UT-BATTELLE

Rapid Thermal Aging of Lean NO_x Traps

Bruce Bunting and Todd J. Toops
Oak Ridge National Laboratory

Ke Nguyen and Hakyong Kim
University of Tennessee at Knoxville

10th CLEERS Workshop
May 2, 2007

Rapid Aging and Poisoning Protocols

- **Goal:**
  - **Accelerated test protocol which simulates longer mileage field-service**
  - **Evaluate durability and understanding mechanisms of deterioration**
  - **If available, compare results to field-aged catalysts**
  - **Generate data that could be used to model deactivation**

- **Benefits include:**
  - **Better 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**

- **Aftertreatment Aging Projects**
  - **Lube-oil effects on DOC (ZDDP-focus)**
  - **Thermal Aging of LNTs (focus of this talk)**
  - **Accelerated Ash loading in DPFs**
  - **SCR (ZDDP, thermal aging, sulfur…system evaluation with DOC and DPF)**

LNT High Temperature Thermal Aging

- **Key concern for Lean NO_x Trap Durability**
  - **high temperature periodically required to desulfate LNTs**

- **Exposure to lean and rich conditions is important characteristic of onboard de-sulfation**

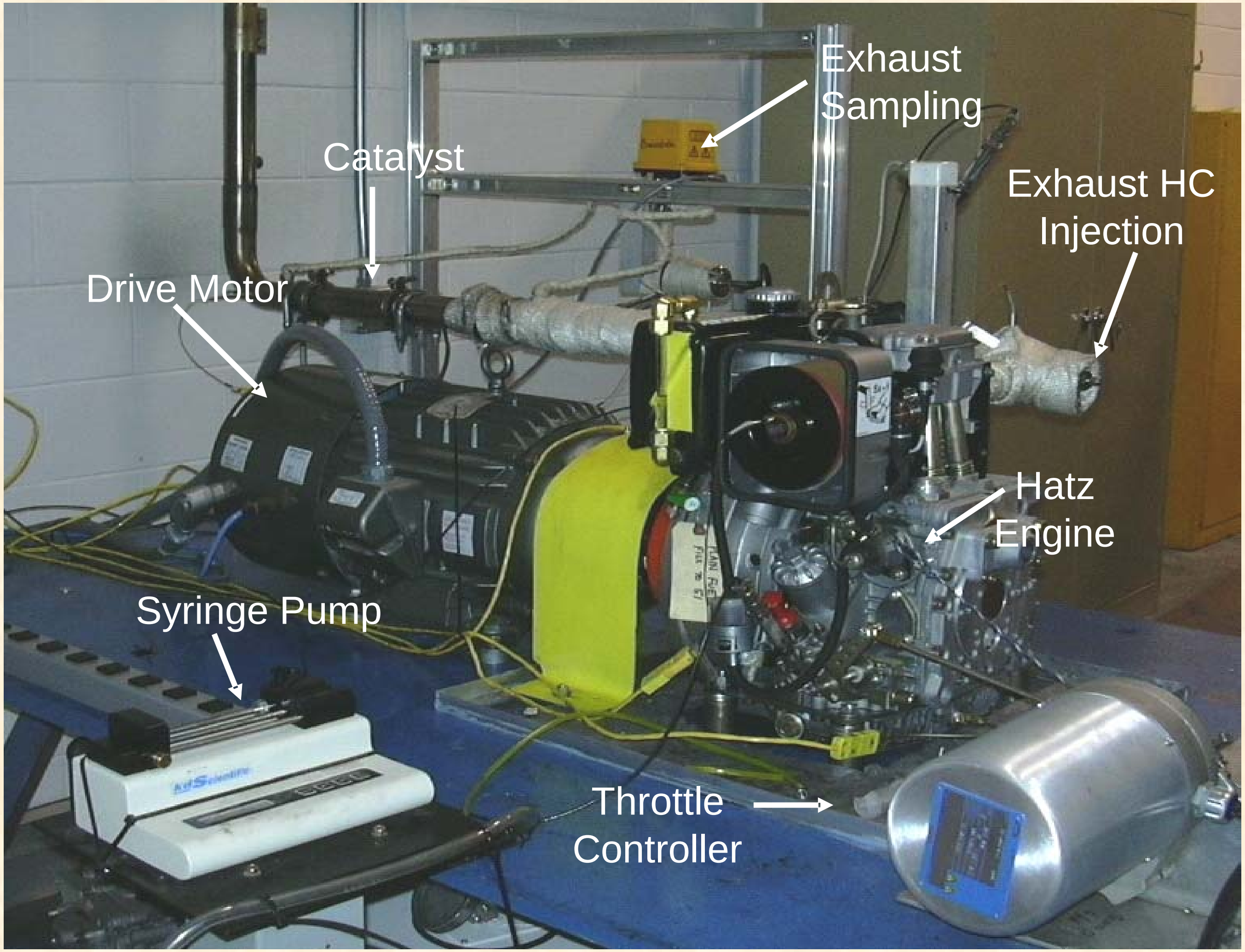
- **Expected deactivation mechanisms**
  - **Precious metal sintering**
  - **Surface area losses**
  - **Solid-state reactions (barium aluminate formation)**
  - **Storage medium migration**

Outline

- **Engine Based Aging**
  - **Model Catalyst**
  - **Observations and Characterization**
  - **Correlation to performance**
- **Bench Reactor (core) Based Aging**
  - **“Fully-Formulated” Catalyst**
  - **Observations and Characterization**
  - **Need for deactivation modeling and correlations**
- **Future Efforts**

Engine-based Thermal Aging

Engine Bench Setup



Key feature for aging:

- **Diesel fuel injected into exhaust manifold**
- **Feature used both for aging and for evaluation**

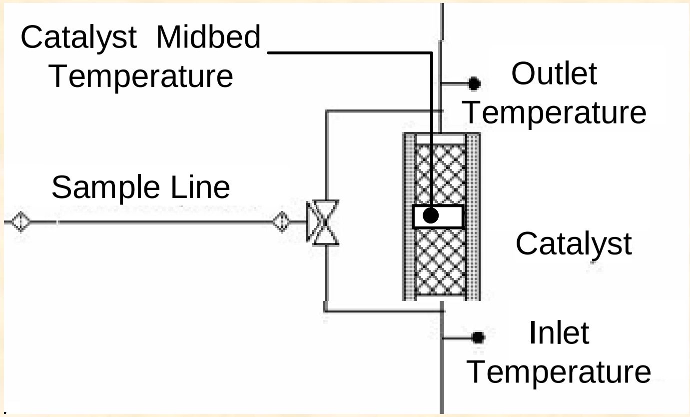
Engelhard (BASF) LNTs

- **Model catalysts (no oxygen storage)**
- **NGK cordierite substrates, 300 cpsi, 2"x3", two bricks used**
- **Barium / PGM / alumina**
  - **150 gm/ft^3 PGM, 14 Pt / 1 Rh**
  - **230 gm/liter total washcoat loading**
  - **~30% barium carbonate**

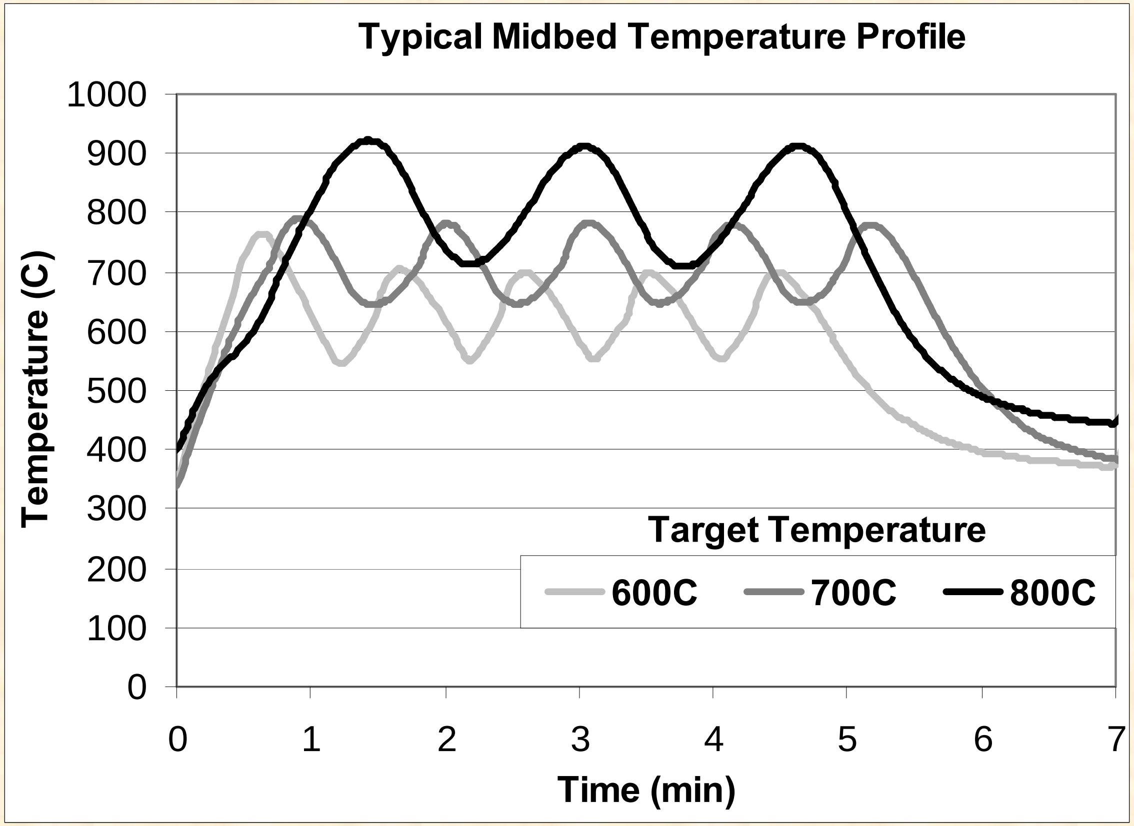
Engine based cycles

- Engine operates steady state at 1000 rpm
  - 1000 ppm NO_x, 60k h^{-1} GHSV
- Diesel fuel injection in exhaust manifold using heated atomizer
  - Target 13:1 A/F
- Degreening procedure
  - 4 hours engine exhaust
- Evaluation Conditions
  - 20 seconds lean, 4 seconds rich
  - 400 C target temperature
- Aging cycle
  - 300 second rich, 120 second lean
  - Inject fuel until target temperature is achieved then cut off fuel
  - Target Temperatures: 600, 700 and 800°C

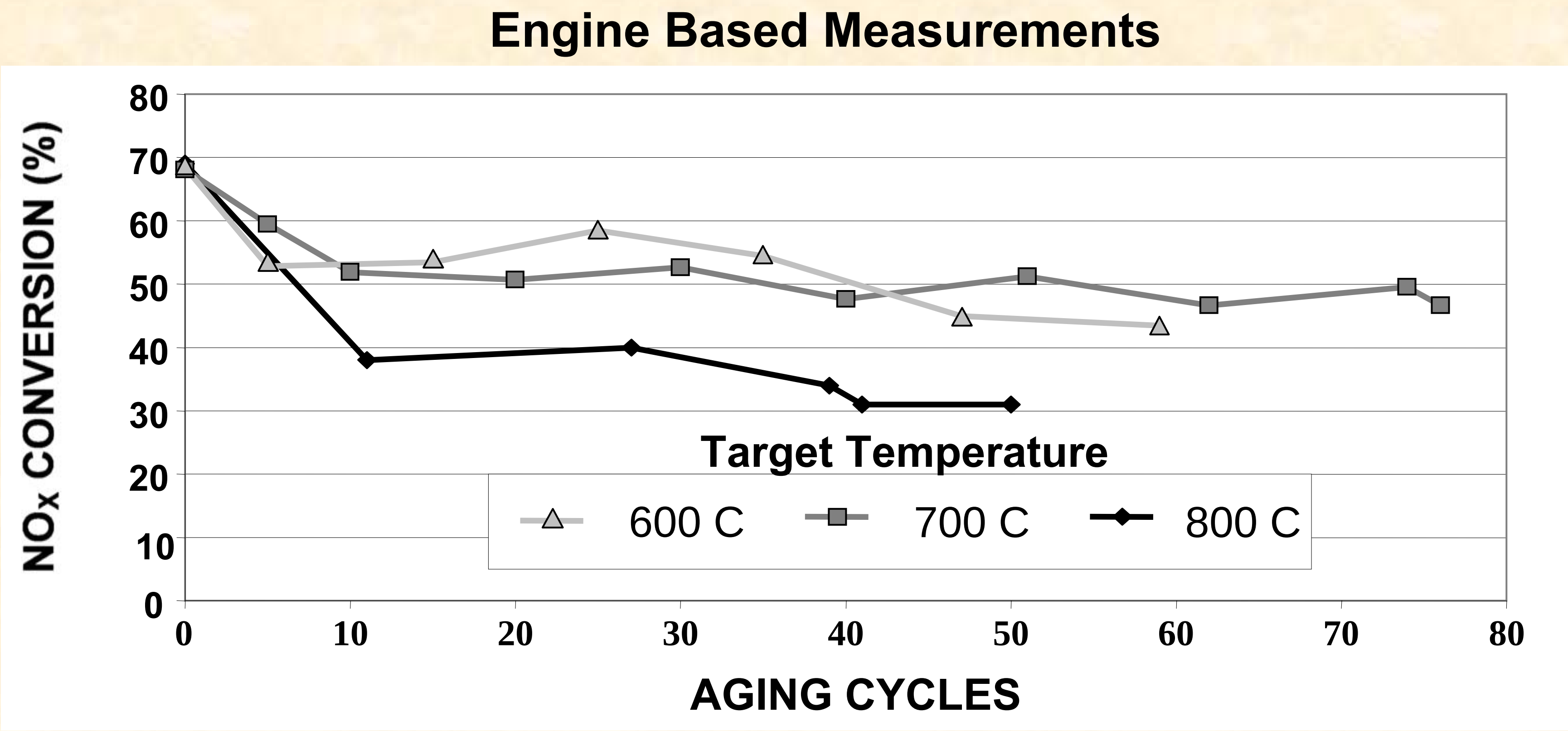
Temperature Profile During Thermal Aging



