Cummins-ORNL\FEERC Emissions CRADA:

NO_x Control & Measurement Technology for Heavy-Duty Diesel Engines,

Self-Diagnosing SmartCatalyst Systems

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Oak Ridge National Laboratory
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Overview

Timeline

- New SOW start: Sept. 2012
- Current end date: Sept. 2015
- ~53% Complete

Budget

- 1:1 DOE:Cummins cost share
- DOE Funding:
  - FY2012: $450k
  - FY2013: $400k
  - FY2014: $350k

Barriers

- *Emissions controls*
  - Catalyst fundamentals,
  - Reactions & mechanistic insights
  - Catalyst models (design tools & imbedded)
  - Control strategies & OBD
- Combustion Efficiency
  - Shift emissions tradeoff to fuel efficiency
- *Durability*
  - Enhanced durability via knowledge-based controls
- *Cost*
  - Lower catalyst & sensor costs
  - Lower development costs

Partners

- **ORNL & Cummins Inc.**
- Several informal collaborators

Objectives & Relevance

Elucidate Practical & Basic Catalyst Nature

for enabling improved Modeling, Design & Control

Objectives

- Develop diagnostics to advance applied & basic catalyst insights
- Understand impact of ageing on catalyst performance
  - Focus on distributed performance
  - NH_3 capacity and utilization
  - Conversion distribution

Relevance – Detailed Catalyst Insights impact:

- Design models
- Control strategies & models
- NH_3 dosing control
- Required engineering margins (engine-efficiency vs. -emissions tradeoffs)
- System capital & operation costs

Milestones

2013 Milestones:

- ✓ Assess distributed performance of DeGreened commercial 2010 Cummins SCR catalyst samples (2010CMI)

2014 Milestone (on schedule for timely completion):

- ✓ Complete assessment of probe-to-probe variations in NH_3 sensors **(Q1)**
- ✓ Assess NH_3 capacity of Lab-Aged 2010CMI sample **(Q2)**
- Assess distributed performance of Lab-Aged 2010CMI sample **(Q3)**
- Compare distributed performance of DeGreened & Lab-Aged 2010CMI **(Q4)**

Global Approach for Improving Energy Security

Develop & apply advanced diagnostics for catalyst characterization to improve: catalyst models, design, state assessment & *controls for fuel-efficient engine systems*

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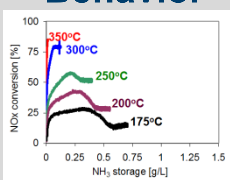
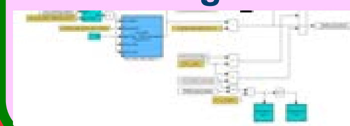
Catalyst Functional Behavior



Control & OBD Strategies



Proprietary Models
- For development
- For OBD

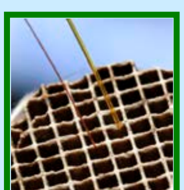
Clean,
Fuel-Efficient,
Durable
Engines
in the Marketplace

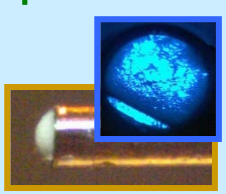
Cummins
2007 6.7L ISB

- ***Focus***
- ***Goals***
- ***Strategy***
- ***Analysis***

ORNL

Diagnostics & Method Development





Catalyst Insights
- Reaction network
- Mechanisms
- Catalyst state & control measures

Improve Models
- With collaborators
- Kinetic parameters
- Use models to study catalysis

Approach

Spatiotemporal Intra-Catalyst Characterization
to Enhance Performance, Control, Cost & Durability

