STATUS REPORT

THE DEVELOPMENT OF RAPID AGING AND POISONING PROTOCOLS FOR DIESEL AFTERTREATMENT DEVICES

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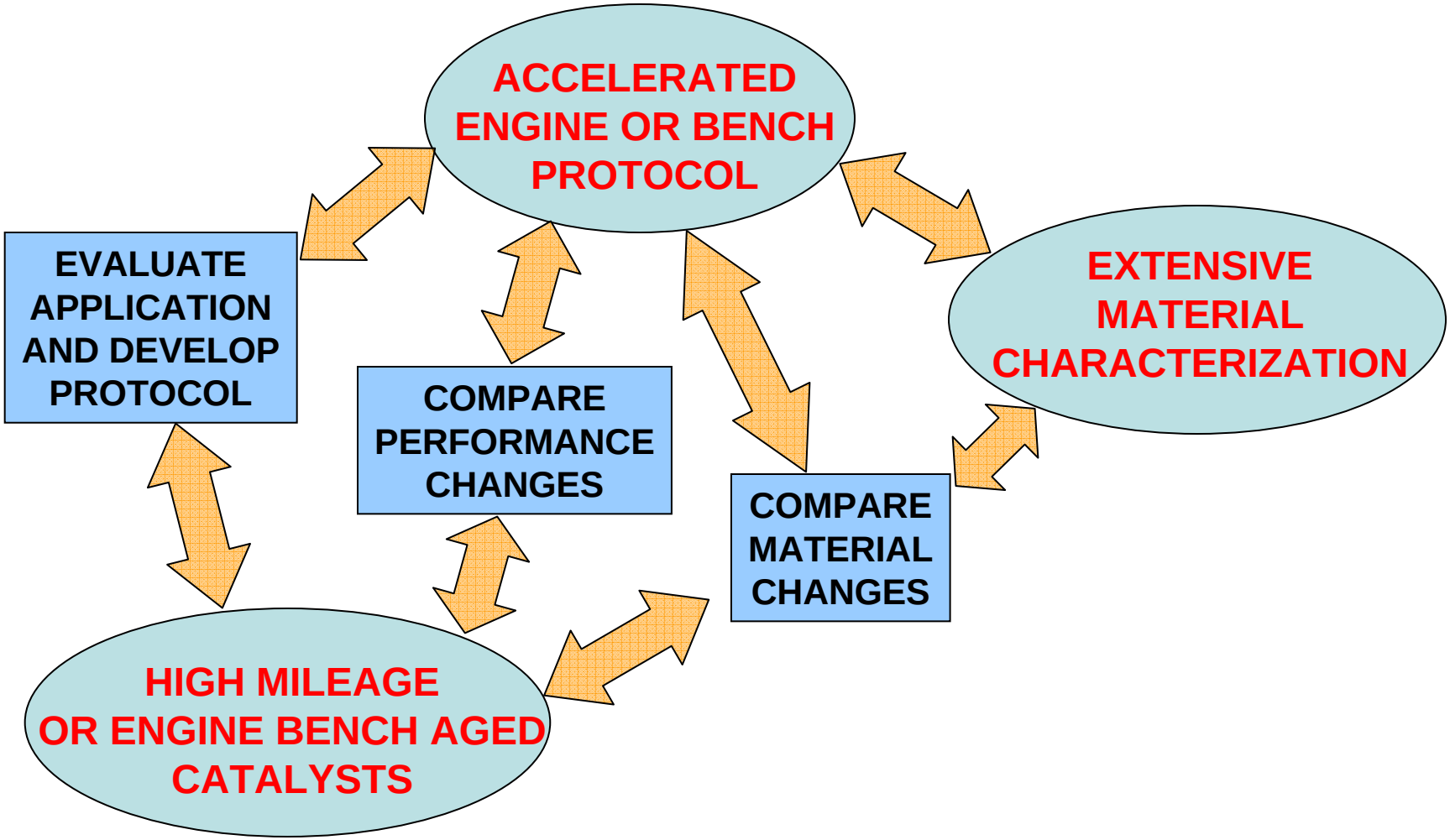
Rapid Aging and Poisoning Protocols

- **An accelerated test protocol which simulates longer mileage field-service for evaluating durability and understanding mechanisms of deterioration.**

- **Benefits include:**
  - **More understanding of processes and mechanisms**
  - **More rapid product development**
  - **Verification of application early in life cycle**
  - **Testing for uncommon situations**
  - **Research basis for new materials or applications**

Development of Rapid Protocols



Current Research Focuses

- Current research was developed through extensive discussion with engine, auto and catalyst companies.
  - Diesel oxidation catalysts - Phosphorous poisoning
  - Lean NOx traps - High temperature lean-rich thermal aging
  - Diesel particulate filters - Ash effects on performance
  - Selective catalytic reduction catalysts - Aging and poisoning of combined DPF-SCR

- Catalysts from Engelhard and Delphi
- Substrates from NGK and Dow

- This research is supported by DOE OFCVT Fuels Technology Program and our program managers are Kevin Stork, Dennis Smith, and Steve Goguen