- **600°C Target**
  - **620°C avg.**
  - **760°C max**
- **700°C Target**
  - **690°C avg.**
  - **790°C max**
- **800°C Target**
  - **780°C avg.**
  - **910°C max**



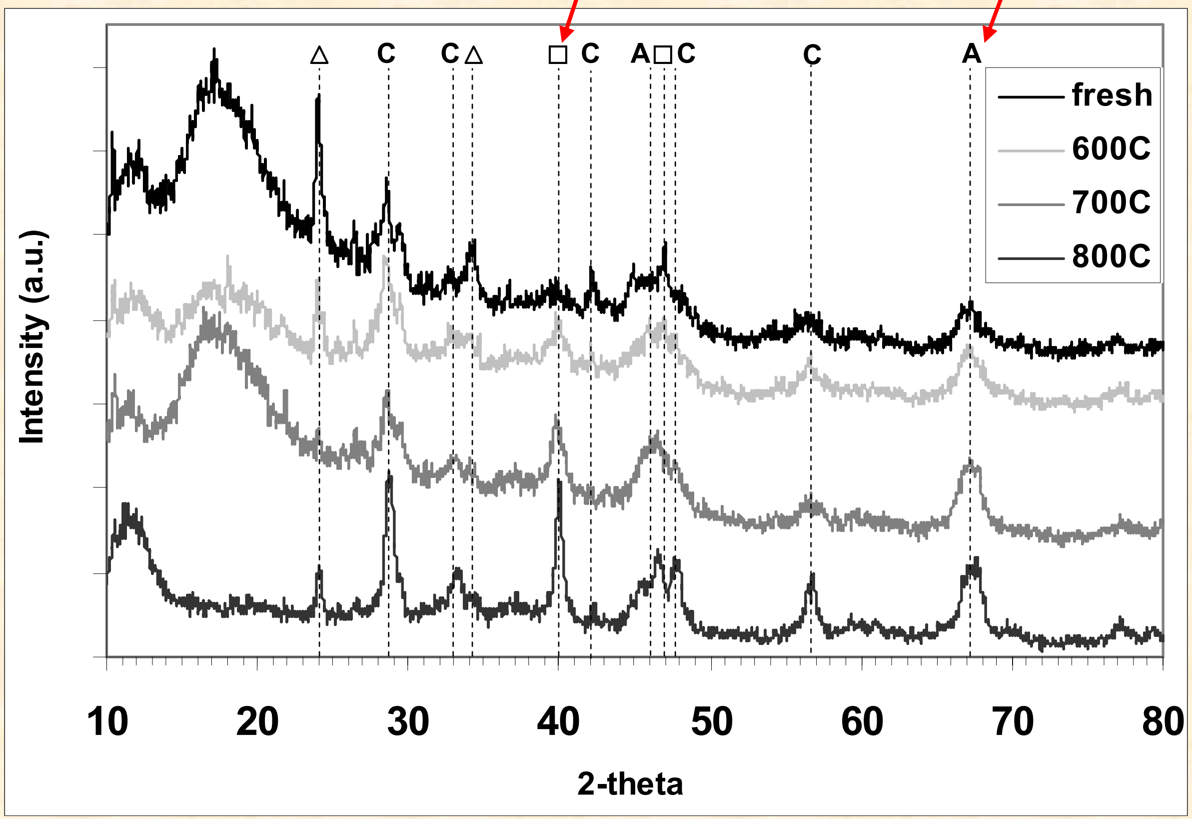
LNT Deactivation More Severe above 800C



XRD Analysis Shows Pt Sintering and Impact on Alumina Morphology

Pt sintering

Al2O3 High shoulder formation



Legend: △ - Ba_2CO_3, □ - Pt, C - Cordierite, A - γ-Al_2O_3

- **Pt sintering Observed**
- **Al_2O_3 impact observed at 800C**
  - **γ to δ Al_2O_3 transition expected at ~850C**

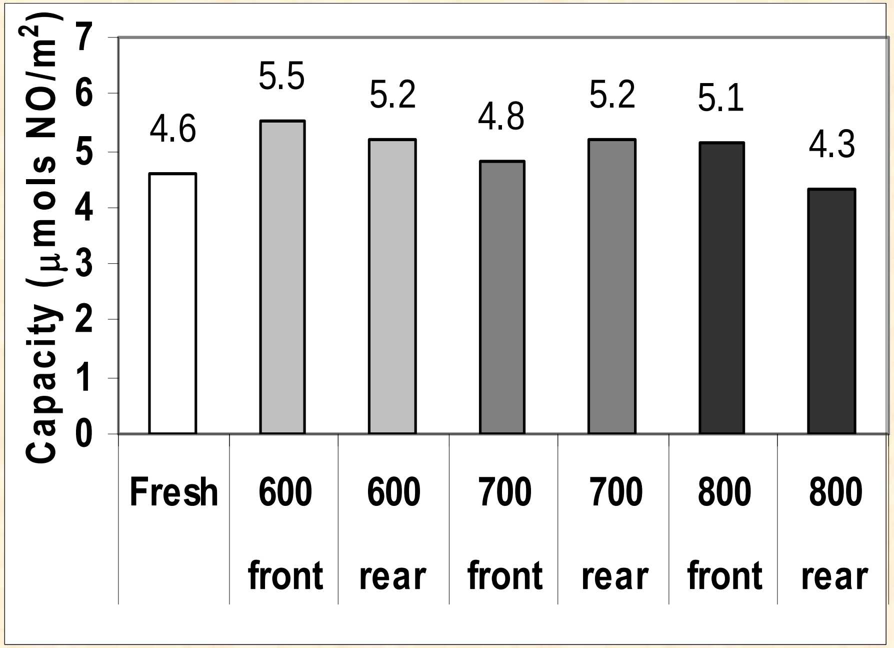
Catalyst Characterization Summary

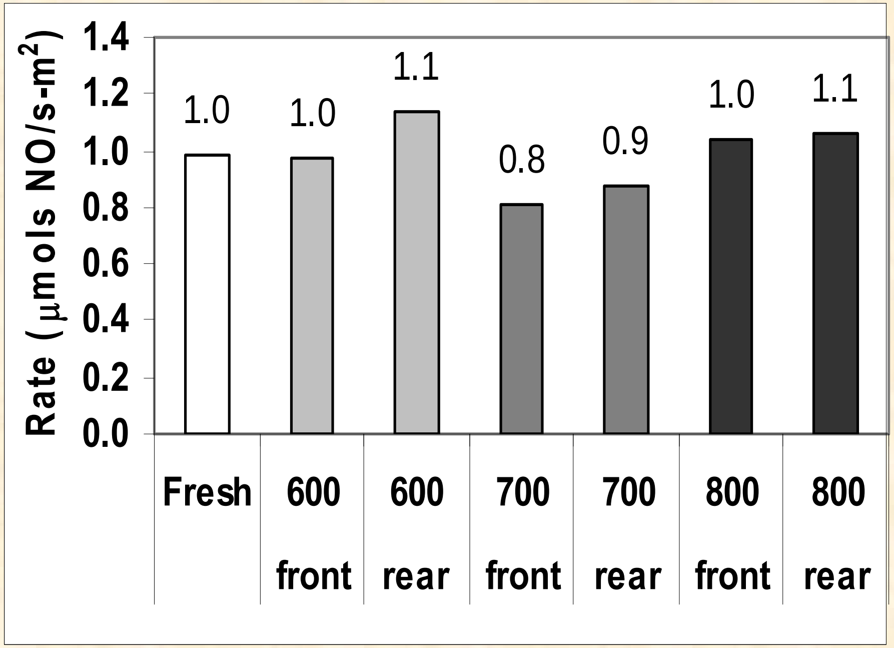
Microreactor Characterization/Measurements

Target Temp. (C)	Average Temp. (C)	Aging Cycles	Brick Position	Total Surface Area (m^2/g)	Est. Washcoat Surface Area (m^2/g)	PM Size-XRD (nm)	PM Size-Chemisorption (nm)	Storage Capacity (µmols NO/g)	SS NO_x Conversion
Fresh	n/a	0	n/a	28	99	n/a	1.1	129	68%
600	620	60	front	25	89	3.6	3.0	138	64%
600	620	60	rear	26	92	4.2	2.7	135	72%
700	690	76	front	27	95	3.6	3.0	128	54%
700	690	76	rear	28	99	3.9	2.7	146	62%
800	780	46	front	16	57	6.2	5.3	82	43%
800	780	46	rear	17	60	6.6	6.1	73	44%

Decreasing Increasing Decreasing

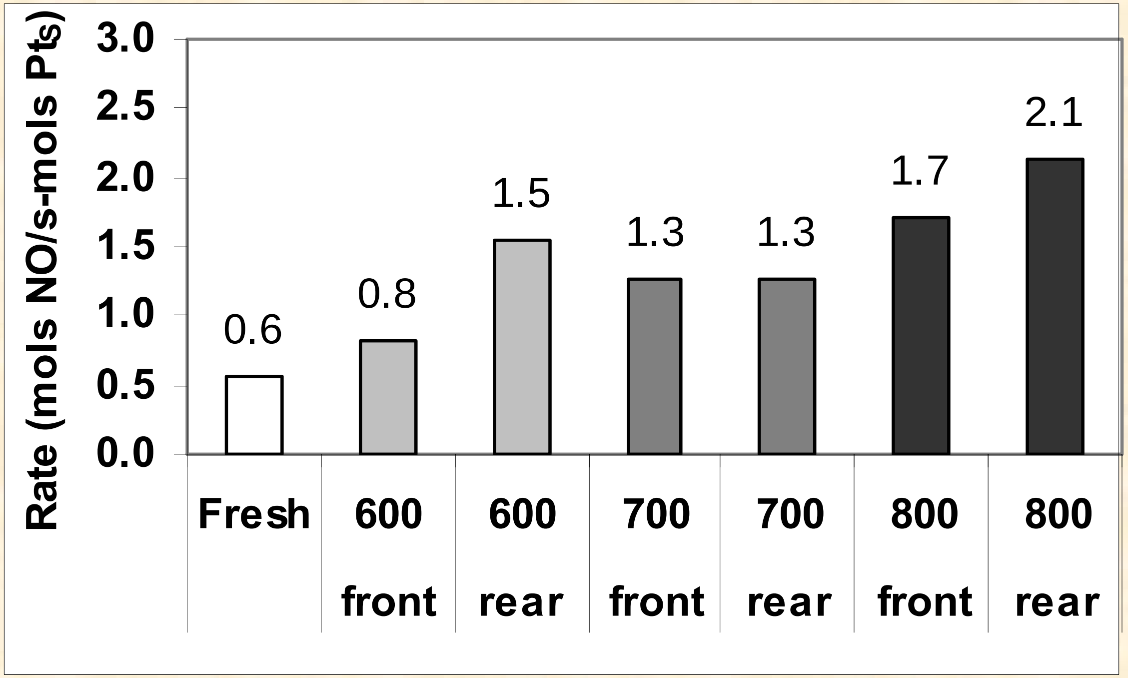
Surface Area Losses Directly Proportional to Performance Losses





- **When normalized to surface area, storage capacity (at t=1h) and overall reaction rate ~constant**
  - **Suggests storage capacity is most important factor at 400C**
  - **Indicates storage capacity and overall rate are dictated by total surface area**

Performance Losses not Directly Linked to Pt Surface Losses at 400C



- **Rate Normalized to Exposed PGM increases**
  - **Deactivation can not be directly correlated to Pt surface sites at 400C**

Engine-Aging Summary

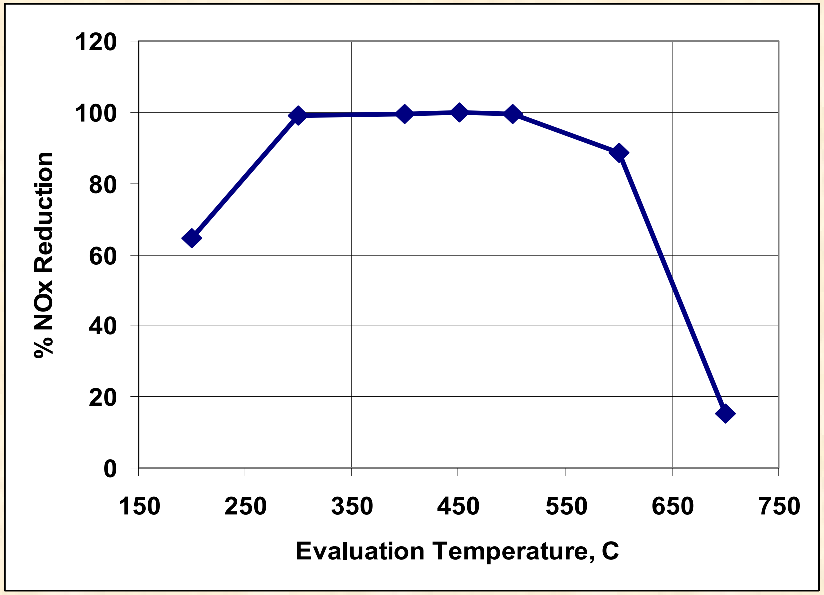
- **Greatest impact occurs for T>800C**
  - **Midbed of LNT reaches 900C**
  - **Alumina γ to δ transition begins at 850C**