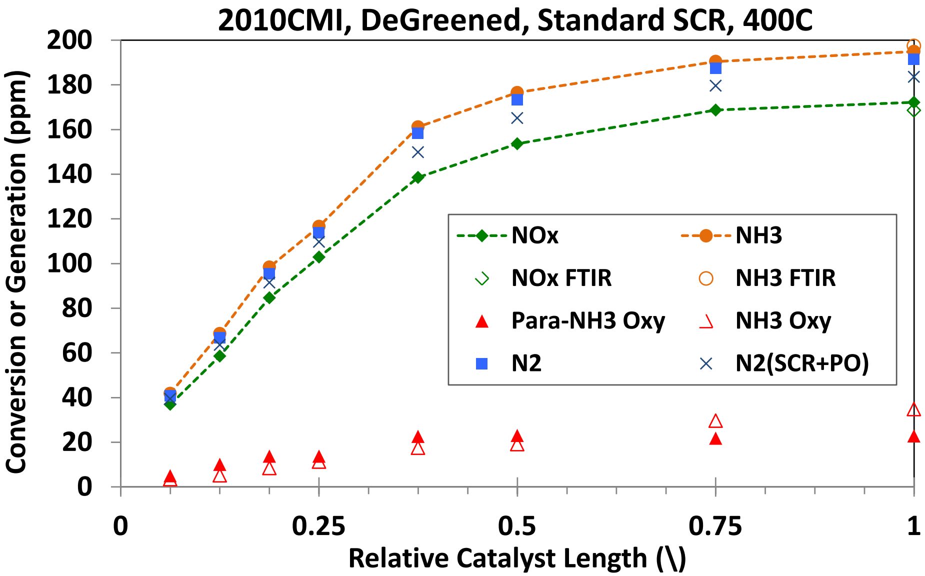
- Cummins-ORNL CRADA Team identifies catalyst-performance barrier
  - ***Understand distributed impacts of ageing on various catalyst functions***
- Develop procedures to measure intra-SCR distributed performance
  - Analysis methods, hardware, diagnostics as necessary
- Assess commercial catalyst in various states & conditions
  - DeGreened, Lab Aged, Field Aged, other specific lab- or field-condition states
  - Standard & Fast SCR; Various temperatures
- Apply diagnostics to characterize distributed SCR performance
  - Focus on NH_3 capacity, SCR, parasitic NH_3 oxidation, NO & NH_3 oxidation
- Correlate impacts to gain insights into controlling chemistry
  - Sensitivity of various functions to state & condition changes
  - Mine insights for diagnostic and control indicators
- Compare experimental results to catalyst-simulation models
  - Model validation, improvements & tuning

Technical Progress: *Summary*

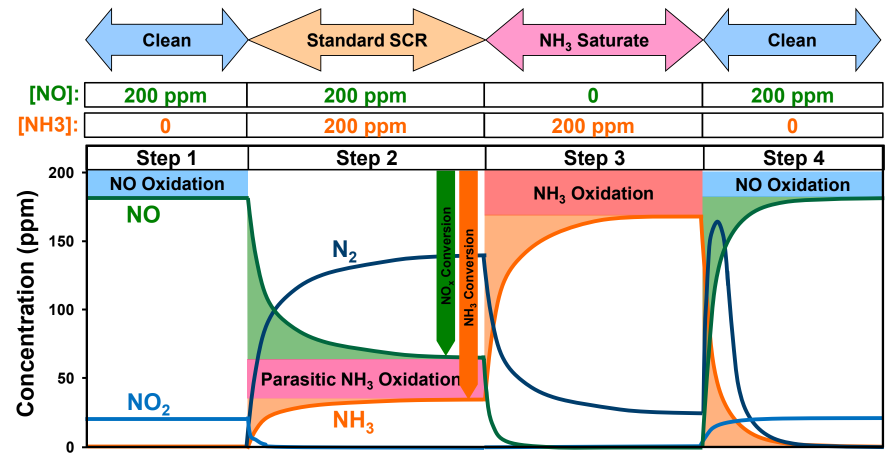
- **Characterize Performance of Commercial SCR Catalyst**
  - Focus on Hydrothermal Ageing impacts
    - Lowers NH_3 capacity
    - Increases NH_3 oxidation
    - Does not change Parasitic NH_3 oxidation
    - Does not change integral SCR conversion
    - Does not change intra-catalyst SCR distribution
      - For Standard SCR at 300°C
      - In back 3/4L of catalsyt for Standard SCR at 400°C
    - Degrades 400°C Standard SCR in front 3/16L of catalyst

