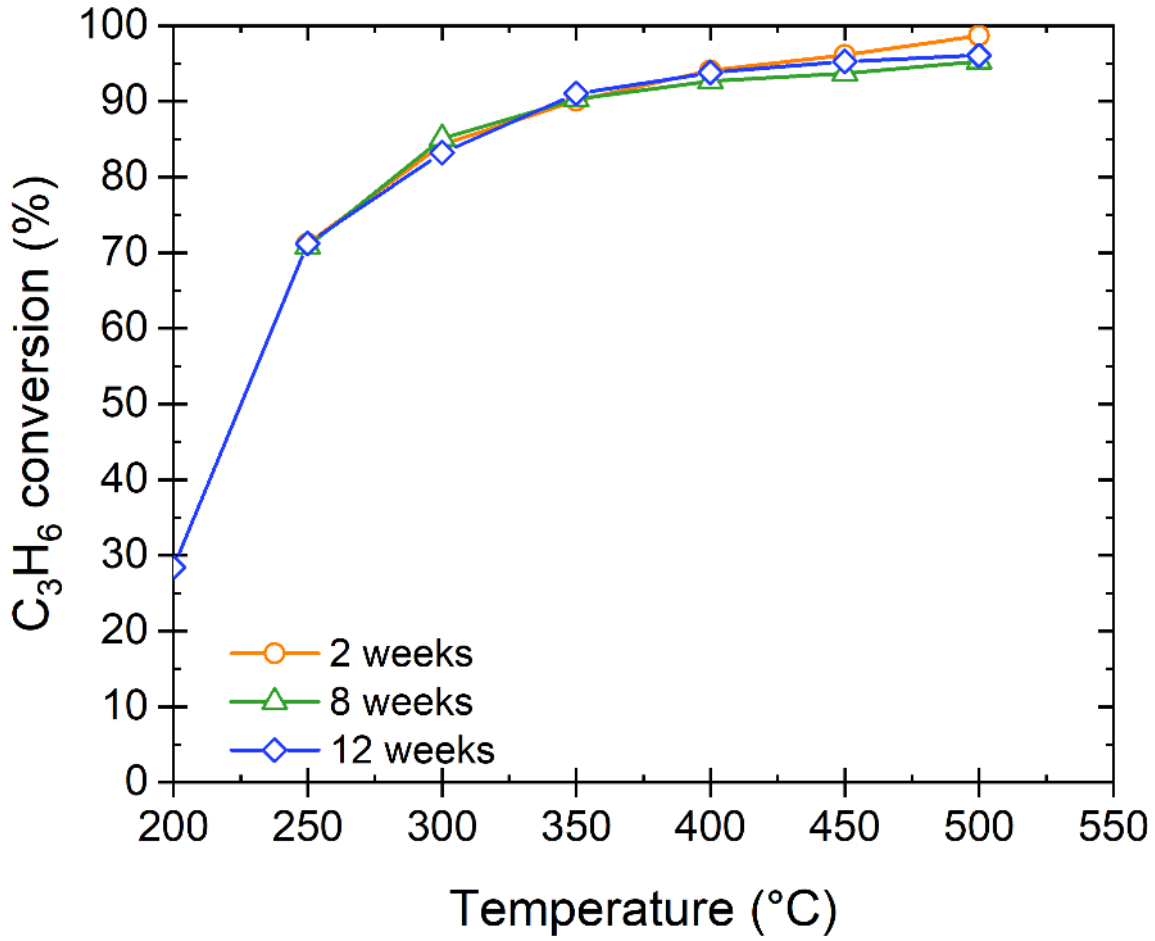
NH_3 oxidation (step 3) – NO_2

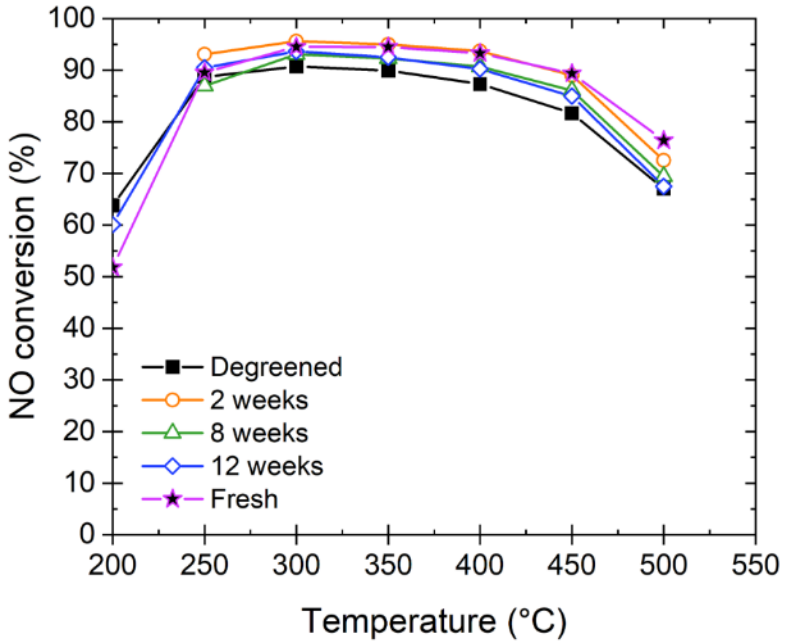


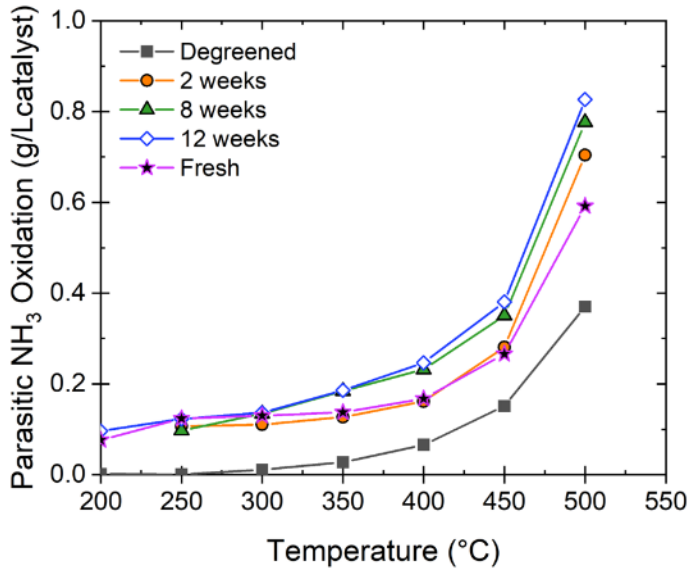
NH_3 oxidation (step 3) – N_2O

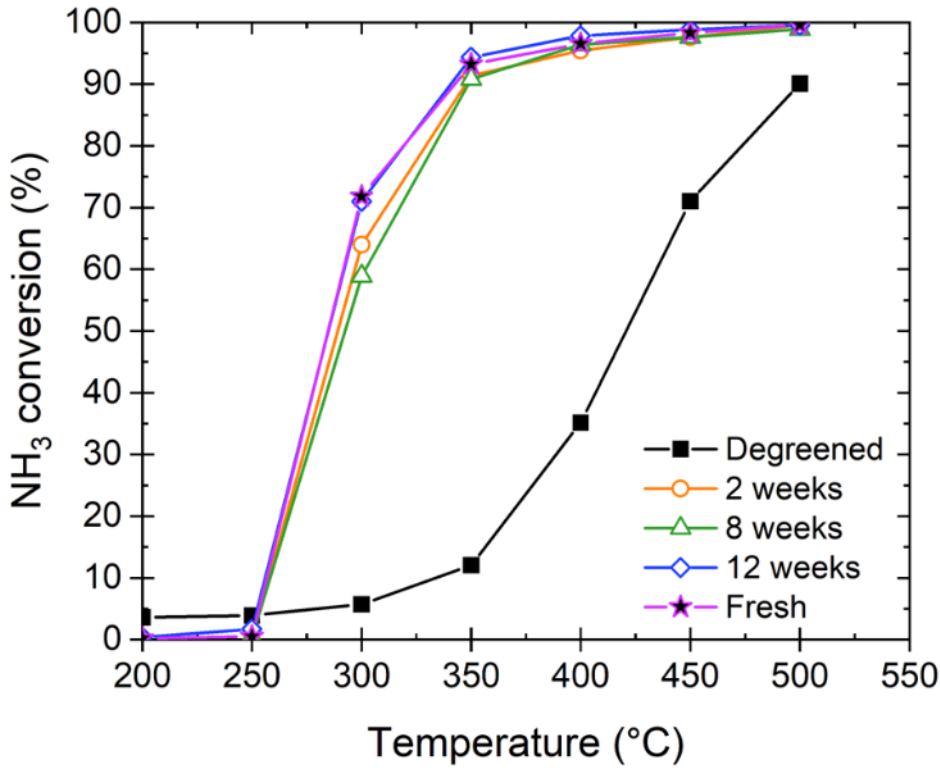


Step 6 – C_3H_6 Conversion




NO conversion (%)
Temperature (°C)
Degreened
2 weeks
8 weeks
12 weeks
Fresh


Parasitic NH3 Oxidation (g/Lcatalyst)
Temperature (°C)
Degreened
2 weeks
8 weeks
12 weeks
Fresh


NH3 conversion (%)
Temperature (°C)
Degreened
2 weeks
8 weeks
12 weeks
Fresh