- **Performance loss at 400C can be directly correlated to surface area loss**
  - **Storage capacity and overall rate decrease is directly proportional to surface area decrease**

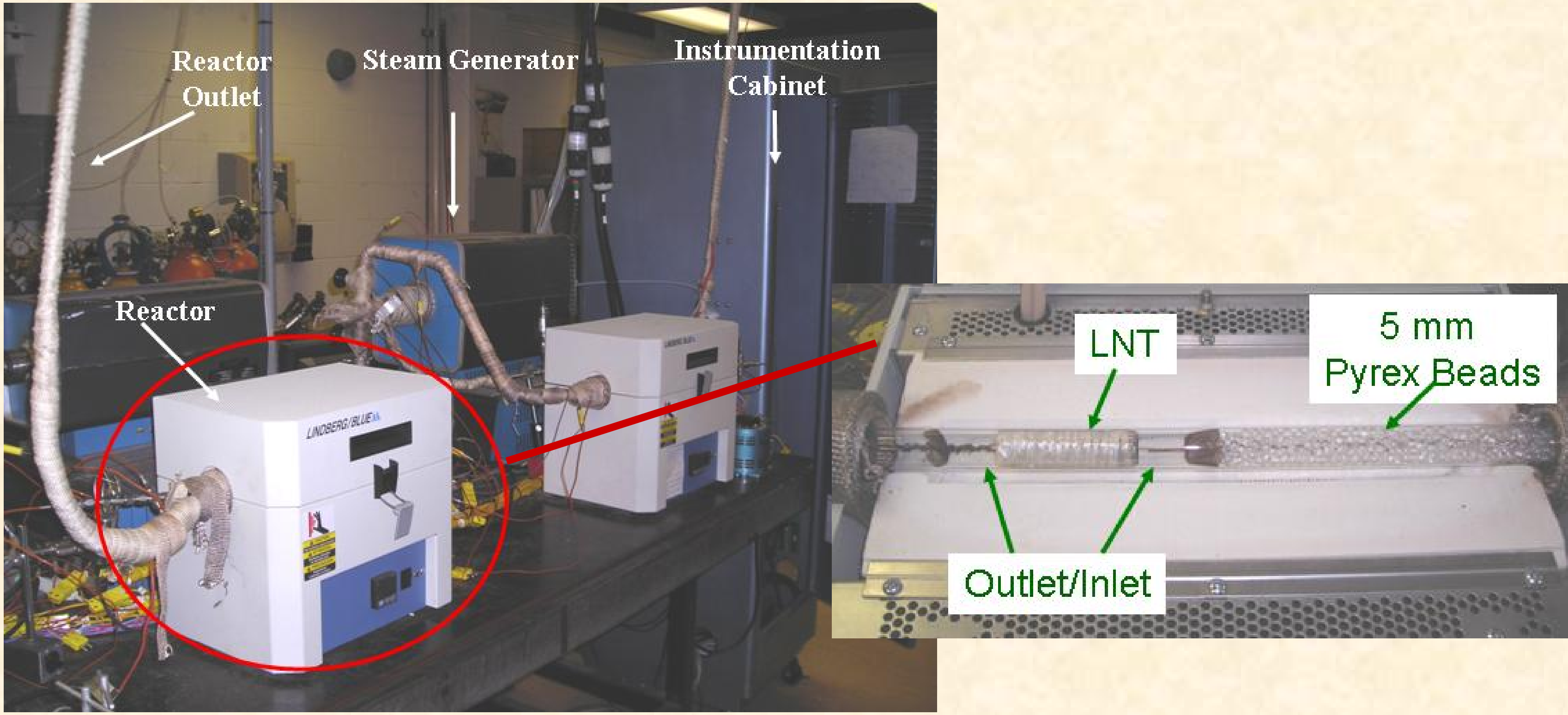
Bench Aging (core)

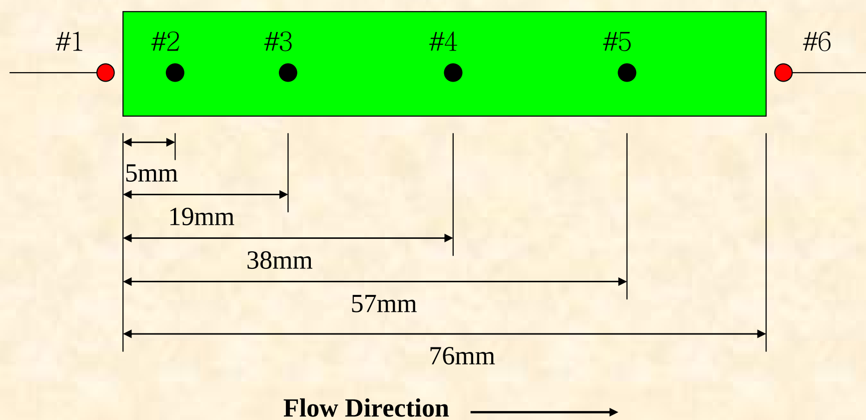
Bench Reactor Thermal Aging

- **Implementation of engine-based thermal aging has limitations**
- **Core bench reactor used to perform thermal aging**
  - **Temperatures of 700, 800, 900 and 1000°C**
  - **Simulated diesel exhaust gas**
  - **NO_x reduction performance evaluated at 400°C**
  - **Materials characterization**
    - **TEM, XRD and EPMA**
- **"Fully-Formulated" catalyst with oxygen storage component**
  - **High temperature LNT formulation (Delphi)**
    - **Ba, K, Pt, Rh, Ce**



UT Bench-Flow Reactor for LNT Aging





Bench reactor gas compositions

THERMAL AGING MIXES

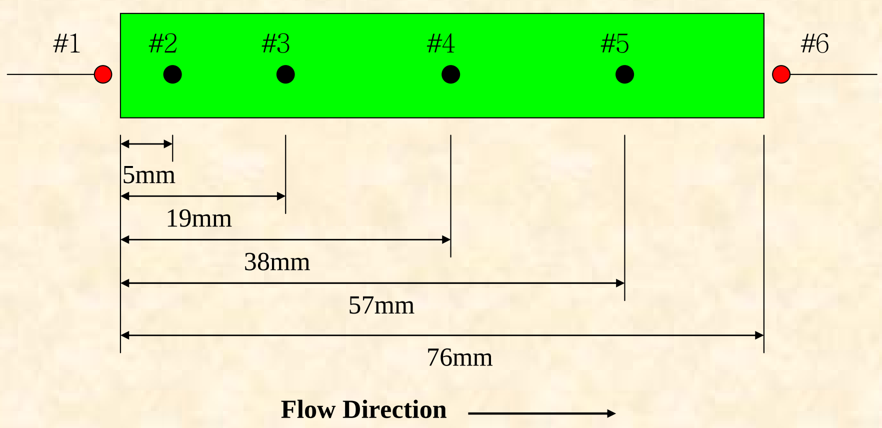
Aging Temperature	Lean Gas Mix	Rich Gas Mix
700°C	CO_2 5% NO 1000 ppm H_2O 10% O_2 10% N_2 Balance	CO_2 5% NO 1000 ppm H_2O 10% CO 4% H_2 1.33% O_2 2% N_2 Balance
800°C	CO_2 5% NO 1000 ppm H_2O 10% O_2 10% N_2 Balance	CO_2 5% NO 1000 ppm H_2O 10% CO 4% H_2 1.33% O_2 2% N_2 Balance
900°C	CO_2 5% NO 1000 ppm H_2O 10% O_2 10% N_2 Balance	CO_2 5% NO 1000 ppm H_2O 10% CO 6% H_2 2% O_2 3% N_2 Balance
1000°C	CO_2 5% NO 1000 ppm H_2O 10% O_2 10% N_2 Balance	CO_2 5% NO 1000 ppm H_2O 10% CO 9% H_2 3% O_2 5% N_2 Balance

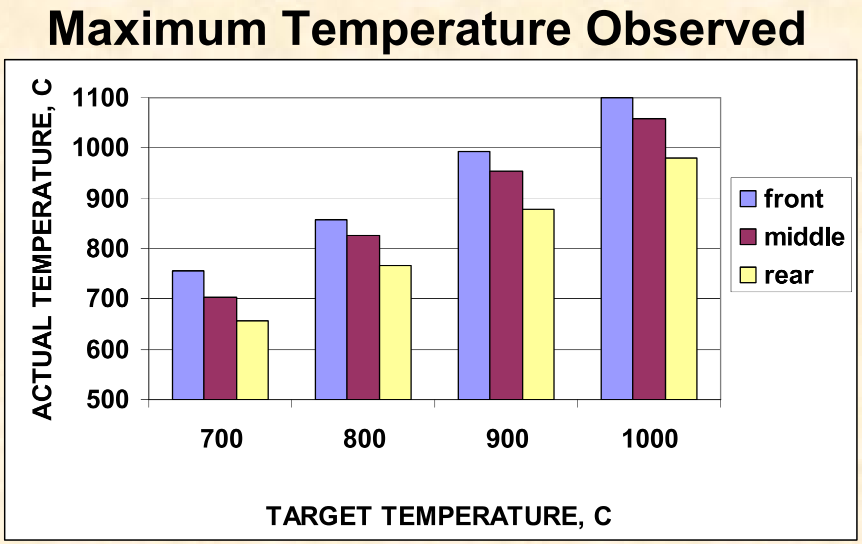
PERFORMANCE EVALUATION MIXES

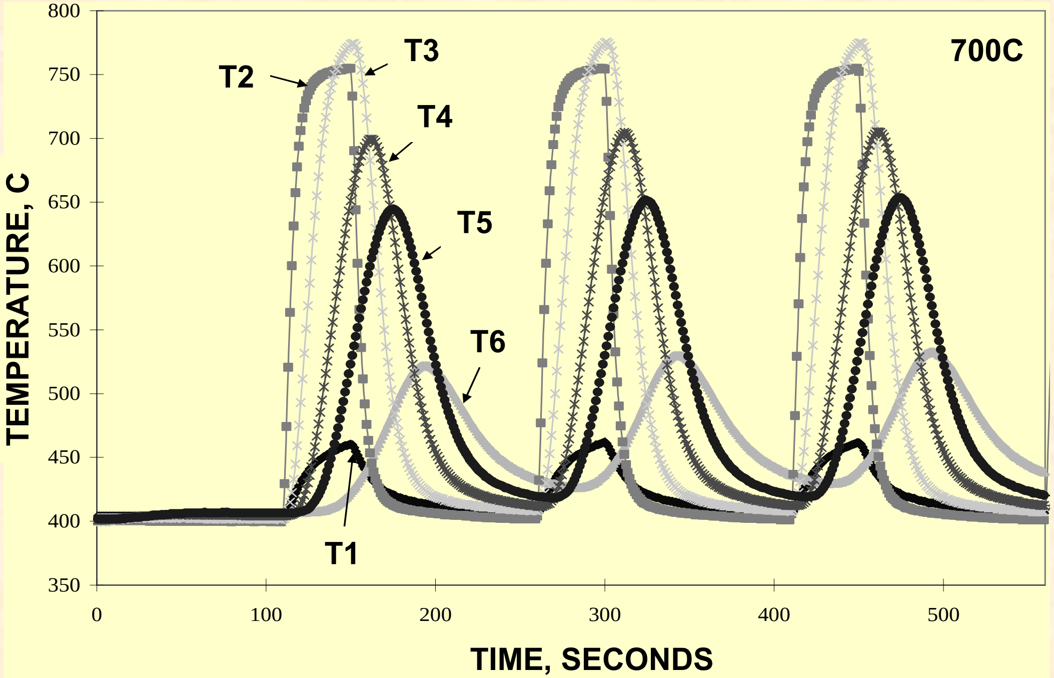
Lean Gas Mix	Rich Gas Mix
CO_2 5% NO 1000 ppm H_2O 10% O_2 10% N_2 Balance	CO_2 5% NO 1000 ppm H_2O 10% CO 4% H_2 1.33% N_2 Balance

