Accelerated Aging and Characterization of Emissions Control Devices

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CLEERS Workshop

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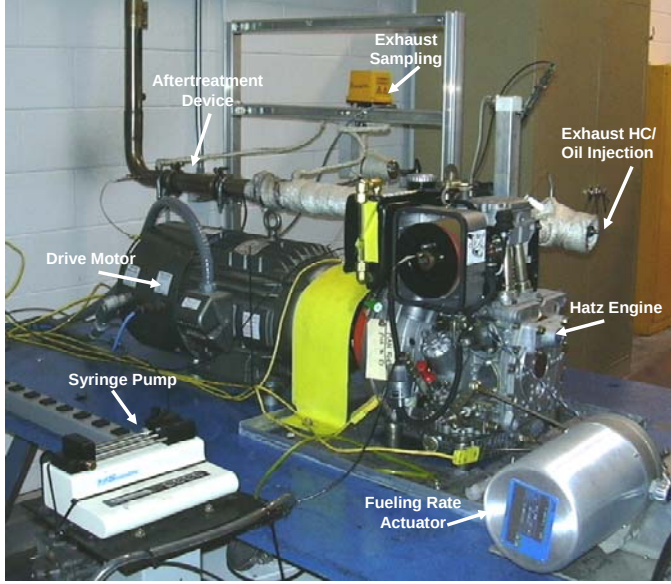
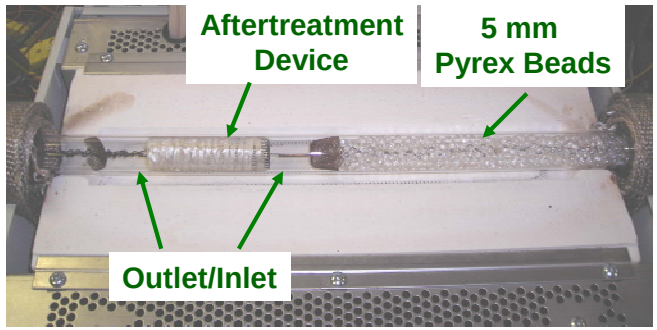
History of rapid aging protocol project

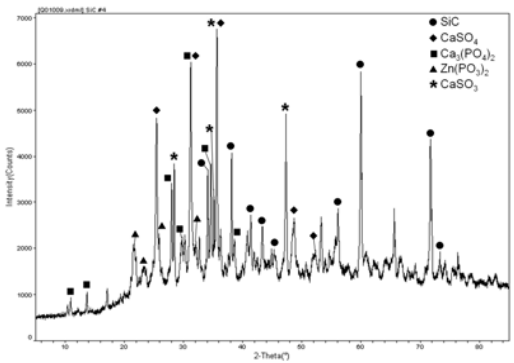
- **DOE funding from Fuels Technology - APBF**
- **Started with survey of industry in 2003**
  - **Catalyst, engine, auto, lube industries, and universities**
- **Goals focused by survey and further discussions**
  - Phosphorous poisoning of DOC
  - **Thermal aging of LNT**
  - **Ash loading of DPF**
  - **Thermal aging of zeolite SCR resulting from DPF regeneration**
- **Overall Vision:**
  - **As fuels and catalyst formulations change, can a simple easy to implement protocol be developed that adequately replicates typical on-road conditions without running end-of-life tests**
- **Secondary vision:**
  - **Can the results be used for general emissions control models**
    - **Both materials changes models and kinetic models**