- **Analytical Development**
  - Improved analysis with better species & nitrogen balances
  - Demonstrated non-invasive nature of intra-catalyst sampling technique
  - Demonstrate Fast-SpaciMS with improved transient response

Technical Progress: NH_3 Divided Between SCR & Parasitic Oxidation



Use 4-Step Protocol & SpaciMS to resolve distributed catalyst performance

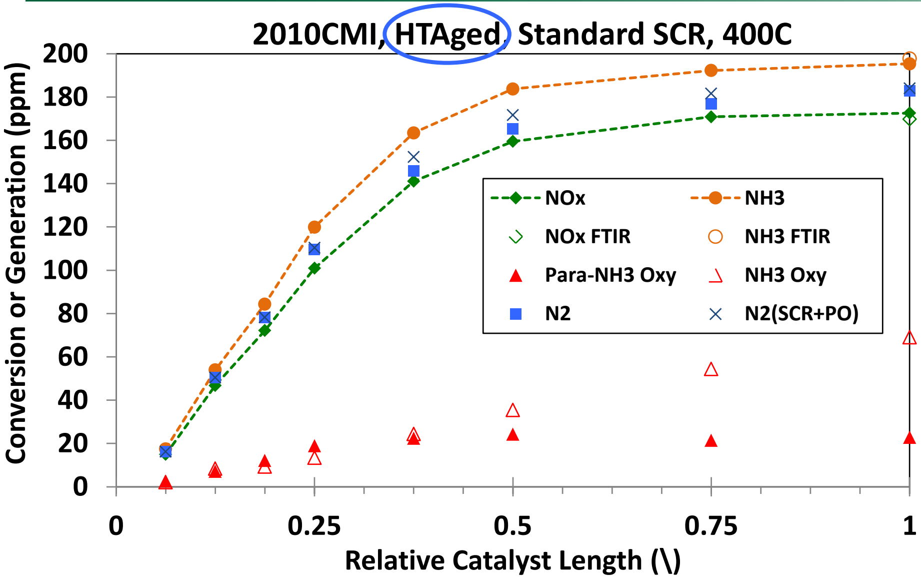


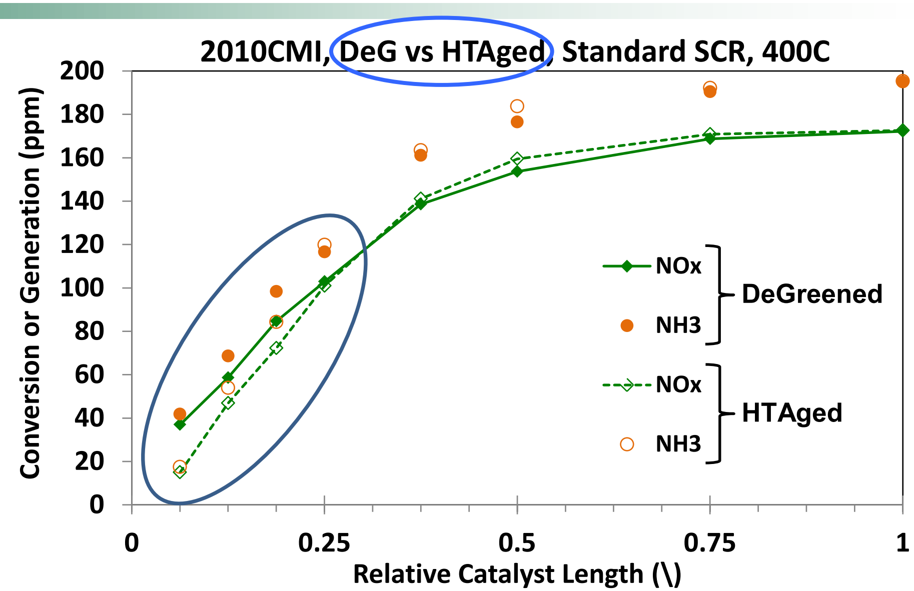
- **DeG**: 700°C, 4hrs, 10% O_2 + 5% H_2O
- Variable SCR along catalyst length
- Effluent Spaci & FTIR match (NO_x & NH_3)
- 12% Parasitic NH_3 oxidation (PO)
  - NO_x/NH_3 conversion ca. 88% throughout
  - Makes N_2 here; PO→N_2
- (NO_x-free) NH_3 oxidation linearly increases