GHSV = 60,000 h^{-1}

Typical Temperatures During LNT Bench Aging





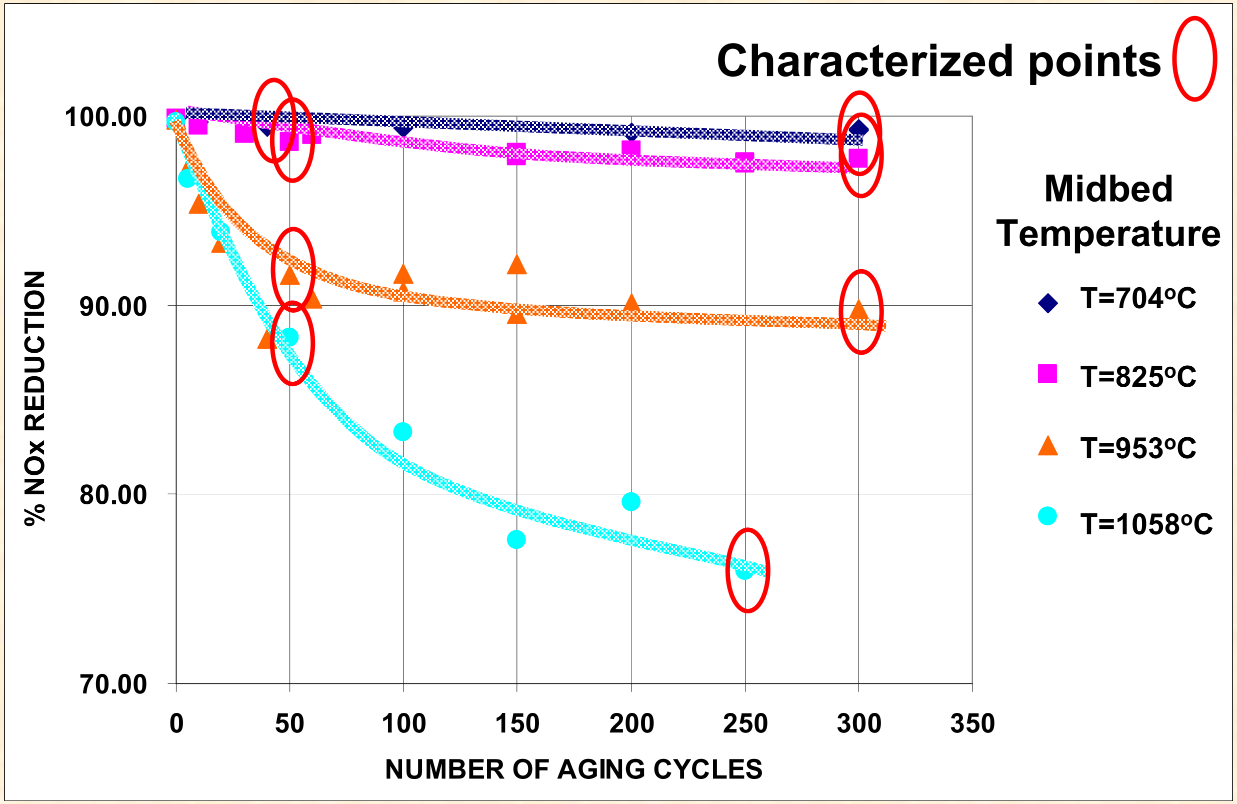


110-130s Rich, 35-60s Lean

- **Reproducible profile obtained for each target temperature**
  - **Detailed 800-1000C profiles included on website version**
- **Max temperature observed at 19 mm**
  - **25% of length**

UT-BATTELLE

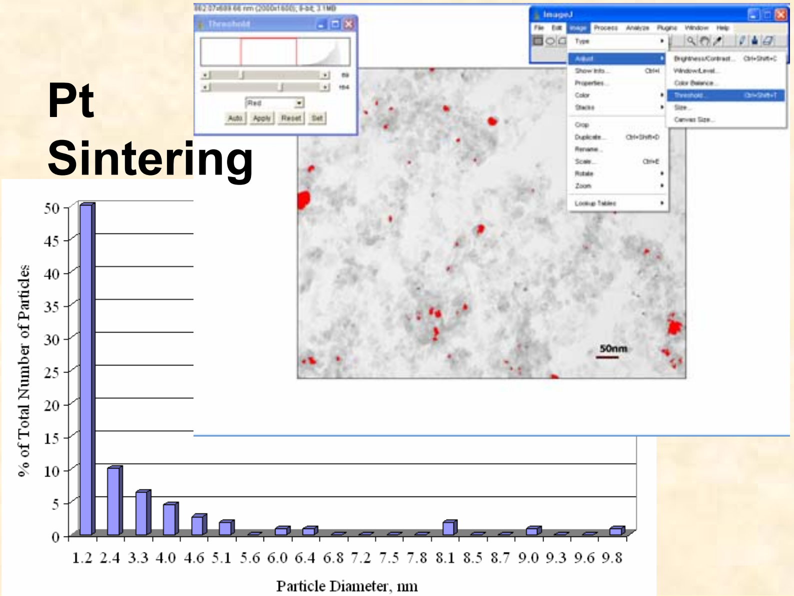
“Fully-Formulated” LNTs Demonstrate Increased Durability Compared to Model



- **Nominal impact up to 825C**
- **Above 950C, deactivation more significant**
  - **above γ to δ Al_2O_3 transition**
- **Above 1000C**
  - **new deactivation mechanism likely**

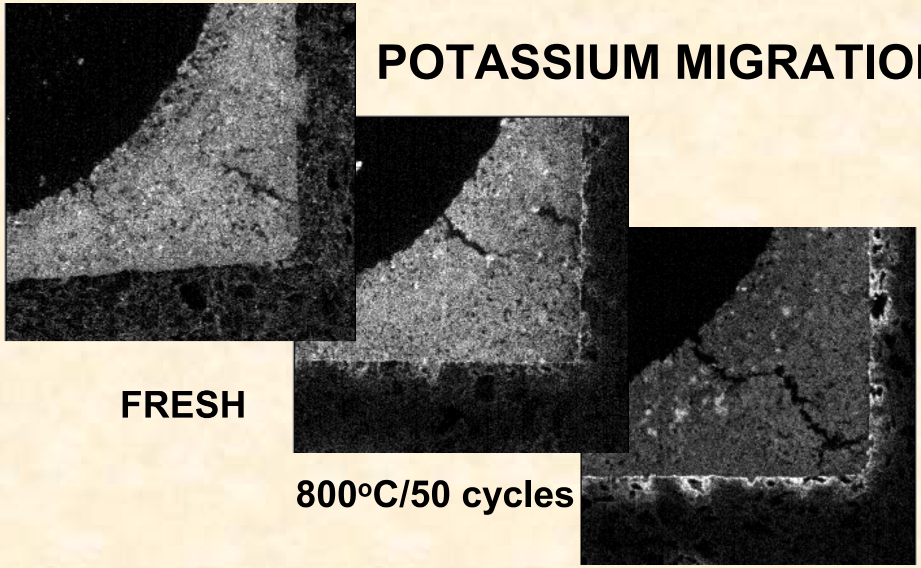
LNT Material Changes

Pt Sintering



PARTICLE SIZE DISTRIBUTION OBTAINED FROM TEM

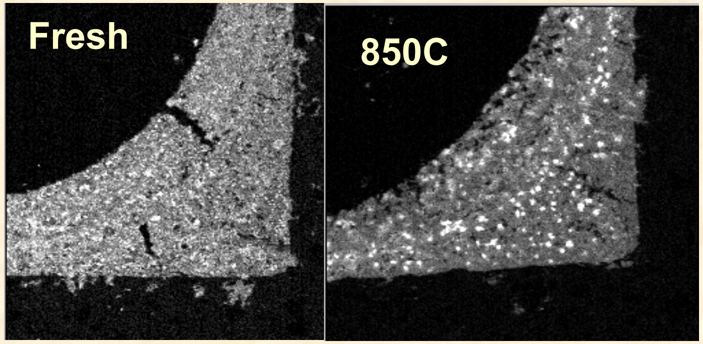
POTASSIUM MIGRATION



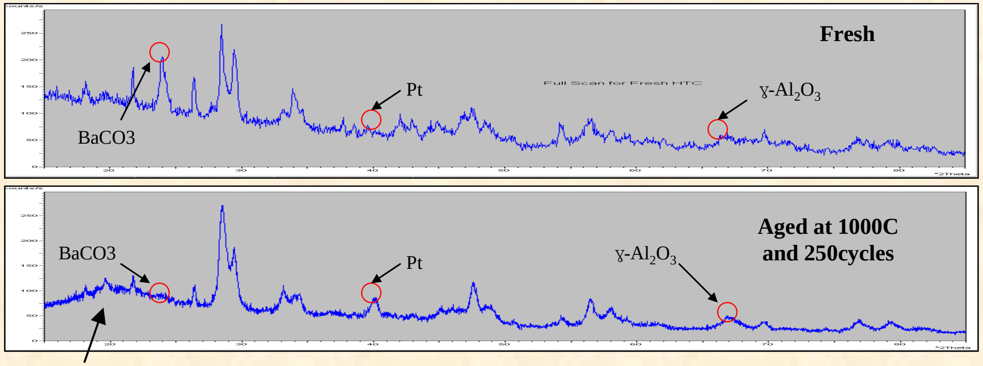
FRESH

800°C/50 cycles

800°C/300 cycles



APPARENT BARIUM AGGLOMERATION

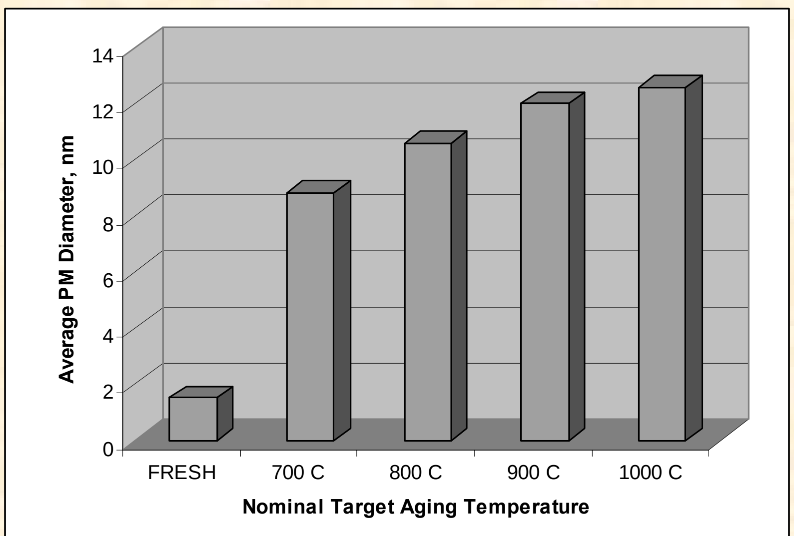


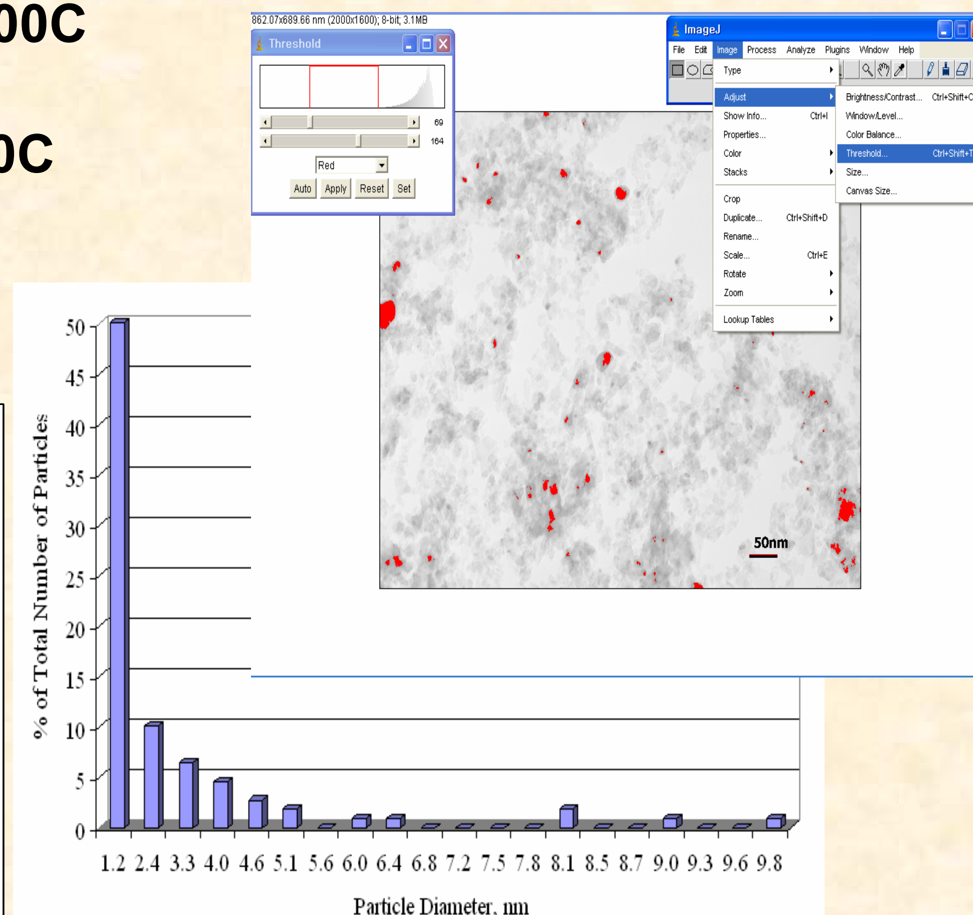
$BaAl_2O_4$

TRANSFORMATION OF $BaCO_3$ (TO $BaAl_2O_4$)

Precious Metal Particle Size Steadily Increases (TEM-based)