Catalyst and DPF Holder Assemblies

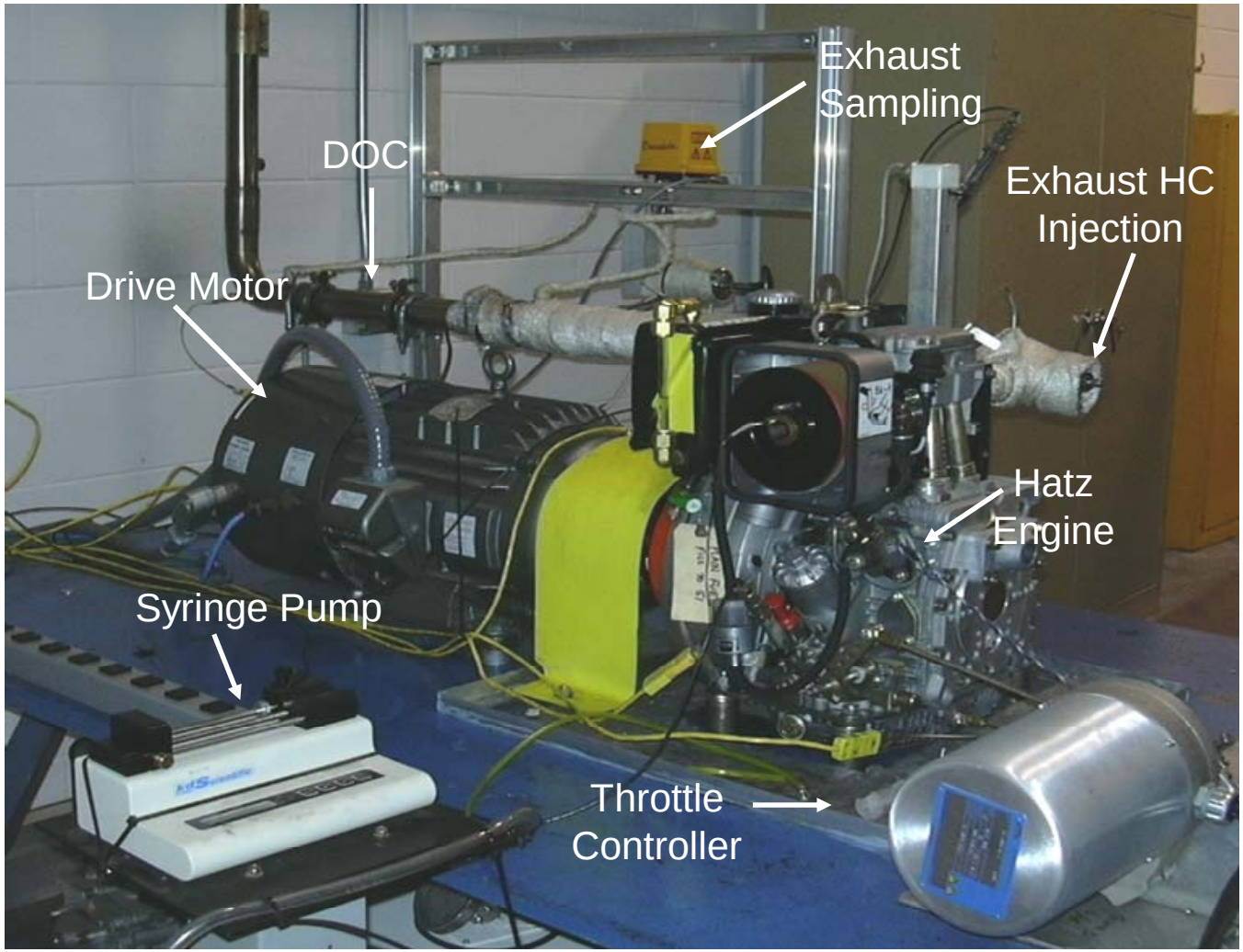
CATALYST CAN

DPF CAN

CATALYST BRICK

DPF BRICK

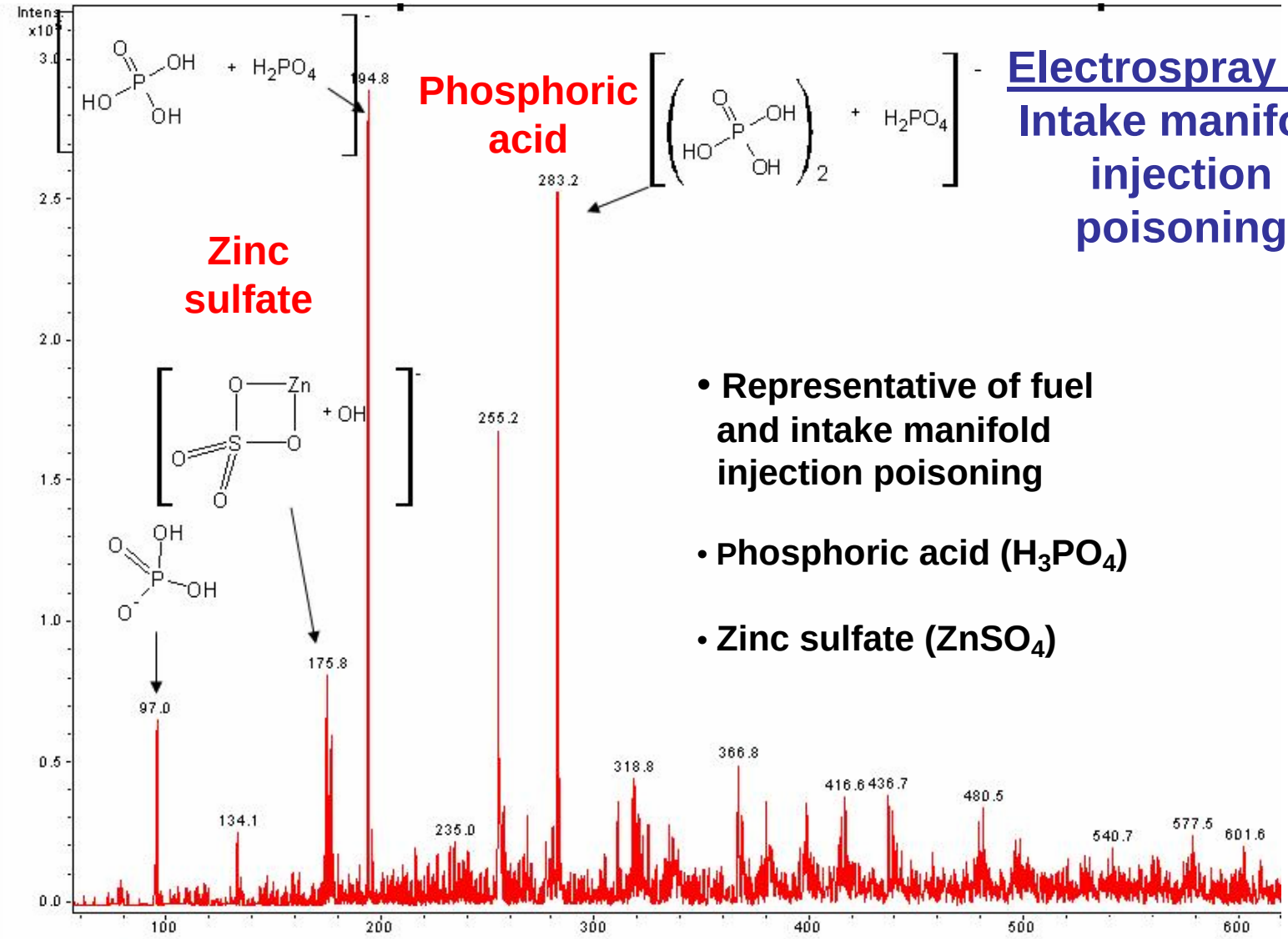
Engine Bench Setup



Summary of DOC Poisoning Effects

DEACTIVATION METHOD	METHODOLOGY	FIELD-SERVICE EQUIVALENCE	PERFORMANCE DEGRADATION
PHOSPHORUS/SULFUR ADSORPTION (CERIUM AND ALUMINUM PHOSPHATES)	INJECTING INTO INTAKE MANIFOLD	NORMAL BUS OPERATION	HYDROCARBON OXIDATION
DENSE SOOT OVERLAYER	MIXING LUBE-OIL WITH FUEL	EXCESSIVE LUBE-OIL CONSUMPTION	CARBON MONOXIDE AND HYDROCARBON OXIDATION
ZINC PHOSPHATE GLAZE	INJECTING INTO EXHAUST MANIFOLD	NOT OBSERVED (POOR OIL CONTROL?)	CARBON MONOXIDE OXIDATION