- Good overall N balance ~4%
- PO causes N_2 < NH_3 conversion
  - 1:1 N_2:NH_3 via SCR, but 1:2 via PO
- Simple NO:NH_3:N_2 stoichiometry
  - N_2 ~2% below NH_3 conversion
  - Predicted N_2 ~4% below measured N_2
  - NH_3 neatly split between SCR & PO→N_2
  - Consistent with zero N_2O generation

Species Distributions Correlate Throughout Catalyst Length & Can Be Used to Study Ageing Impacts

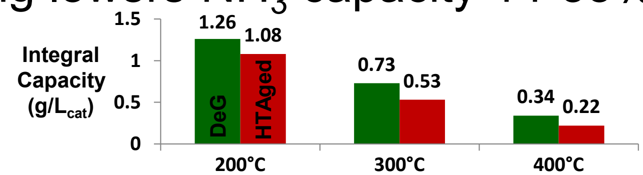
Technical Progress: HTAgeing Does Not Impact Integral SCR Performance



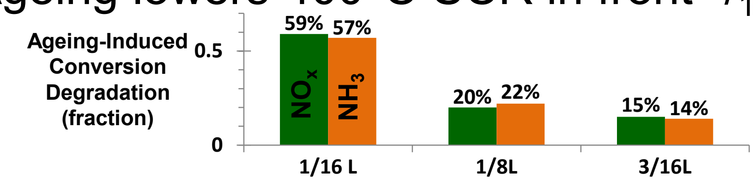


- **HTAge**: 800°C, 50hrs, 14%O_2 + 8%H_2O
- Overall SCR distribution looks similar
- Similar 14% Parasitic NH_3 oxidation
  - NO_x/NH_3 conversion ~86% throughout
- NH_3 reacts via SCR or PO→N_2
  - NO:NH_3:N_2 stoichiometric within ~5%
- NH_3 oxidation increases significantly

- Ageing lowers NH_3 capacity 14-35%



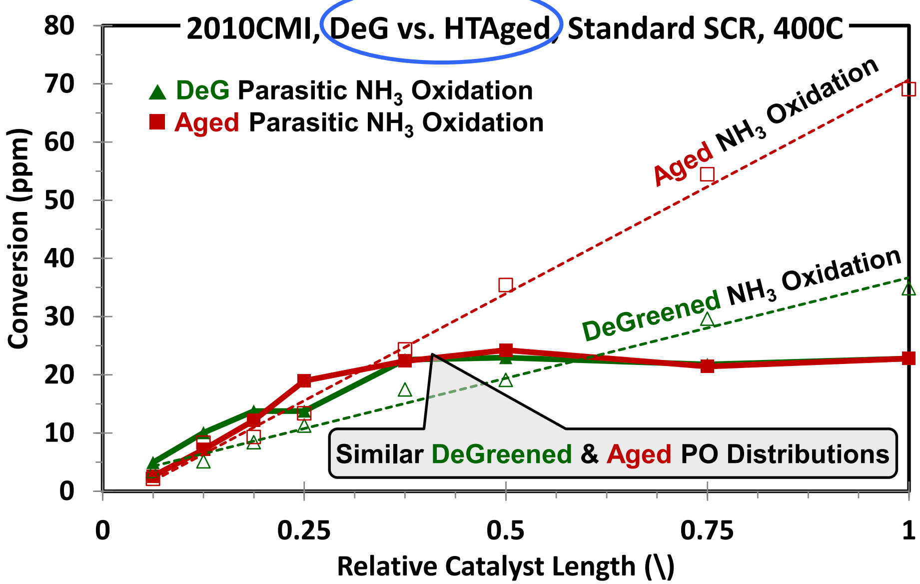
- Ageing lowers 400°C SCR in front 3/16 L