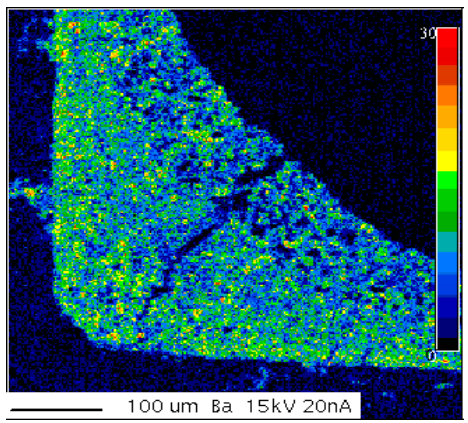
Approach

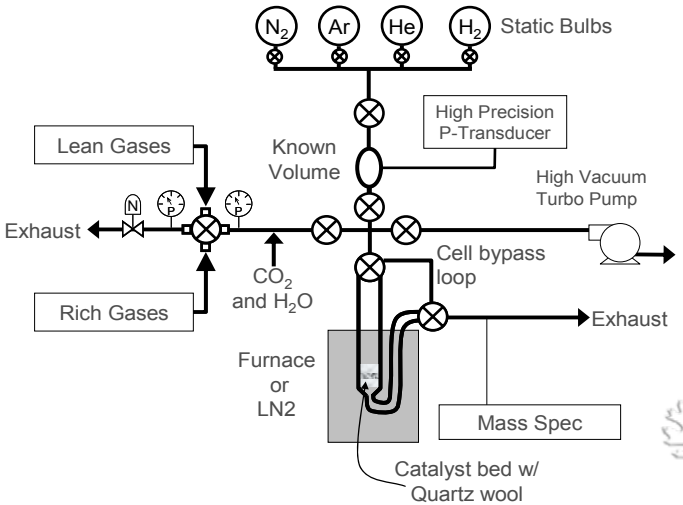
- **Small engine and bench reactor tests**
- **Commercial catalysts, real suppliers**
- **Extensive materials characterization**
- **Develop rapid protocols for aging and poisoning**
- **Determine what materials characterization most useful, how materials changes relate to performance changes**
- **Compare rapid protocols to field aged parts**
- **Model aging results to provide more insight and usefulness**