Phosphorus Exhaust Chemistry



Phosphoric acid

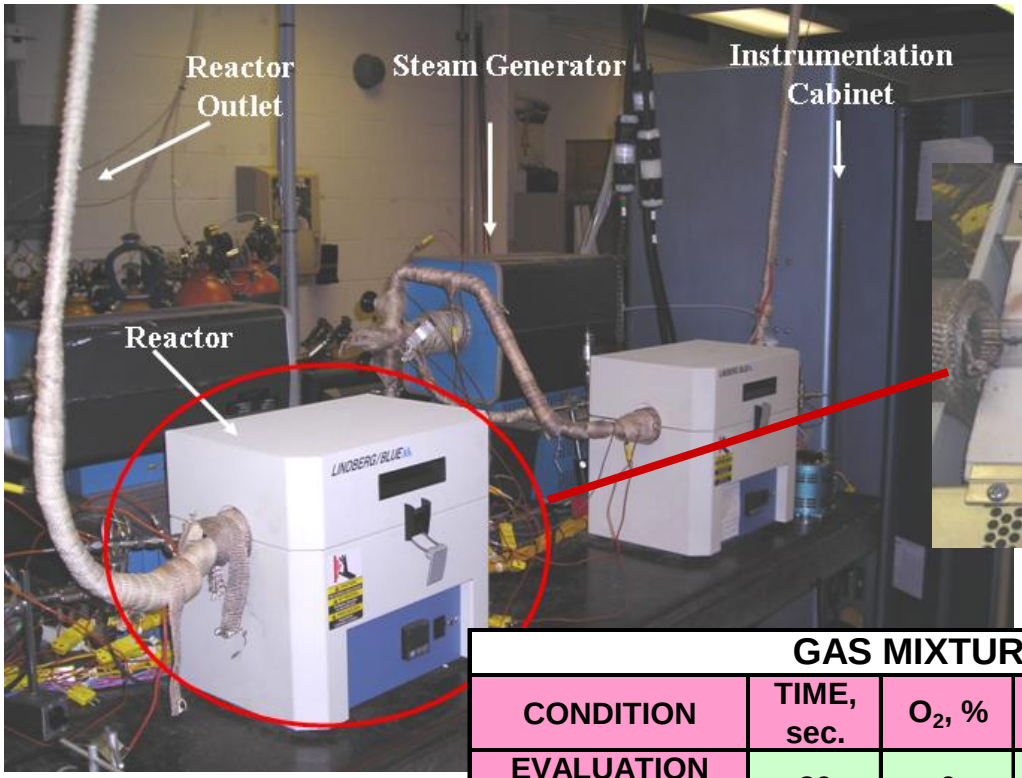
Zinc sulfate

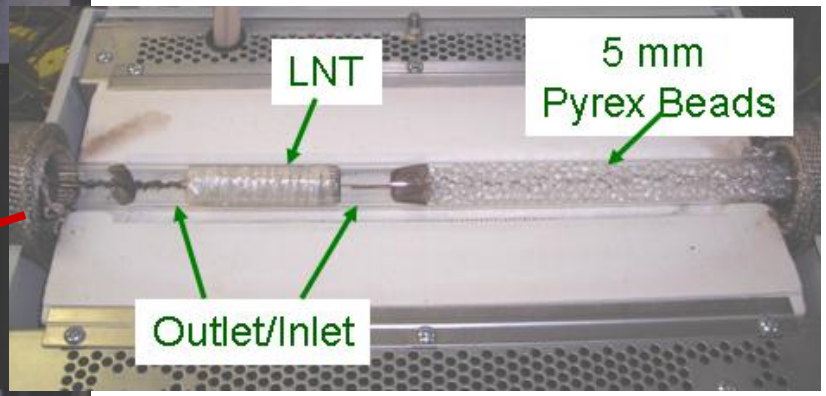
Electrospray MS

Intake manifold injection poisoning

- **Representative of fuel and intake manifold injection poisoning**
- **Phosphoric acid (H_3PO_4)**
- **Zinc sulfate ($ZnSO_4$)**