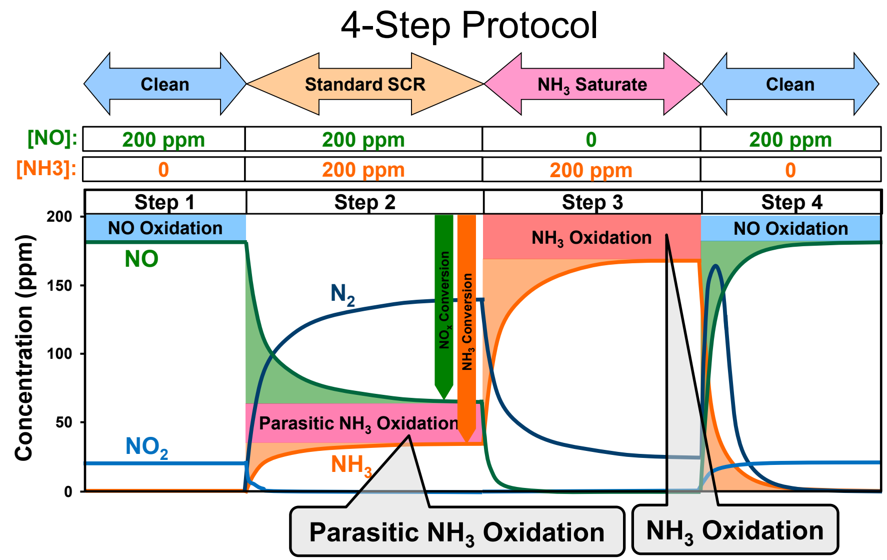


- Ageing has little impact on 300°C SCR
- Additional HTAgeing needed

Ageing Impact is Distributed & Varies with Catalyst Function

Technical Progress: Different Ageing Impacts on Parasitic & NH_3 Oxidation





- HTAgeing doubles NH_3 Oxidation
- Parasitic-NH_3 Oxidation unchanged by HTAgeing
  - Thus: consistent N-Balance & simple NH_3 reaction via SCR or PO→N_2
  - Further ageing may change Parasitic oxidation: PO→N_2 & PO→N_2O
    - Impact balances & N_2O selectivity (low N_2O difficult to measure)
- Parasitic & NH_3 Oxidation have different ageing responses
  - Demonstrates that these are different reactions
  - Design & control models need to incorporate both for NH_3 management

Aging Impacts Catalyst Significantly, but Not Integral SCR Performance

Need to Understand Various Ageing Impacts to Advance Efficiency

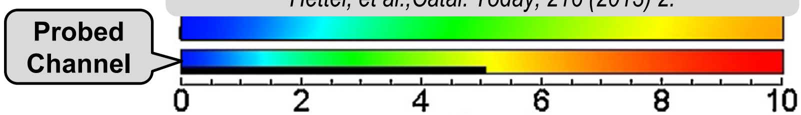
Technical Progress: Invasive Nature of Intra-Catalyst Capillaries