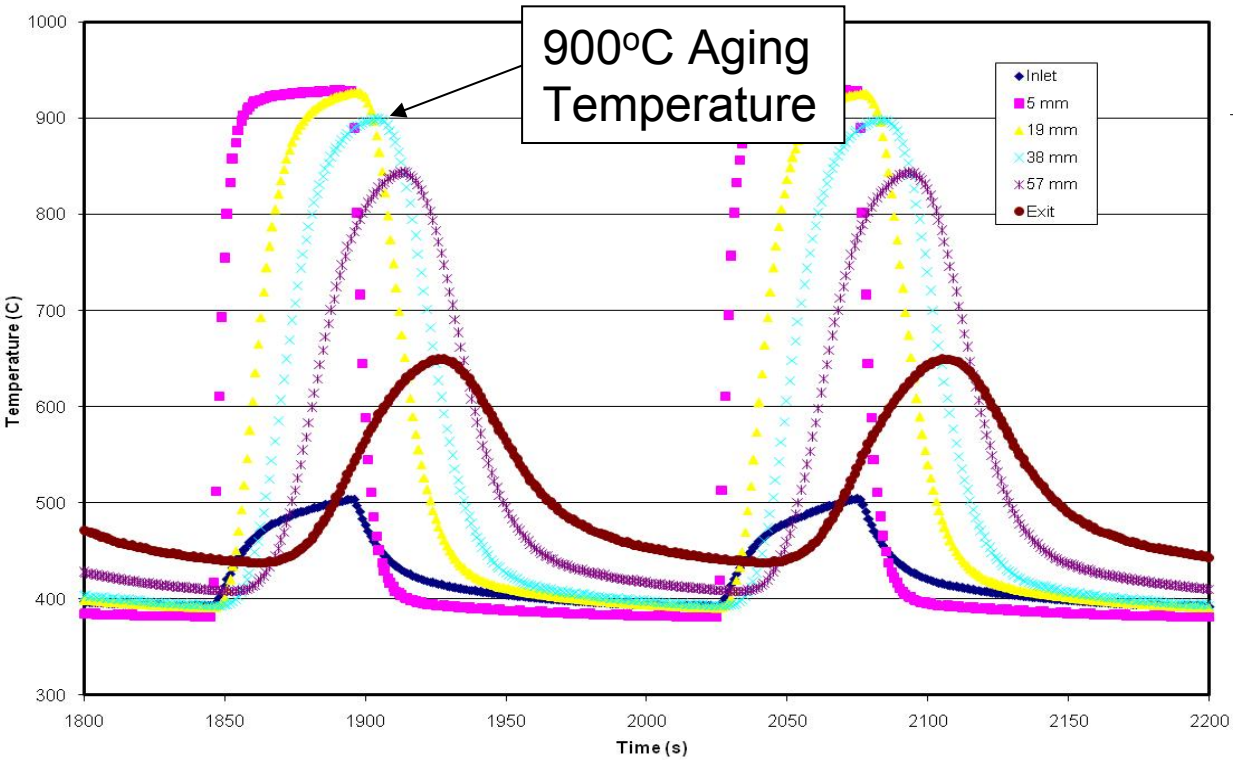


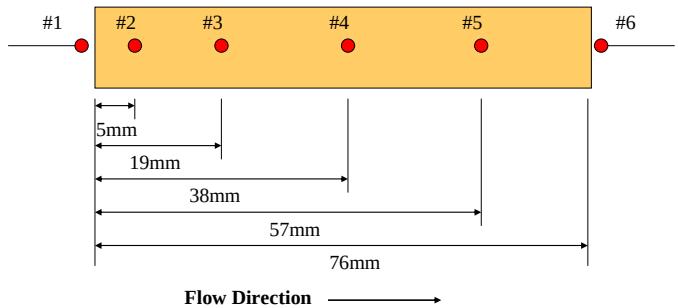


LNT

Bench Core-Reactor Based Thermal Aging

Thermal-Aging with Exotherm in a Furnace

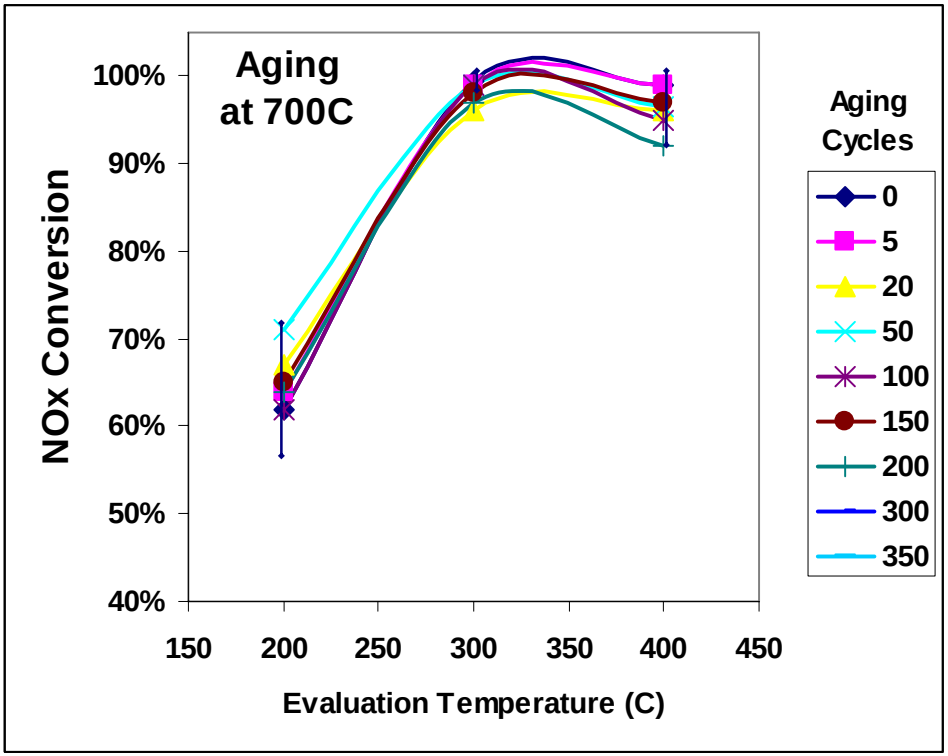


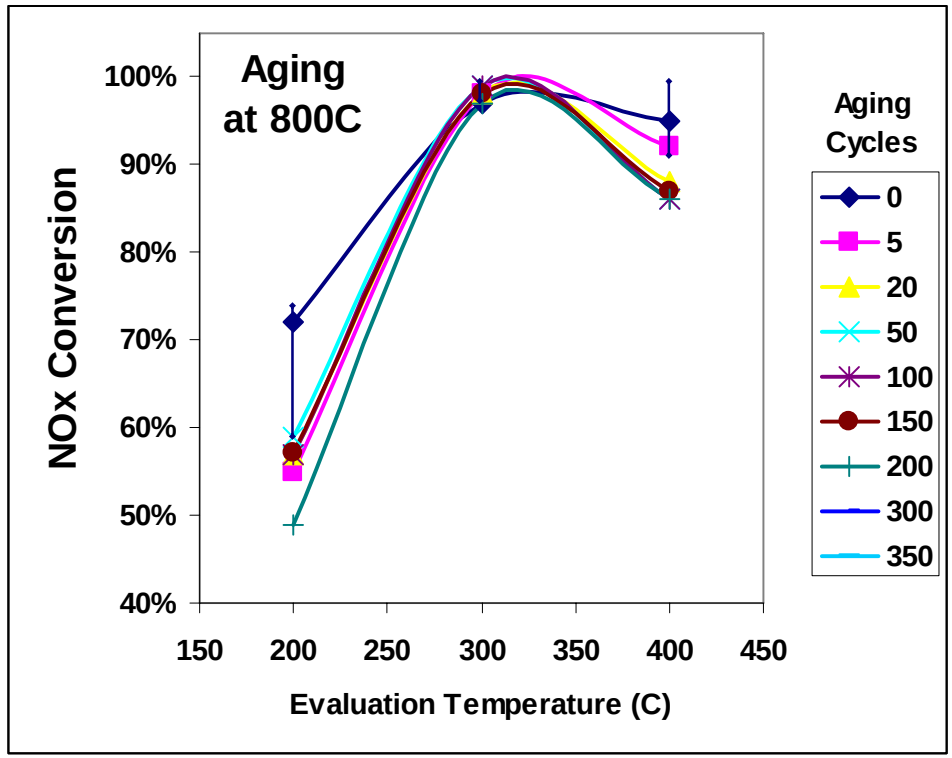


	Lean (130s)		Rich (50s)
NO_x	**300 ppm**		**300 ppm**
CO_2	**5%**		**5.00%**
CO	**0**		**5.10%**
H_2	**0**		**3.25%**
O_2	**11%**		**4.00%**
H_20	**4.2%**		**4.20%**
N_2	**balance**		**balance**

- **Low Temperature Ba-only LNT (fully-formulated)**
- **The center of the catalyst reaches a nominal aging temperature of ~900°C**
- **The front section of the catalyst experiences higher aging temperature**
- **Similar to profiles seen in our single cylinder engine**