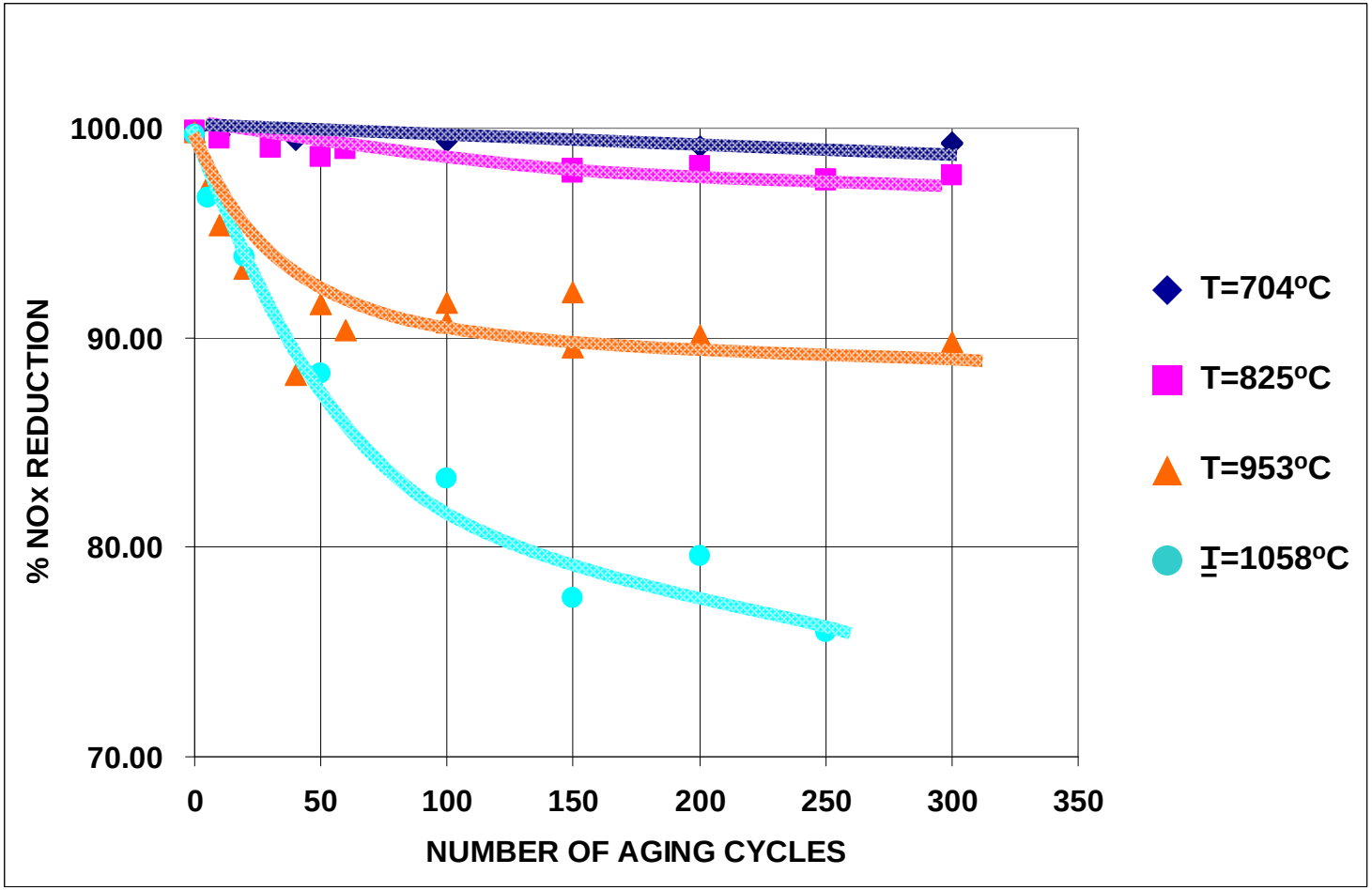
UT Bench-Flow Reactor for LNT Aging



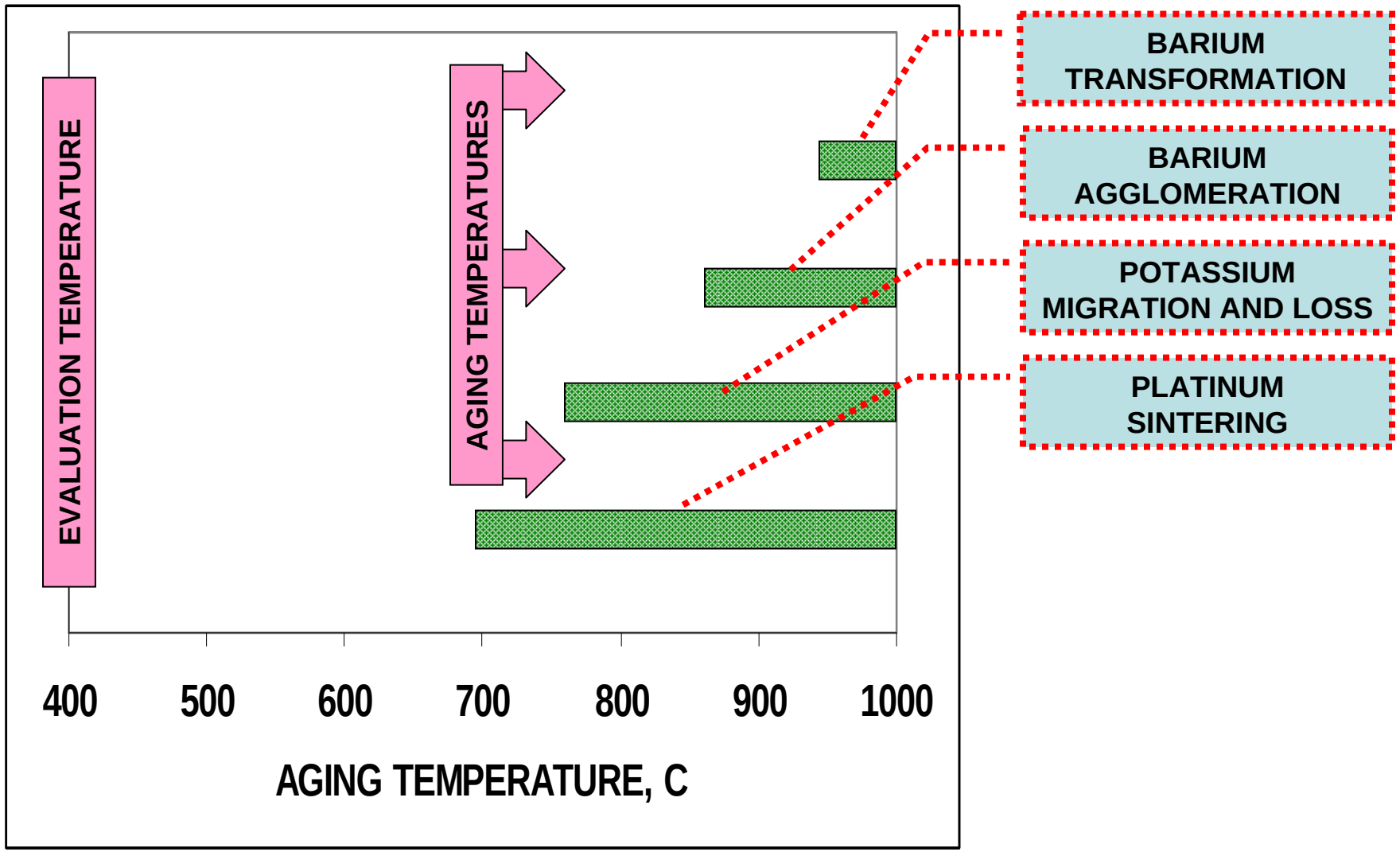


GAS MIXTURES USED FOR LNT AGING								
CONDITION	TIME, sec.	O_2, %	CO_2, %	H_2O, %	NO, ppm	CO, %	H_2, %	N_2, %
EVALUATION LEAN	20	0	5	10	1000	0	0	bal
EVALUATION RICH	4	0	0	0	0	4	1.3	bal
AGING LEAN, 800ºC*	158*	0	5	10	1000	0	0	bal
AGING RICH, 800ºC*	22*	3*	0	0	0	6*	2*	bal
* TIMES AND CONCENTRATIONS VARY SLIGHTLY WITH TARGET AGING TEMPERATURE								