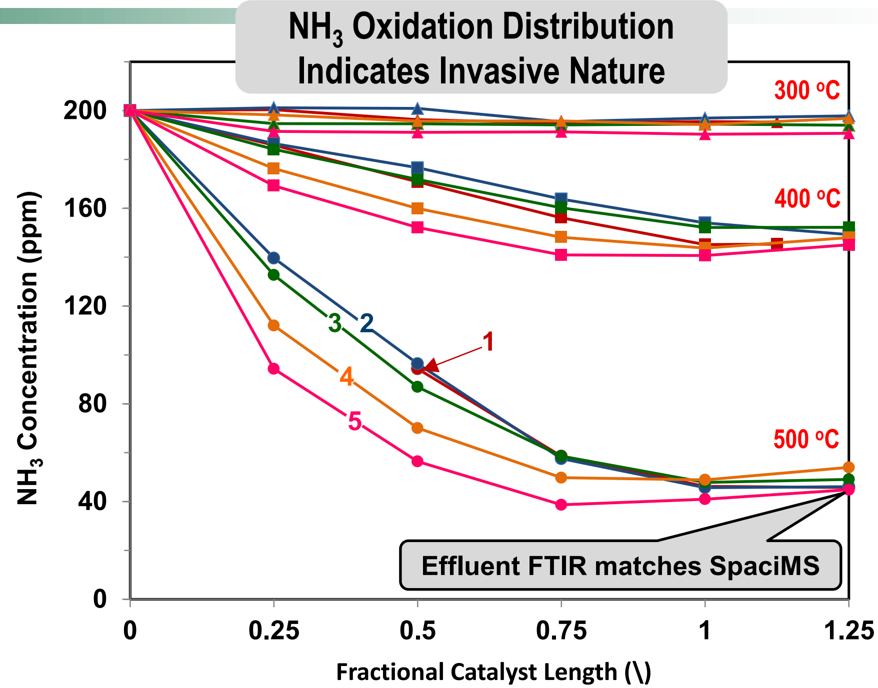
Varying Probe Invasive Nature

No.	OD (um) Cap.	OD (um) Fiber	Blocking Channel (%)	Capillary Position
1	150	-	1.2	
2	200	-	2.2	
3	375	-	7.7	
4	200	700	29.2	
5	375	700	34.7	

Simulated Reaction Product Distribution

Hettel, et al.,Catal. Today, 216 (2013) 2.





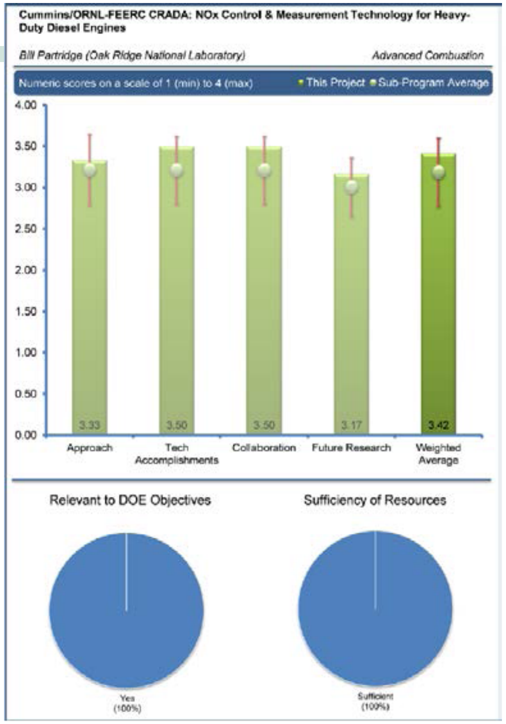
- More people are using SpaciMS
  - Different implementations
  - More discussion of invasiveness
- Evidence of invasiveness
  - Greater conversion gradients
  - Conversion step at outlet
    - A simple check we commonly use

NH$_3$ Oxidation Invasiveness Study

- No. 4 & 5 clearly invasive
  - Greater intra-catalyst gradients
  - Blocks ca. 30-35% channel area
- No. 1 & 2 are non-invasive
  - Equivalent conversion profiles
  - We use 200μm capillaries (No.2)

Our SpaciMS Approach is Effectively Non-Invasive

Responses to 2013 Review Comments



Numerous Positive Comments:

- “instrumental work in this project was very good”
- “very good & comprehensive approach covers real-world challenges”
- “strong collaboration with industry partner keeps work sharply focused on barriers most impacting industry”
- “excellent collaborations with industry and universities and international partners”
- “Good participation in CLEERS, DEER, etc.”
- “ORNL’s unique expertise has helped in many applications related to meeting DOE’s objectives.”

Recommendation:

- “would be nice to see more catalyst ageing”
- “more work on catalyst aging would be really nice”
- “incorporation of laboratory and field aged catalysts..critical”
- “more work on how aging affects the correlation between SCR efficiency and NH_3 storage..recommended”
  - ***Work over the last year has focused on lab-aged catalyst***
  - ***Future work will focus on field-aged catalyst***
  - ***Analysis has and will continue focus on correlating aging-induced distribution changes to elucidate degradation pathways; including NH_3 capacity components.***

- “2014 plans are pretty bland”
  - ***We have tried to better communicate our research plans vis-à-vis remaining barriers.***