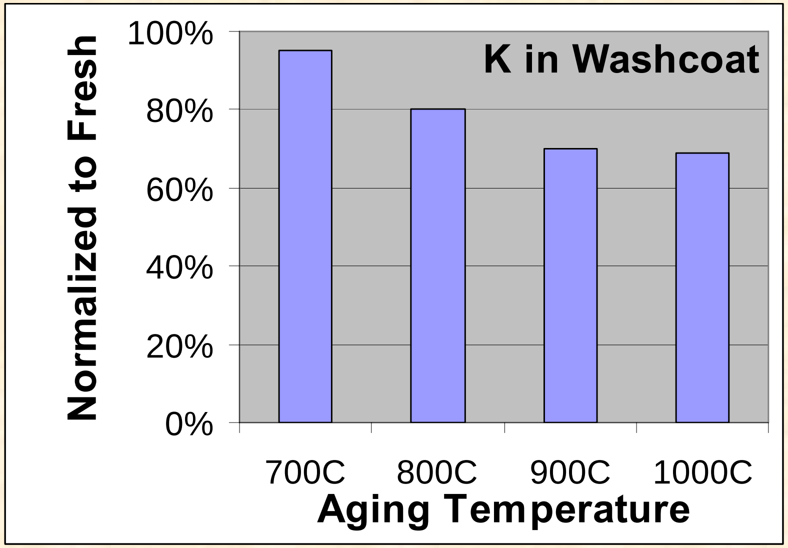
- **Essentially degreening at 700C**
- **Nominal increase above 700C**
- **Particle size distribution data also collected**

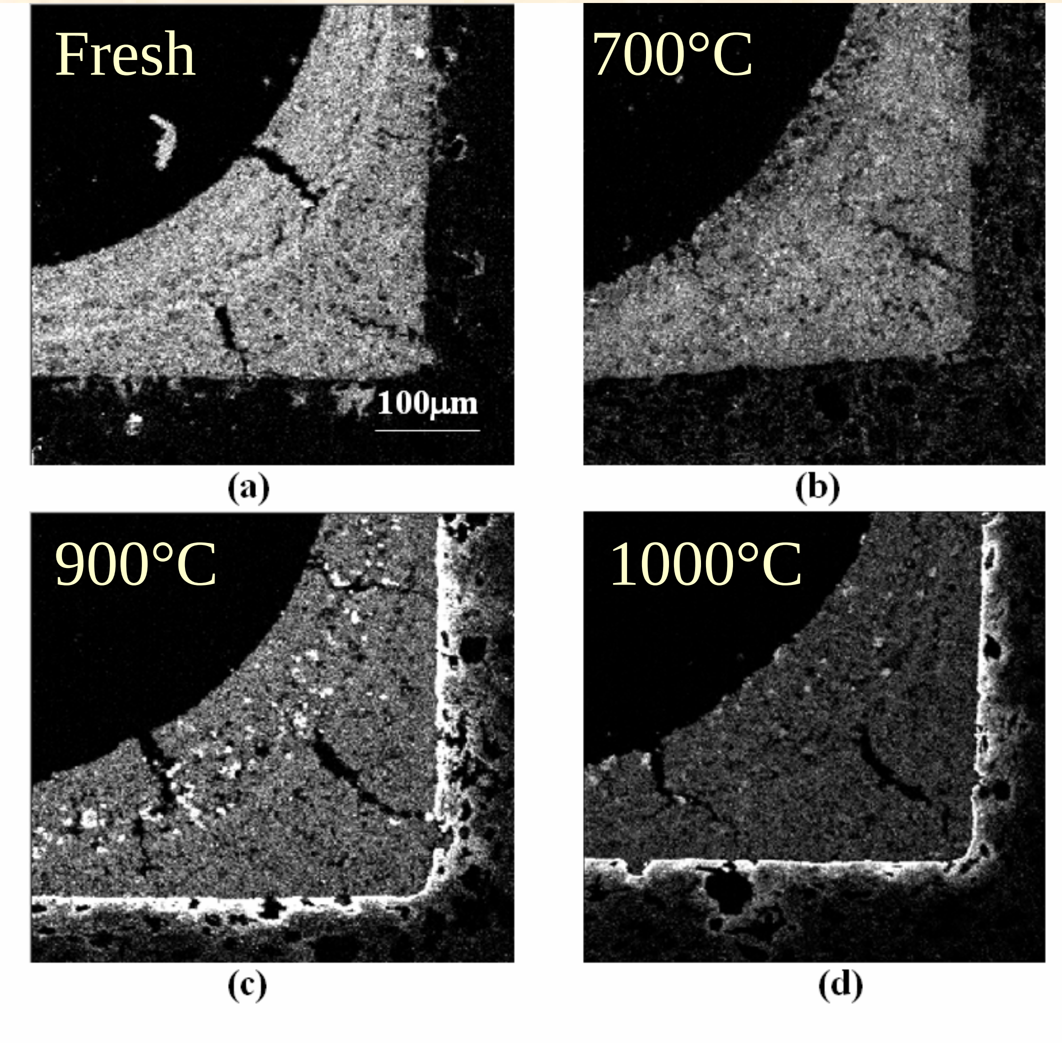




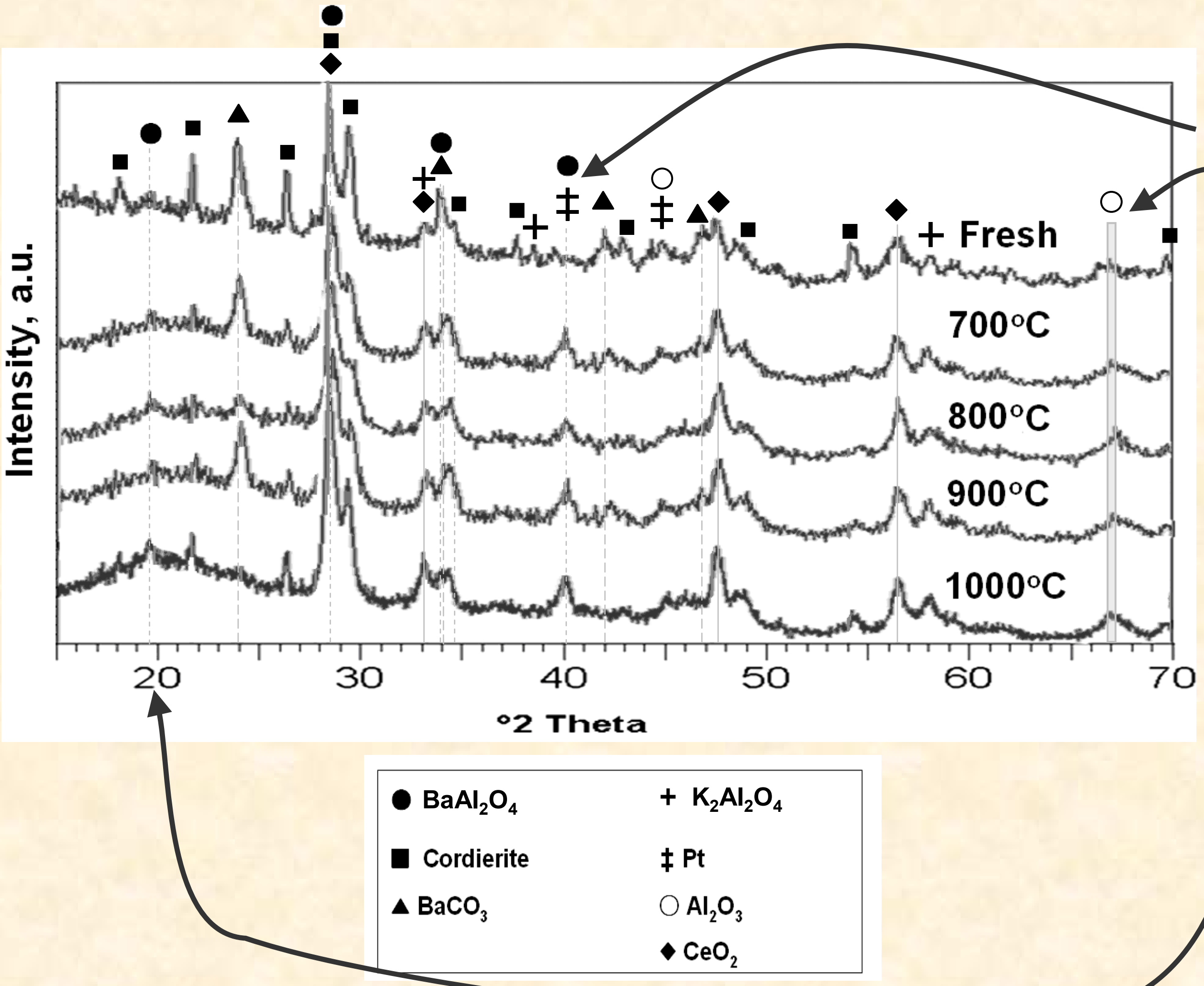
Elemental Map Shows K migration for Thermally-Aged LNTs

- **K initially well-dispersed**
- **K clearly migrates into Cordierite after aging at 900 and 1000°C**
  - **30% of K has migrated from washcoat**



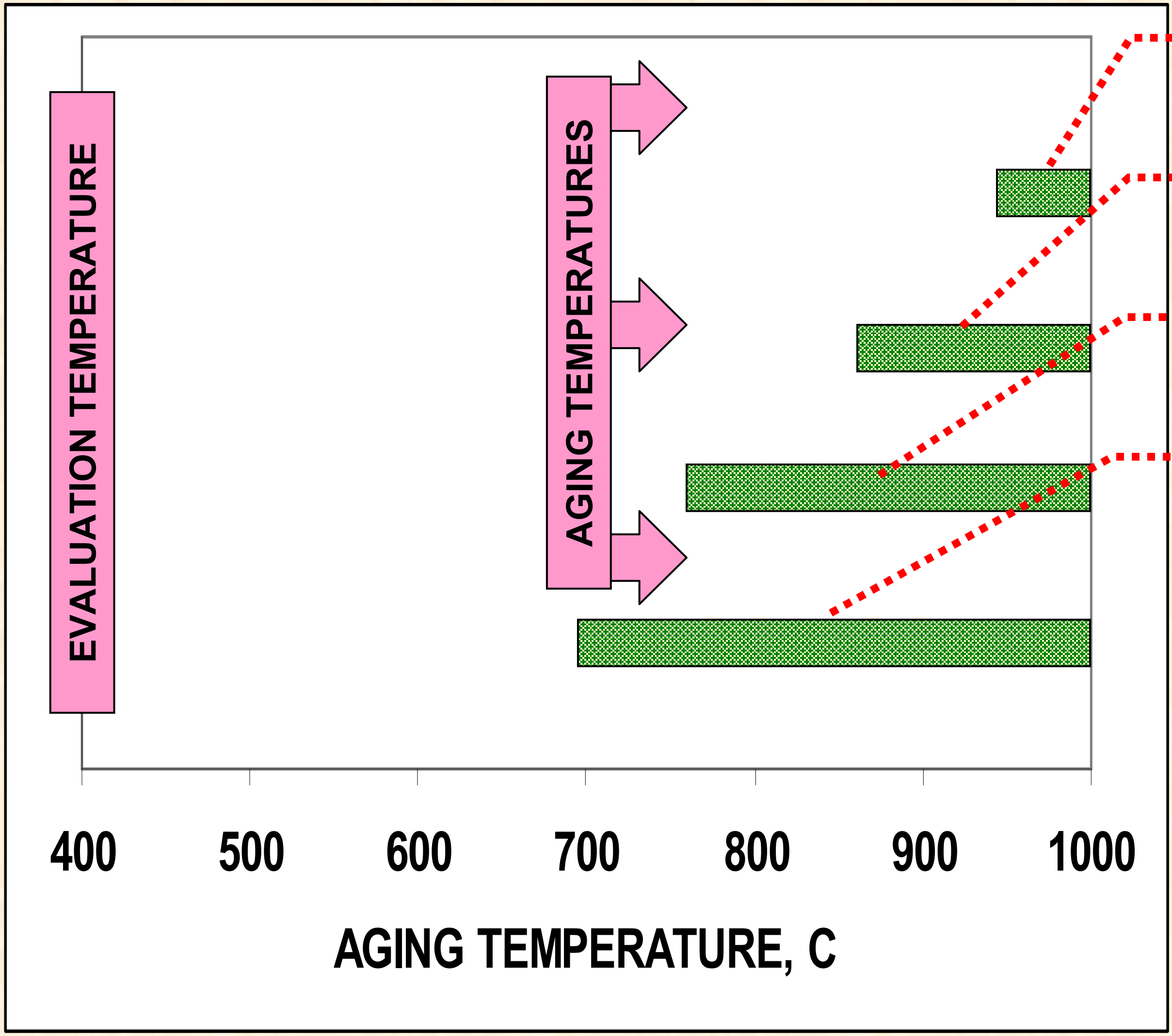


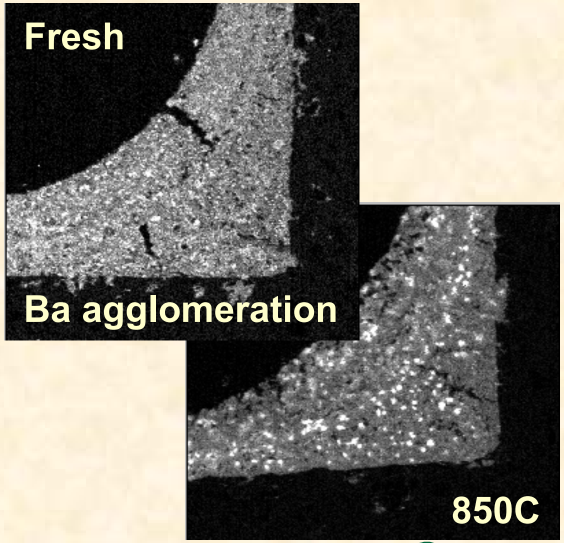
XRD Patterns Corroborate Pt Sintering and suggest possible $BaAl_2O_4$ formation