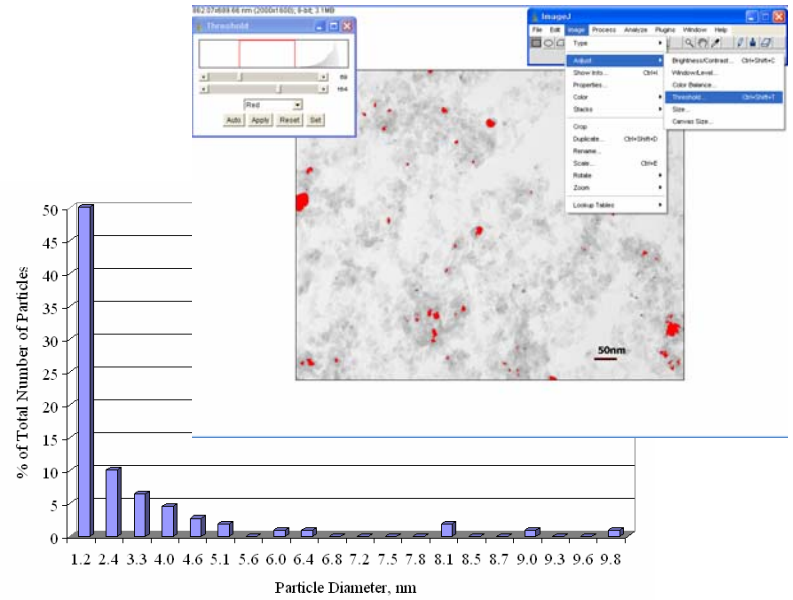
Deterioration of Hi-Temp LNTs as Function of Temperature and Number of Aging Cycles



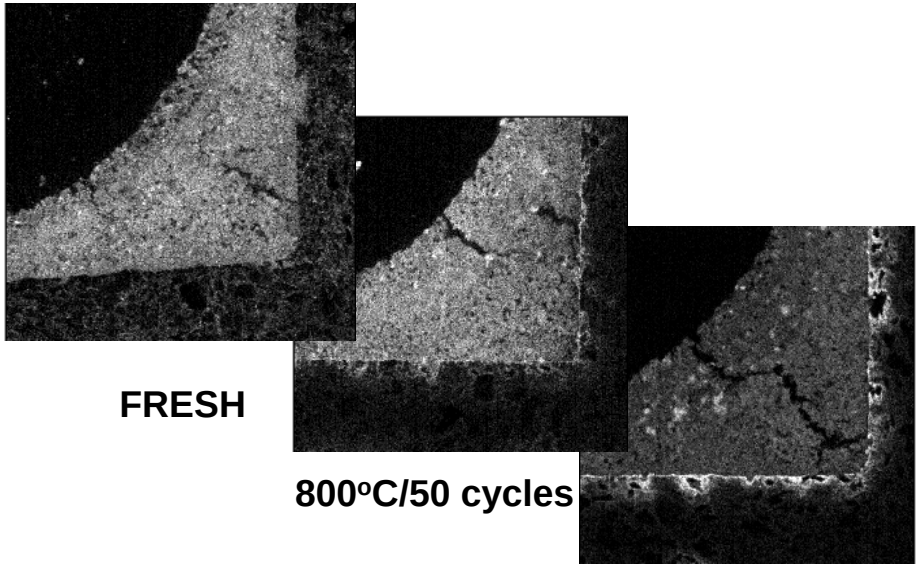
Mechanisms of Deterioration for Hi-Temp LNTs



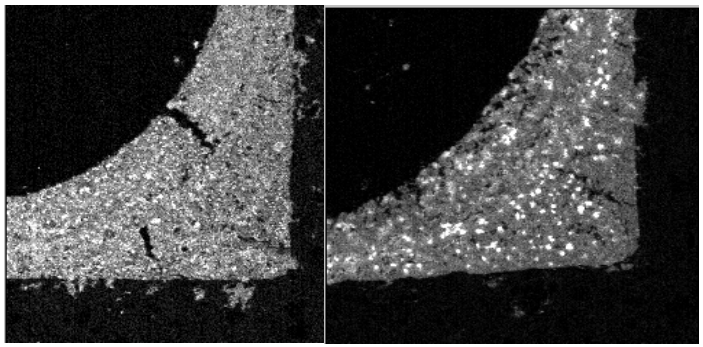
LNT Material Changes



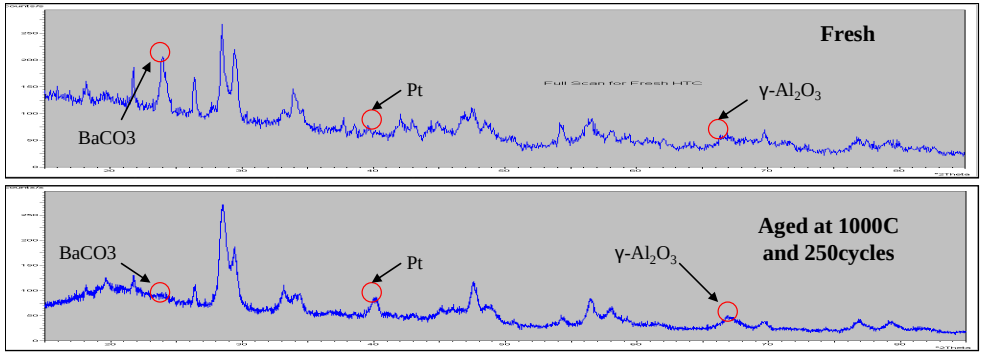
PARTICLE SIZE DISTRIBUTION OBTAINED FROM TEM