- “not much results from collaboration partners especially from universities”
  - ***With the limited time, we primarily focus on the main work within the CRADA partnership.***
  - ***Several publications and presentations from these collaborations are called out in this year’s presentation and cited in the ‘Additional Slides for Reviewers.’***

Collaborations & Coordination with Other Institutions

- **Cummins**
  - CRADA Partner, Neal Currier (Co-PI)
- **Chalmers (Prof. Olsson)**
  - SCR kinetic analysis & modeling (Xavier Auvray)
  - See Shwan publication; Auvray SCR publication submitted
- **CLEERS (ACE022, Pihl, Wednesday 4:15pm)**
  - Diagnostics, analysis & modeling coordination
- **Politecnico di Milano (Profs. Tronconi & Nova)**
  - Precompetitive study of selected SCR mechanisms (with CLEERS)
  - See Ruggeri presentation; publication in process
- **Institute of Chemical Technology, Prague (Prof. Marek & Dr. Kočí)**
  - Precompetitive study of LNT N_2O chemistry (with CLEERS)
  - KONTAKT II Grant from Czech Republic Government
  - Dr. Kočí working at ORNL (May 28-31, 2013 & Sept. 1-5, 2014)
  - ICTP PhD student working at ORNL (David Mráček, Sept.-Nov. 2013 & May-June 2014)
  - Using Fast-SpaciMS to resolve N_2O vs. reductant transients
  - See 2 publications (Kočí, Bártová) & 2 presentations (Bártová, Mráček)
- **Dissemination via Publications & Presentations**
  - 3 Archival Journal Publication, 1 Book Chapter & 9 Presentations

Remaining Challenges & Barriers, and Proposed Future Work

Remaining Challenges:	Future Work:

• Characterize distributed impact of ageing on SCR-catalyst functions & performance	• Study HydroThermally Lab-Aged sample
	• Complete experimental matrix & analysis
	  - DeG & HTAged 2010CMI SCR samples
	  - Standard & Fast SCR
	  - 200, 300 & 400°C

• Resolve NH_3 Capacity distributions via transient analysis - Resolve Dynamic-, Unused- & Total-Capacity	• Determine capacity distributions using an improved transient analysis method incorporating instrument isotherms

• Understand mechanisms of ageing-induced performance degradation
  - Mine insights for improving catalyst development models & control
	• Correlate impacts of Temp., SCR Reaction & Ageing on distribution of specific functions
	  - E.g., further work as presented here
	• Comparison of measurements to SCR models
	  - Assess model performance and sensitivity vs. specific parameters, ageing and functions
	• Continue University collaborations