- **Pt sintering corroborated**
- **Al_2O_3 impact also observed at 1000C**
  - **Increased stability likely due to OSC**
- **Possible $BaAl_2O_4$ formation observed at 1000C**

Mechanisms of Deterioration for Hi-Temp LNTs





Bench-Aging Conclusions

- **At aging temperatures below 830C:**
  - **Loss of NO_x performance is minimal (100-96%)**
  - **Observed materials changes include**
    - **Sintering of the precious metal**
- **At aging temperatures above this threshold temperature:**
  - **NO_x performance decreases to 89%**
  - **Observed materials changes include**
    - **Continued sintering of the precious metal**
    - **Partial phase change of alumina from γ-Al_2O_3 to δ-Al_2O_3**
    - **Migration of K to substrate interface**
      - **Migration of K to the substrate interface subsides after about 150 aging cycles**
- **At aging temperatures above 1000°C**
  - **NO_x performance decreases to 76%**
  - **Partial conversion of Ba-phase to $BaAl_2O_4$**

Results can be used for Deactivation Modeling

- **Has not been a focus of these projects to date**

- **Data available for modeling deactivation mechanisms**
  - **Temperature profiles down core**
    - **Including time at each temperature**
  - **Quantitative Materials Characterization**
    - **Pt Sintering**
    - **K migration into cordierite**
    - **Not presented here, but we have characterized catalysts at different lengths**

- **Can benefit catalyst lifetime estimates**
  - **Catalyst optimization, modeling aging factors, etc.**

Future plans

- **LNT effort is continuing in following areas**
  - Correlate performance loss to material changes
  - Hopefully…modeling to correlate material changes and rates to aging temperature and time
  - Aging studies with low temperature LNT formulation

- **Other Rapid Aging/Poisoning projects**
  - DOC: nearly finalized, correlation analysis underway
  - DPF: Ash loading rates based on oil consumption
  - SCR: lube-oil effects, thermal aging, sulfur tolerance
    - just getting started; deactivation mechanisms TBD
    - Being implemented on engine-based system with DOC and DPF
      - Two sequences under consideration

Acknowledgements

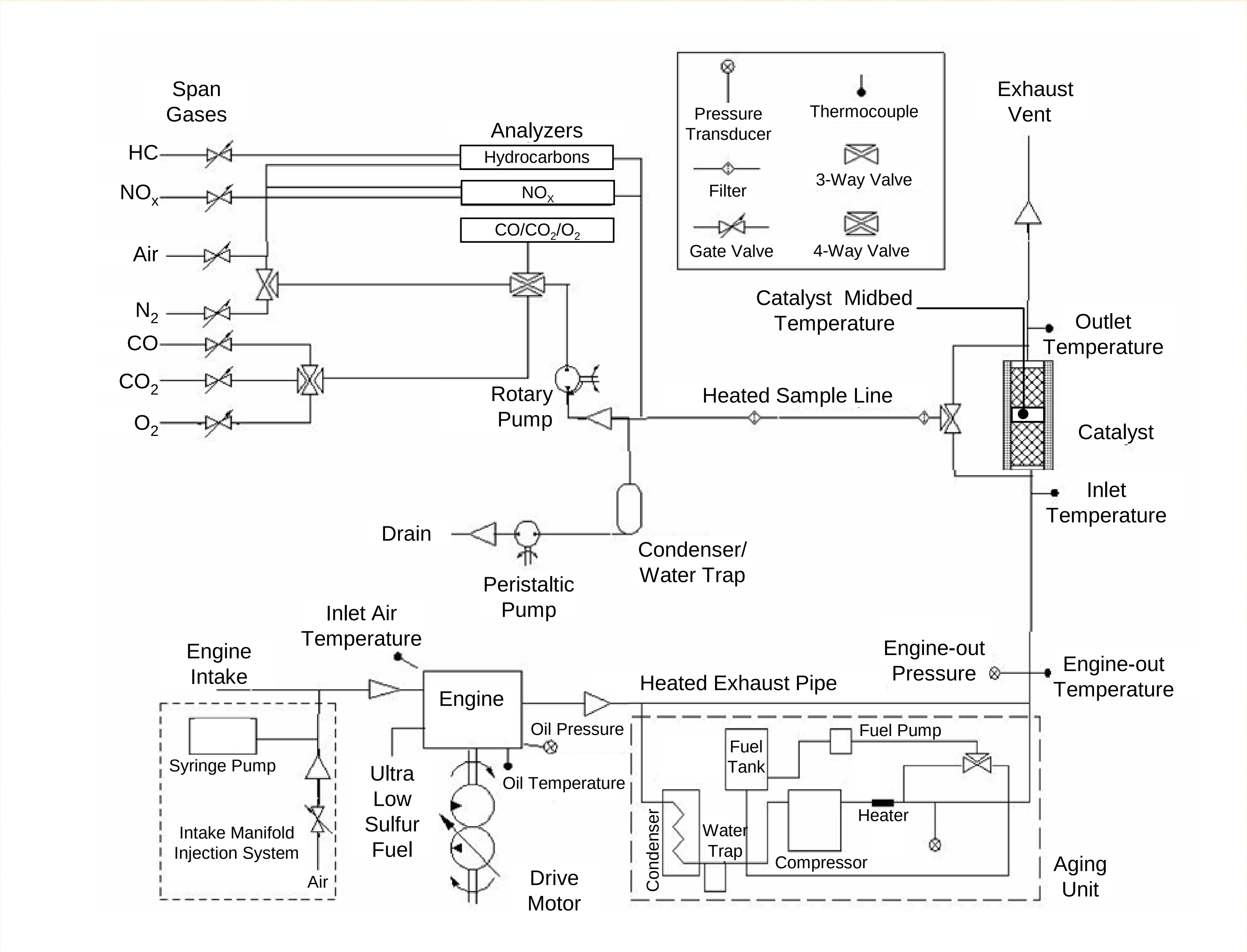
Research is supported by the U.S. Department of Energy (DOE), Office of FreedomCAR and Vehicle Technologies, Fuels Technology Program. Steve Goguen and Kevin Stork are program managers

The model catalysts used in this study were graciously supplied by BASF (formerly Engelhard) and Delphi Corporation

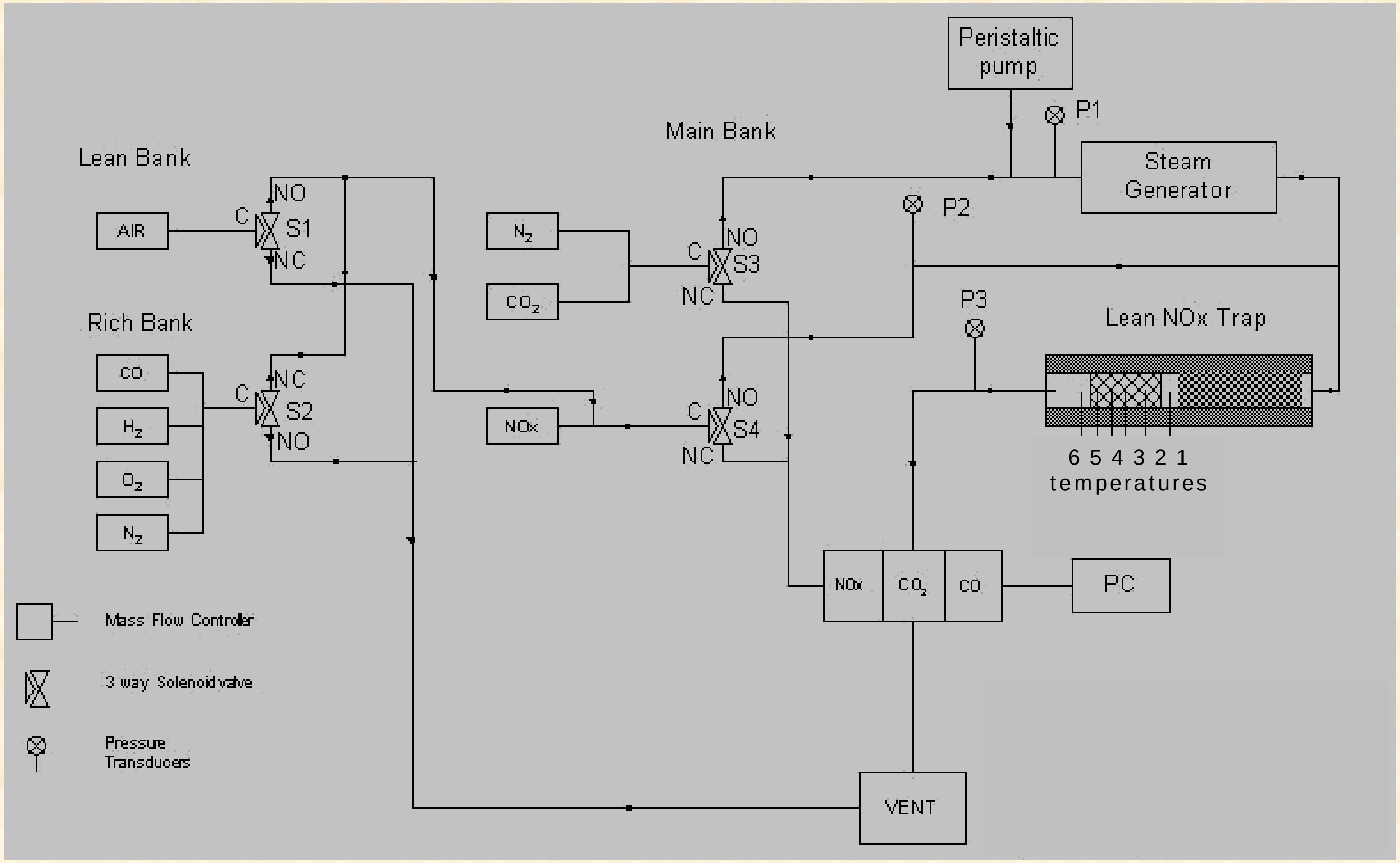
Rapid Aging/Poisoning References

- **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, SAE 2006-32-0035.
- **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, SAE 2007-01-0470.
  - T.J. Toops, B.G. Bunting, K. Nguyen, and A. Gopinath, "Effect of engine-based thermal aging on surface morphology and performance of Lean NOx Traps", Catalysis Today (2007), doi:10.1016/j.cattod.2007.02.027.