POTASSIUM MIGRATION TO INTERFACE



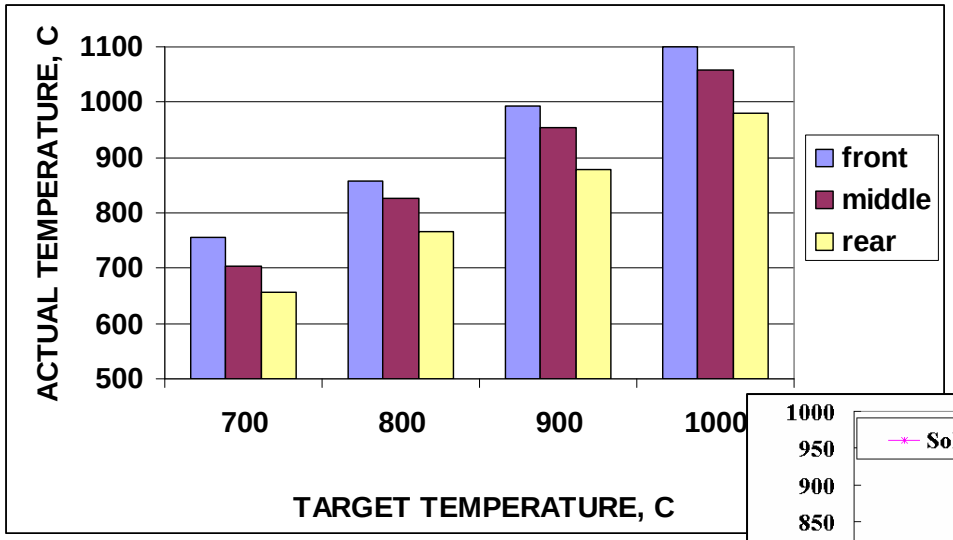
BARIUM AGGLOMERATION



TRANSFORMATION OF $BaCO_3$ (TO $BaAl_2O_4$)

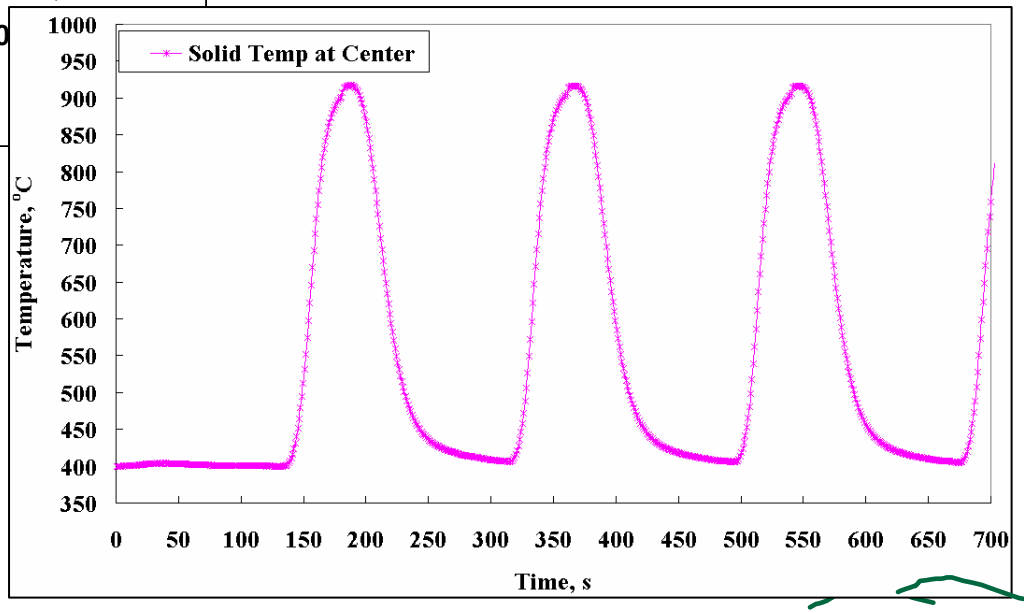
Temperature Profile During LNT Thermal Aging

MAXIMUM TEMPERATURES IN LNT VARY AXIALLY DURING THERMAL AGING



Aging time and temperature are needed to extract deactivation kinetics

TEMPERATURE VARIES DURING AGING CYCLING



Future Plan for LNT Aging

- Continue aging and characterization
  - Barium / Potassium (high-temperature LNTs)
  - Barium (low-temperature LNTs)
- Extract rates for aging mechanisms
  - Performance loss (global deactivation)
  - PGM sintering and NOx storage media agglomeration/loss
  - Applicable temperature ranges
- Model deactivation with simple kinetics