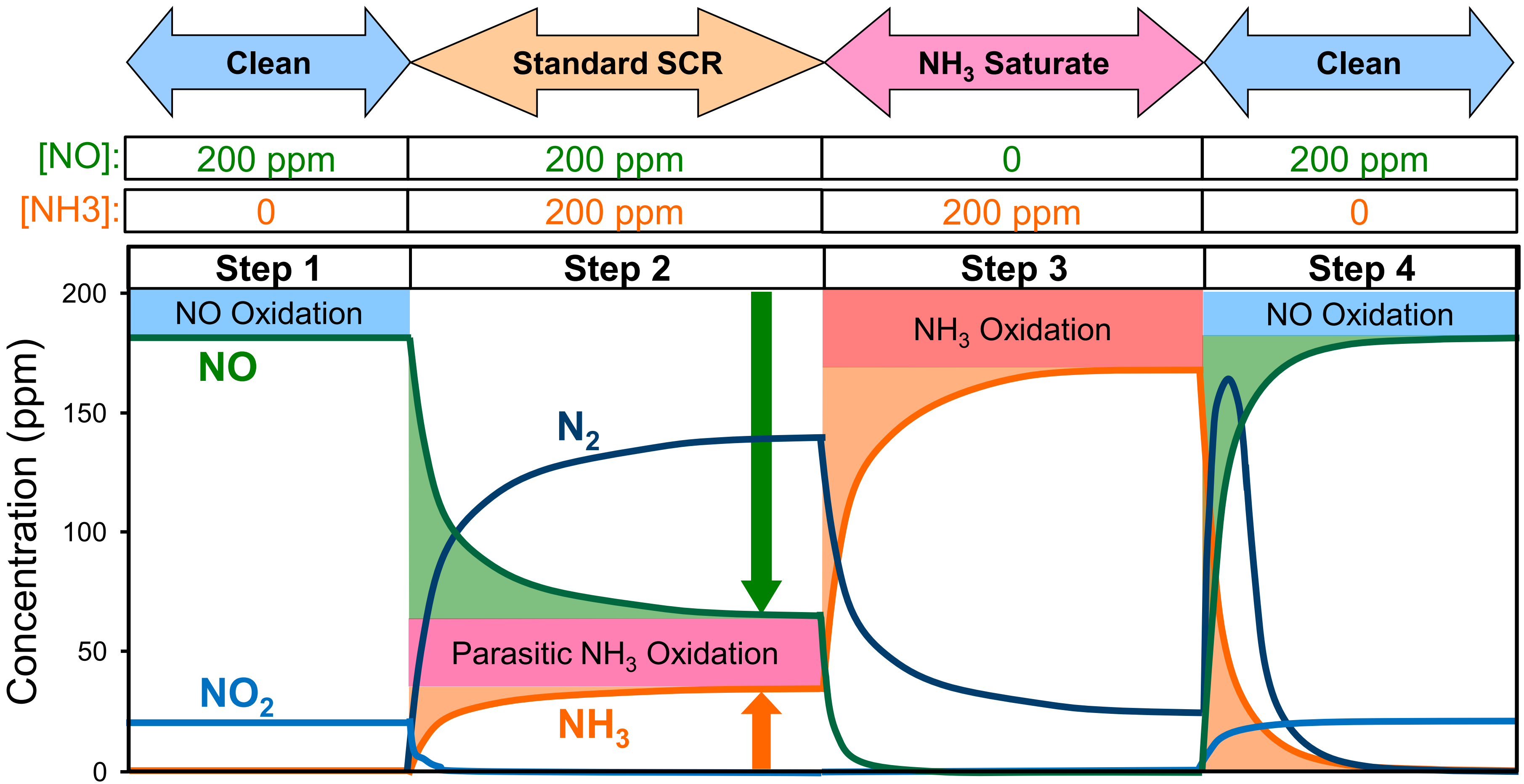
• Advance detailed understanding of ageing
  - Impacts of degree of ageing
  - Impacts of different real-world conditions
	• Similar studies on catalyst in other aged states
	  - Further HT Lab Ageing
	  - Field-aged 2010CMI catalyst samples

Summary

- **Relevance**
  - CRADA work enables improved catalyst knowledge, models, design & control
  - This reduces catalyst system costs & required engine-efficiency tradeoffs
  - This in turn enables DOE goals for improved fuel economy
- **Approach**
  - Develop & apply diagnostics to characterize catalyst nature
  - Analyze data to understand mechanistic details of how the catalyst functions
  - Develop improved catalyst models based on improved catalyst knowledge
- **Technical Accomplishments**
  - Assessed impacts of hydrothermal lab ageing on commercial SCR catalyst functions
    - NH_3 capacity, SCR, Parasitic NH_3 oxidation, NH_3 Oxidation
  - Capillary sampling demonstrated to be effectively noninvasive
- **Collaborations**
  - Numerous university collaborations resulting in presentations, publications and advances
  - Coordination & collaboration with other DOE projects to maximize benefit
- **Future Work**
  - Analyze for distribution of NH_3 capacity components on DeGreened and Aged samples
  - Analyze impacts of further lab ageing and field ageing
  - Assess ageing impacts via experimental correlations and comparison to catalyst models

Technical Back-Up Slides

Cummins 4-Step Protocol Resolves Reaction Parameters



- Step1: NO oxidation
- Step2: SS NO_x & NH_3 conversions, Parasitic NH_3 oxidation, Dynamic NH_3 capacity
- Step3: NO_x-free NH_3 oxidation, Unused NH_3 capacity
- Step4: NO oxidation, Total NH_3 capacity

Total = Dynamic + Unused