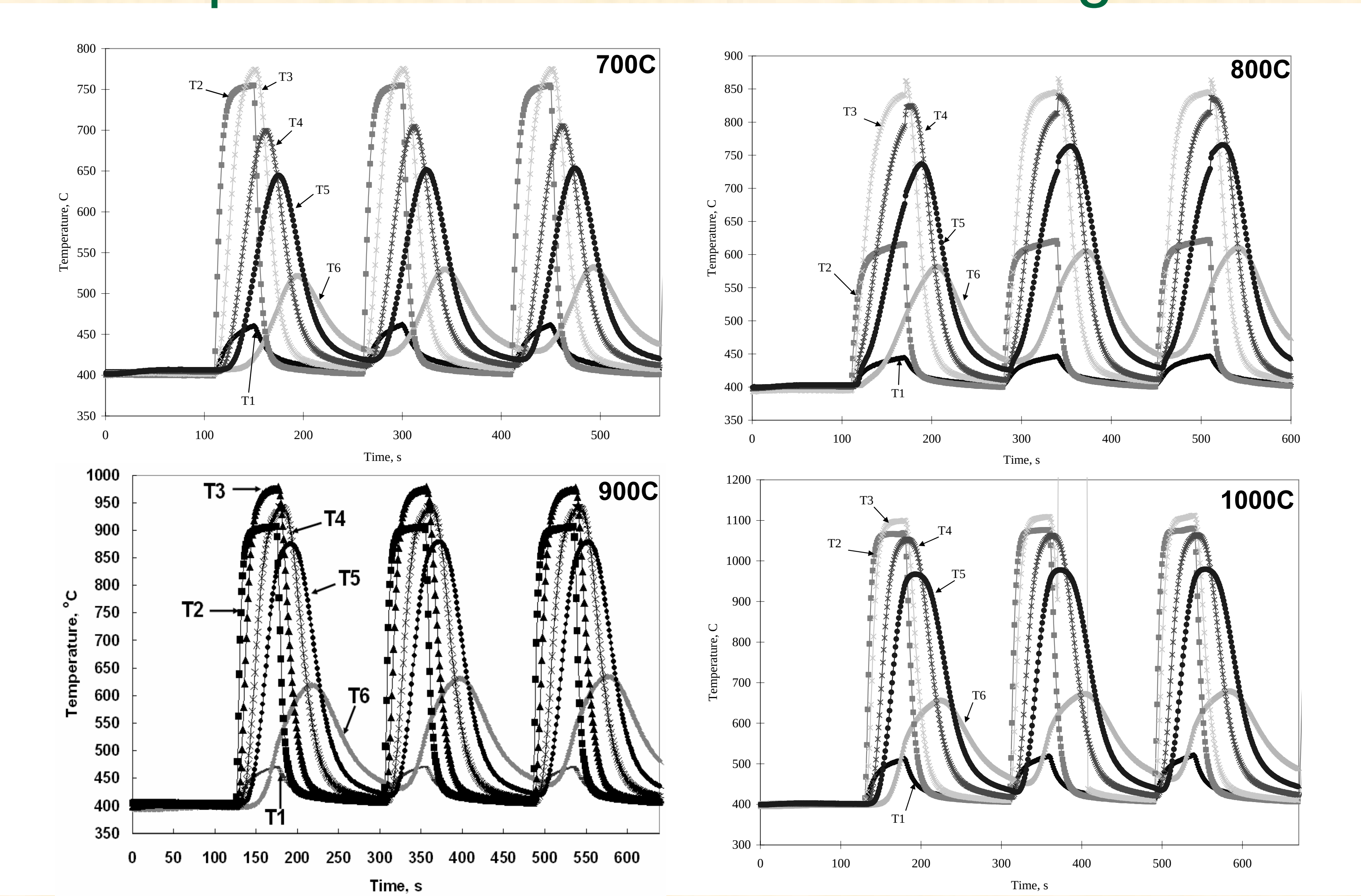
Engine aging and test rig



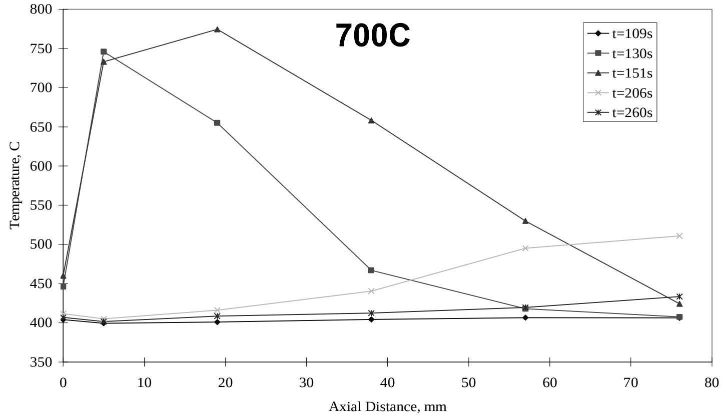
Bench reactor flow schematic

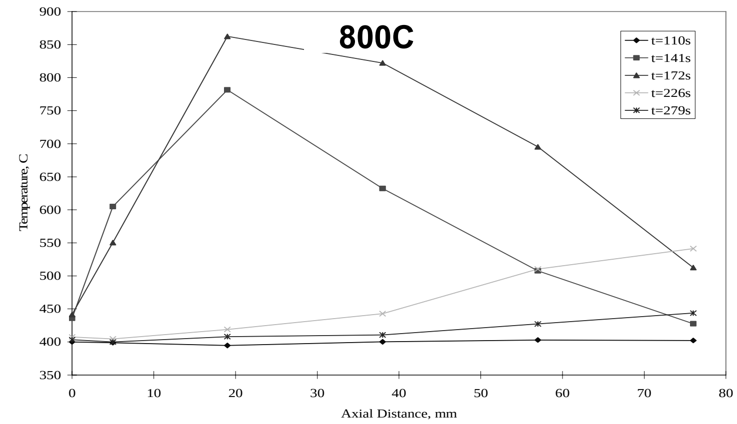


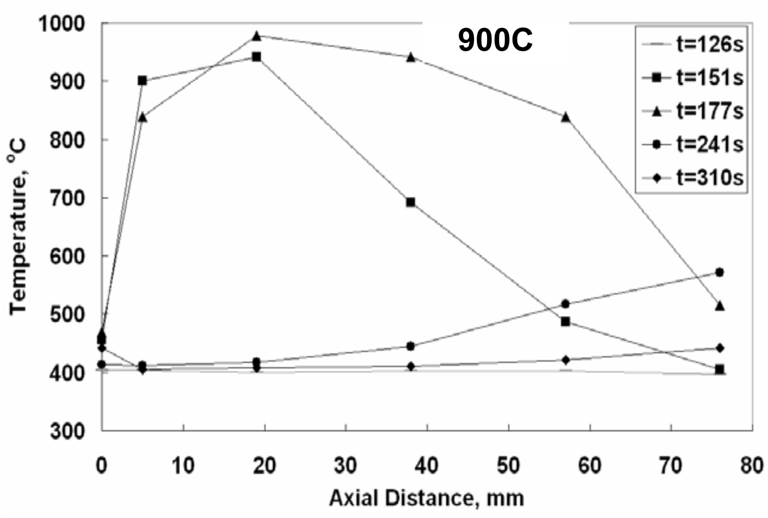
Temperature Variation Along Axis

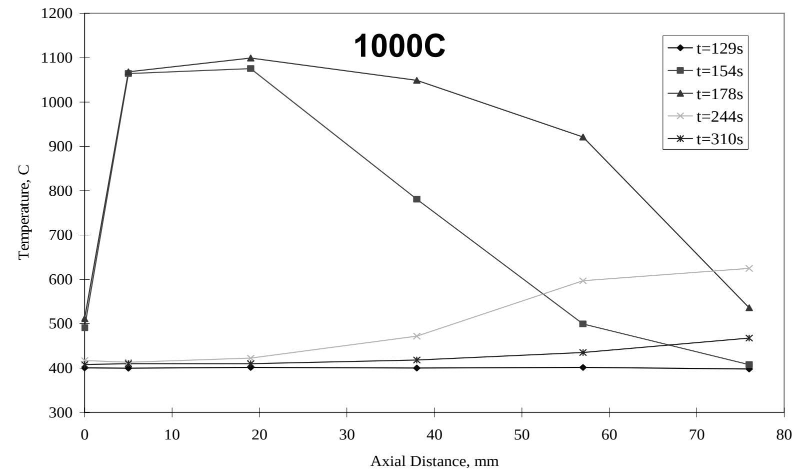


Temperature Variation Along Axis

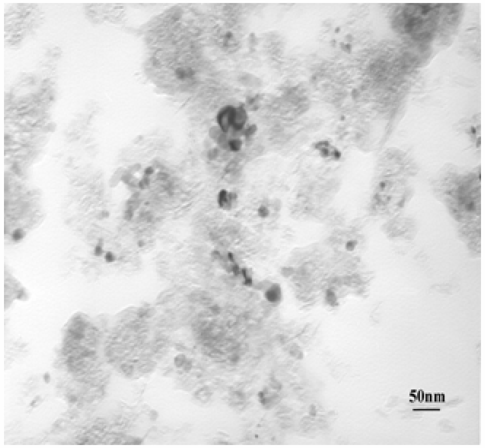




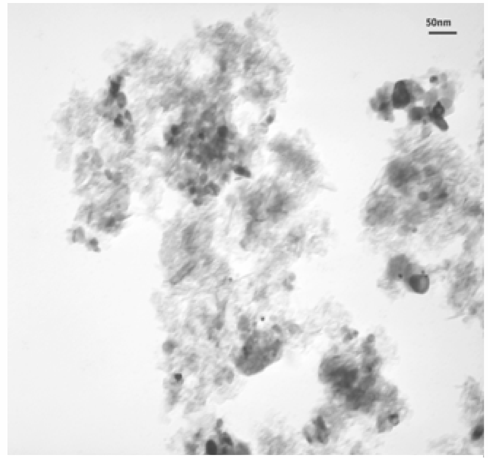




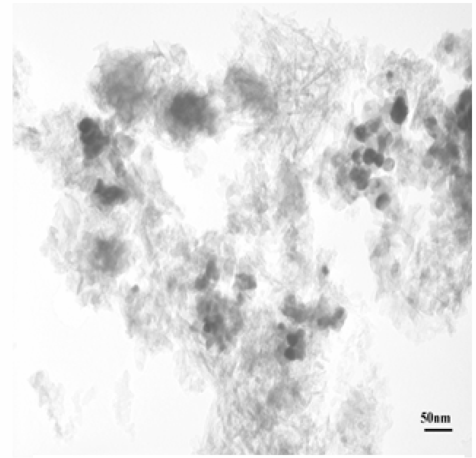
TEM images showing PGM clusters



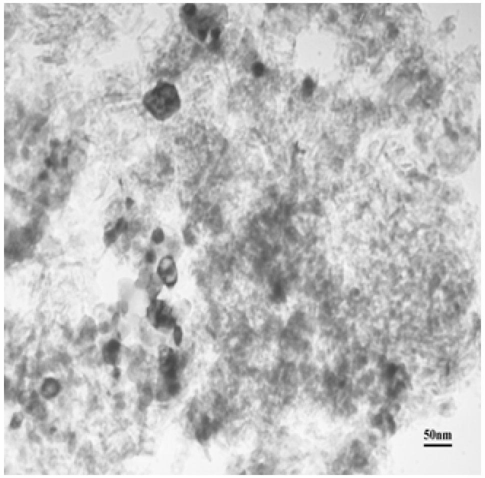
fresh



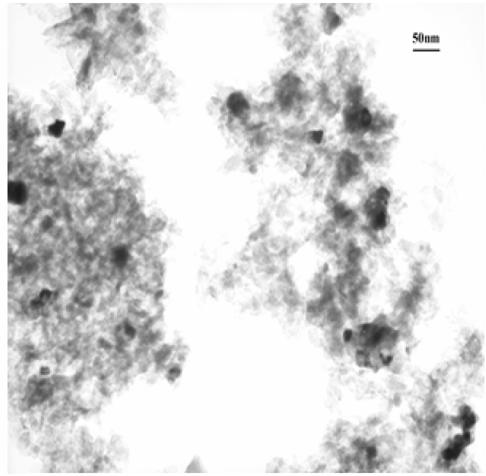
700°C / 300 cycles



800°C / 300 cycles



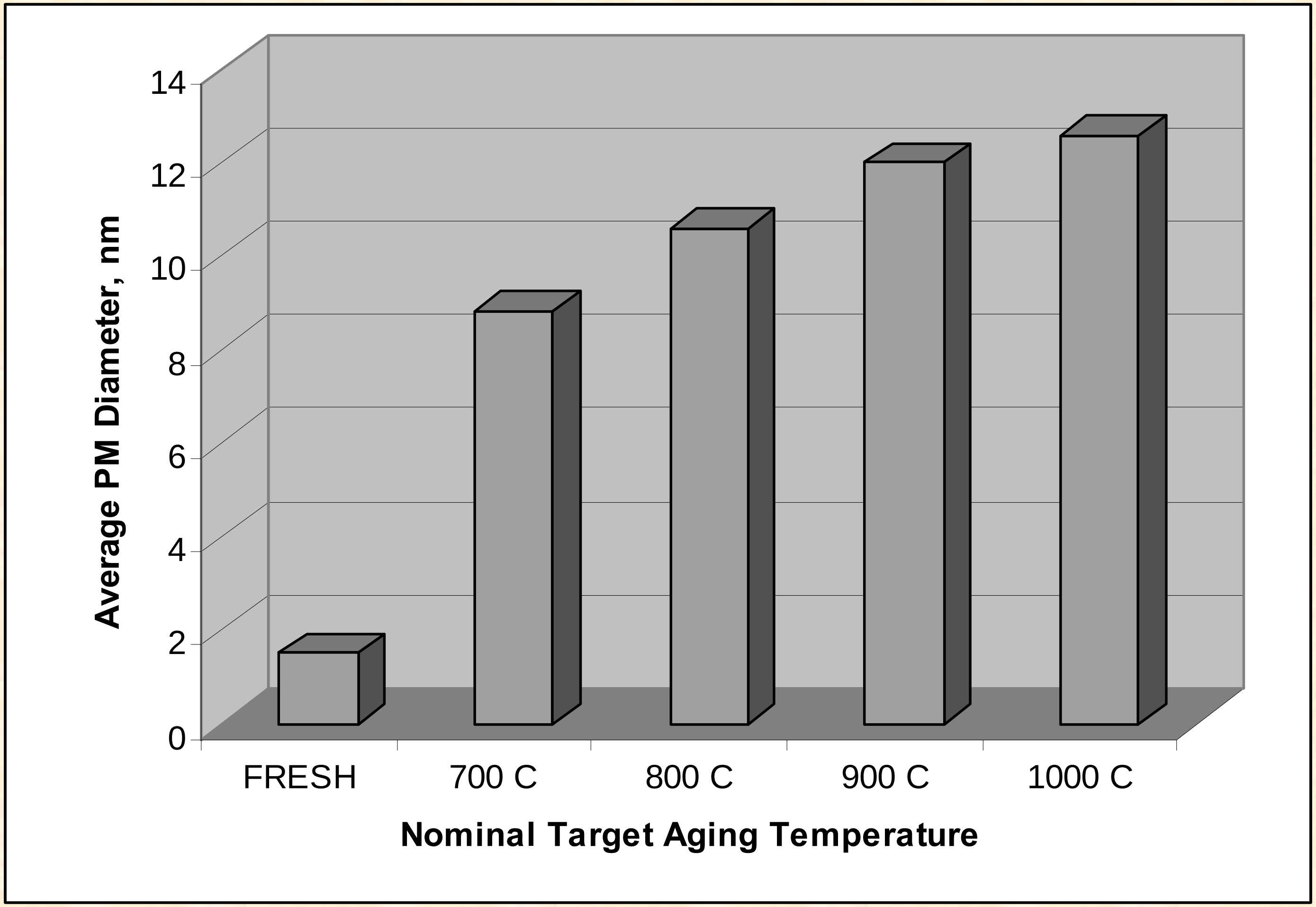
900°C / 300 cycles



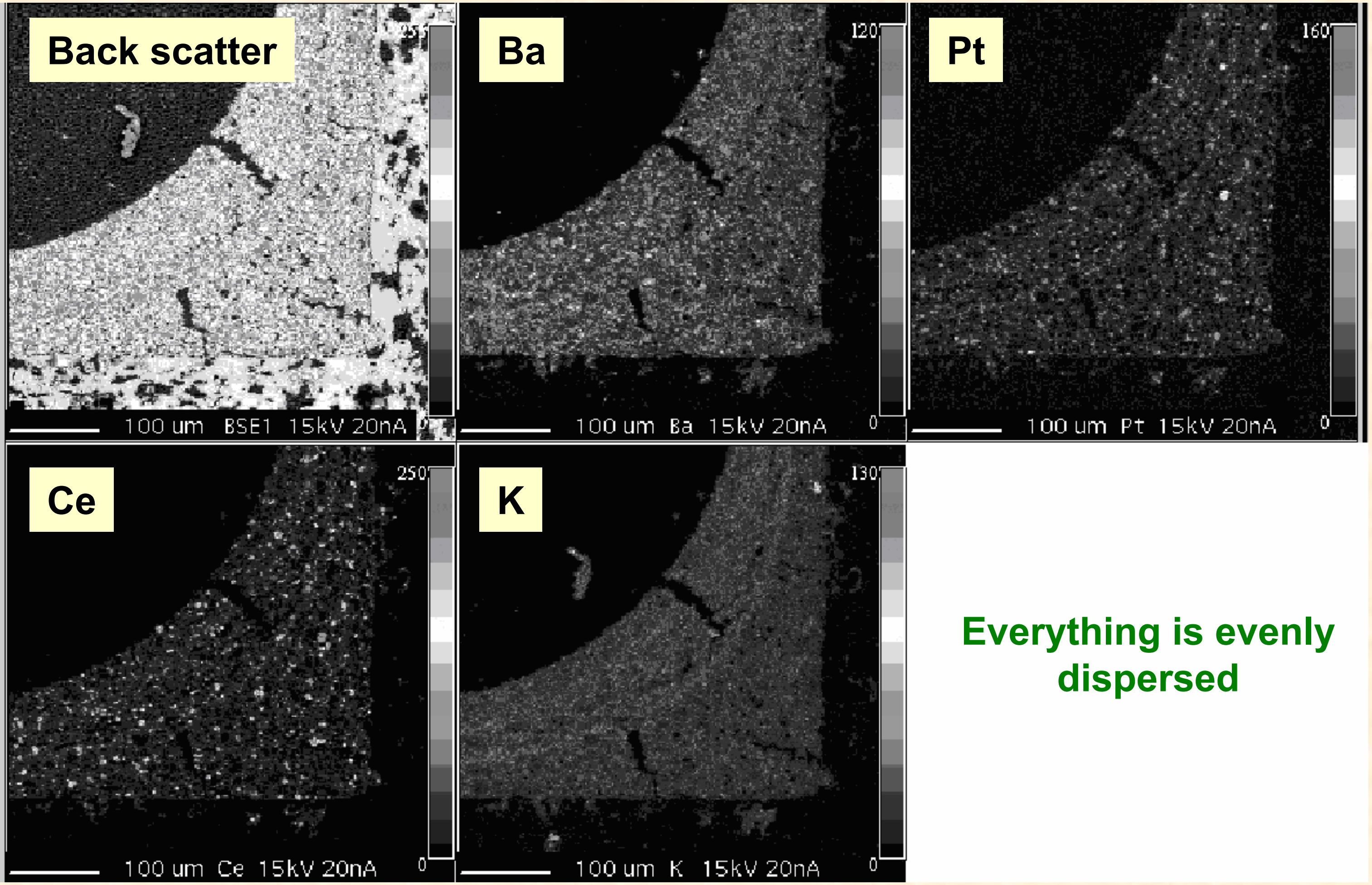
1000°C / 250 cycles

All images taken at 100,000X

Average PGM diameter as function of aging temperature from XRD

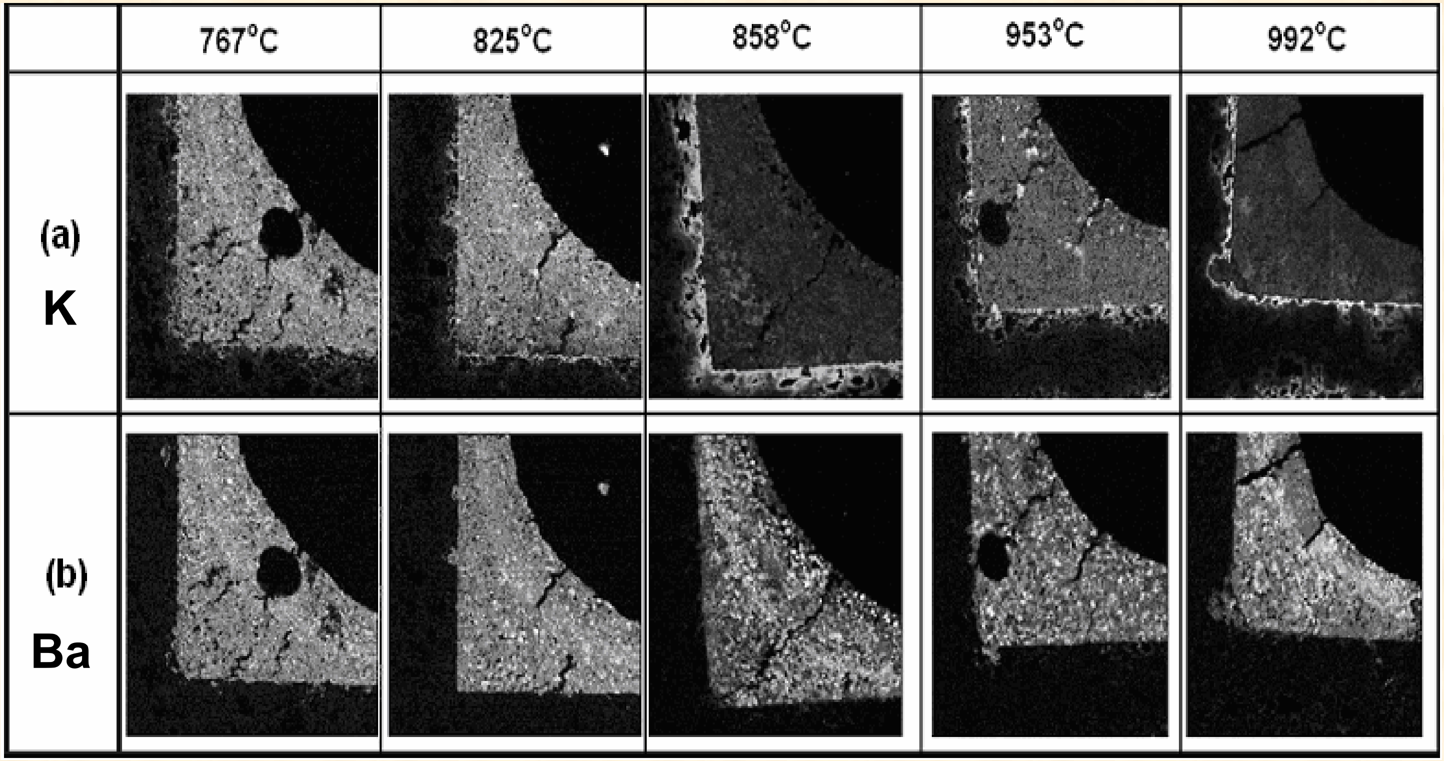