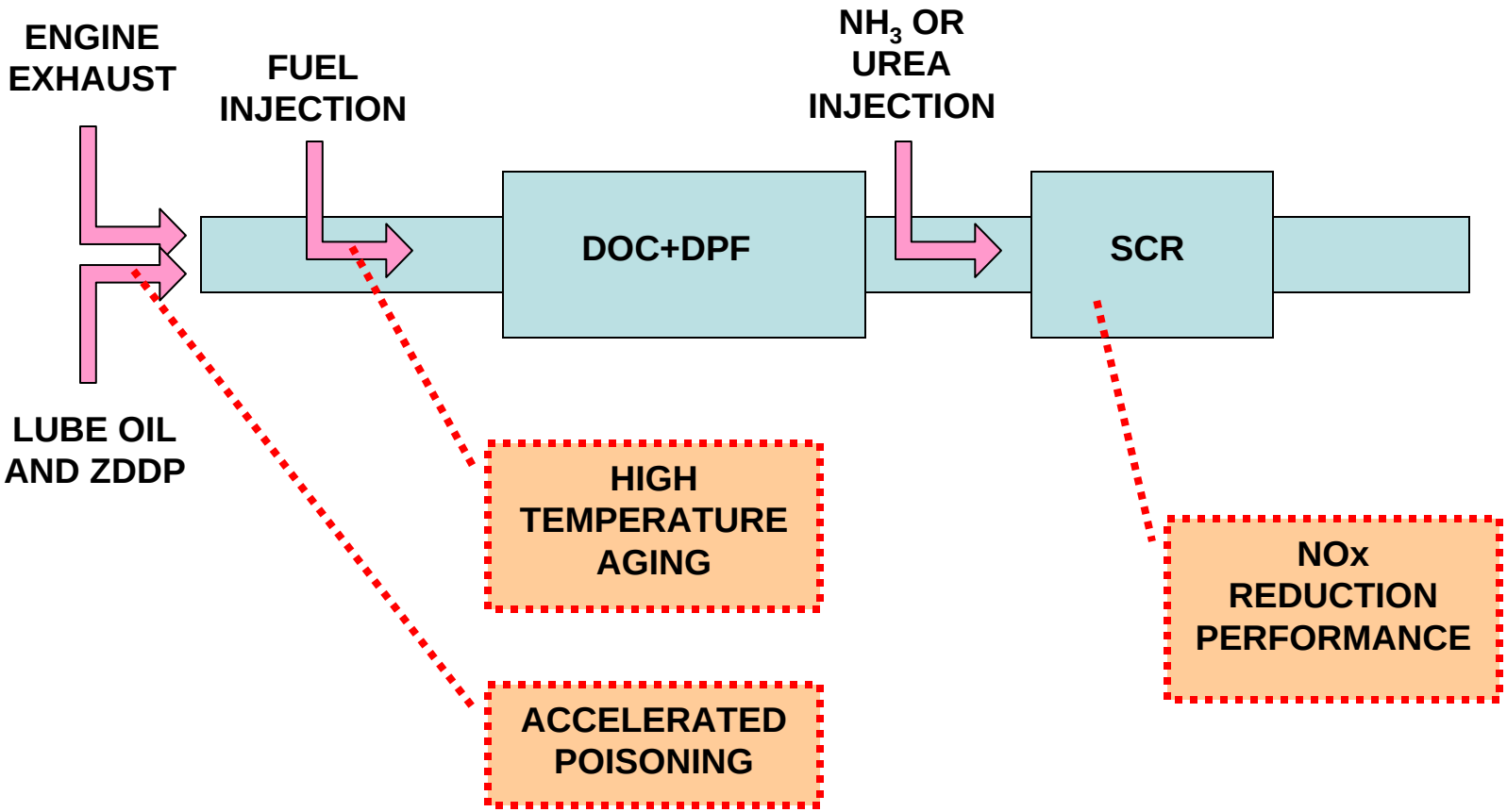
DPF Plan and Progress

- **Plan**
  - **Study confounding issues of phosphorous, ash, and soot**
  - **Evaluate performance and microstructure analysis**
- **Progress**
  - **Received samples**
  - **Performed first tests**
  - **Blended lube oil into fuel to increase ash loading rate**
  - **Performed light-off and forced regeneration**
- **See DEER poster for more information:**
  - **B.G. Bunting and C.G. Li, "The Development of a Small Engine-Based Accelerated Ash Loading Protocol and Application to a New Substrate Material", DEER 2006, Tuesday, 9/22/06**

SCR Aging and Poisoning

- Research just starting
- Inputs from industry gathered so far
  - Focus on zeolite-based SCR
  - Topics of concern
    - Aging of SCR during active DPF regeneration
    - Phosphorous poisoning of SCR catalyst

SCR Aging and Poisoning Concept



Conclusions

- Rapid aging and poisoning protocols require three tasks
  - Develop rapid cycle based on application
  - Compare performance changes to field-aged catalysts
  - Compare material changes to field-aged catalysts
- Rapid aging and poisoning protocols provide an understanding of the processes taking place
  - Extensive materials characterization
  - Kinetic modeling of deactivation mechanisms
- General schemes can be applied to other situations
- It is difficult to obtain field-aged catalysts (hint! hint!) ☺

Upcoming References

- DOC poisoning
  - S.J. Eaton, K. Nguyen, and B.G. Bunting, “Deactivation of Diesel Oxidation Catalysts by Oil Derived Phosphorous”, SAE 2006 International Powertrain Conference, SAE 2006-01-3275.
- General
  - B.G. Bunting, J.P. Szybist, T.J. Toops, K. Nguyen, S.J. Eaton, A.D. Youngquist, and A. Gopinath, “The Use of Small Engines as Surrogates for Research in Aftertreatment, Combustion, and Fuels”, SAE 2006 Small Engine Technology Conference, 06SETC-62.
- LNT aging
  - H. Kim, K. Nguyen, B.G. Bunting, and T.J. Toops, “Rapid Aging of Diesel Lean NOx Traps through High Temperature Thermal Cycling”, SAE 2007 World Congress, 07-PFL-227.