EPMA elemental maps of Pt, Ce, Ba, and K in fresh LNT



Everything is evenly dispersed

EPMA maps of K and Ba at different aging temperatures after 50 cycles

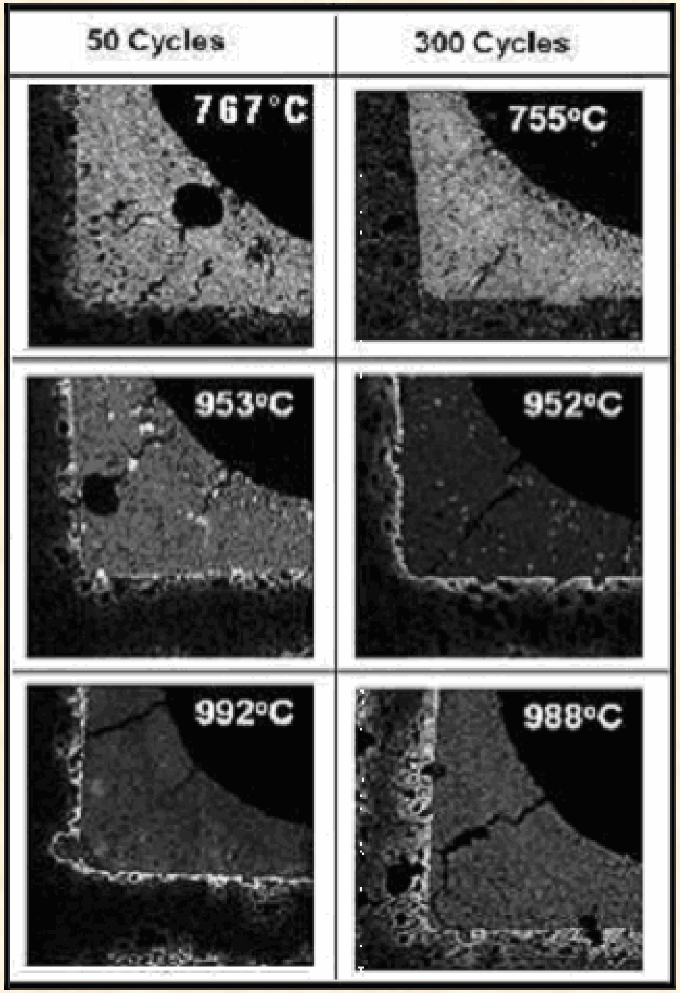


Migration of K

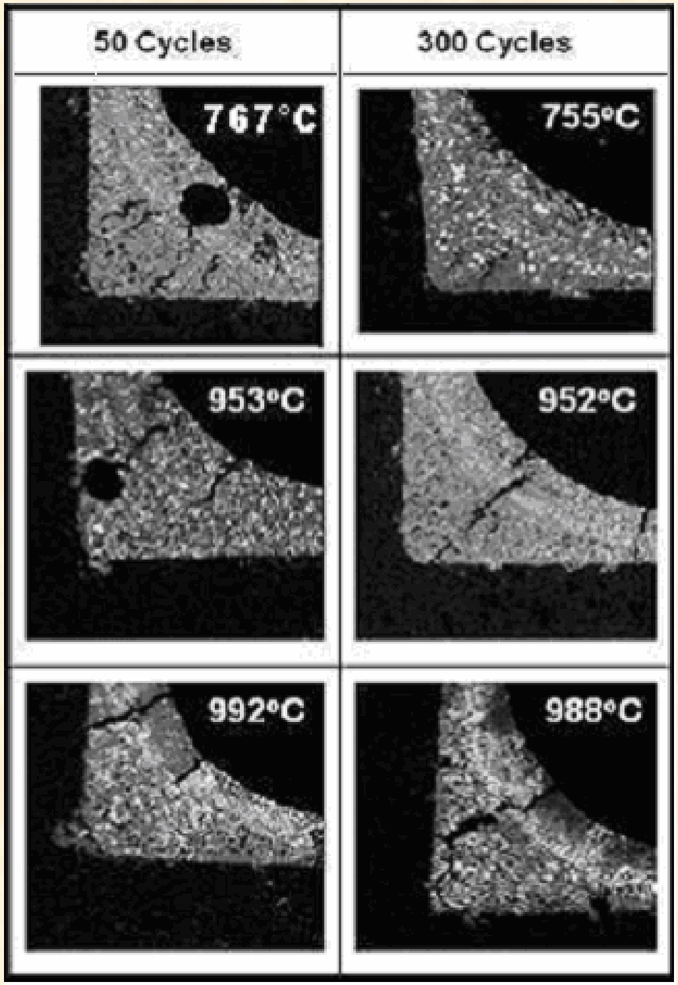
Agglomeration of Ba

EPMA maps as a function of aging temperature and number of aging cycles

K



Ba



Future Plans

- **Continue aging and characterization**
  - Barium/Potassium (high-temperature LNTs)
  - Barium (low-temperature LNTs)
- **Extract rates for aging mechanisms**
  - LNT: PGM sintering and NOx storage media changes
    - Applicable temperature ranges
  - DPF: Ash loading rates based on oil consumption
  - SCR: ZDDP, thermal aging, sulfur tolerance
    - just getting started; key deactivation mechanisms TBD
- **Model deactivation with simple kinetics**
- **Continue modeling efforts to relate deactivation to performance losses**