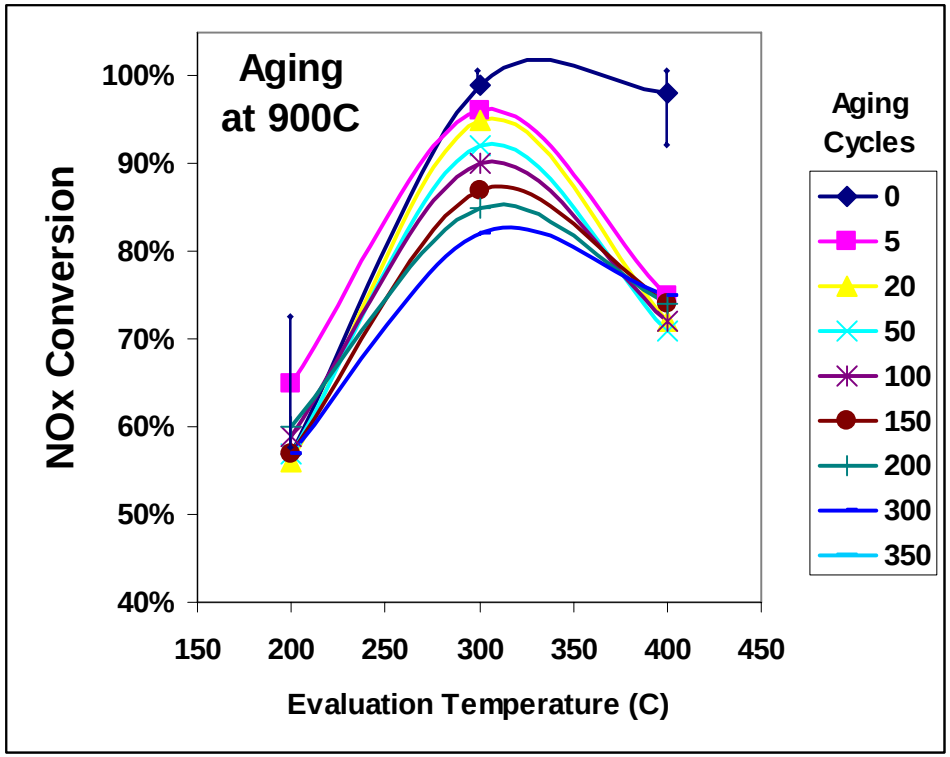
Aging at 700 and 800C has small impact

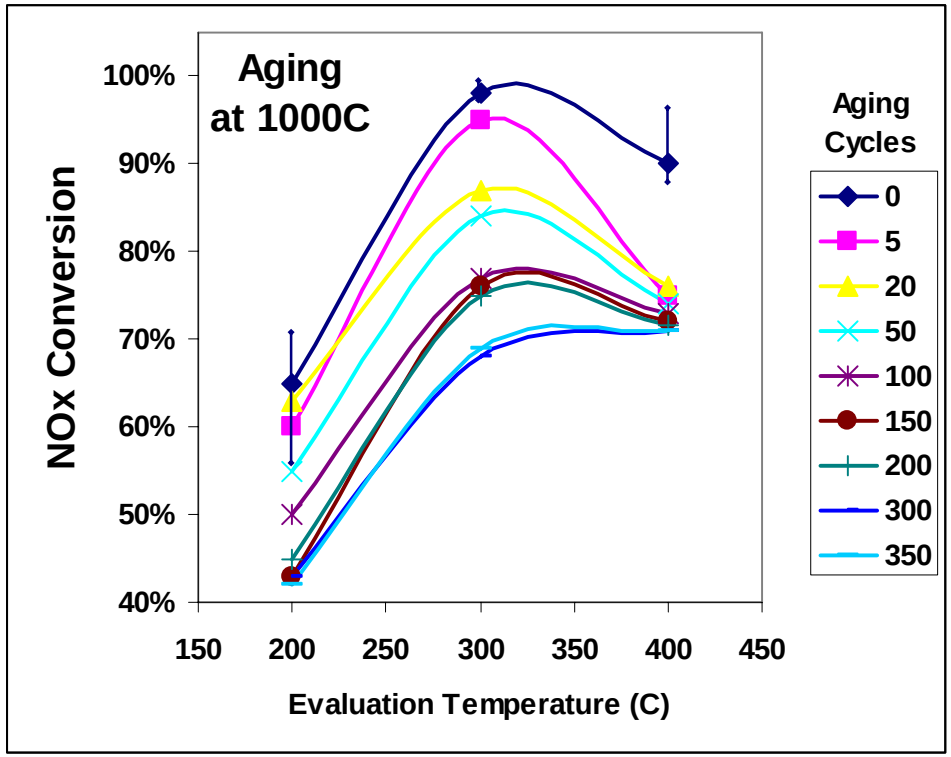




- **Performance measured periodically using CLEERS fast cycling protocol**
- **Minimal effects observed beyond two standard deviations of fresh measurements**
  - **Aging at 800C denotes a mild deactivation at 200 & 400C**

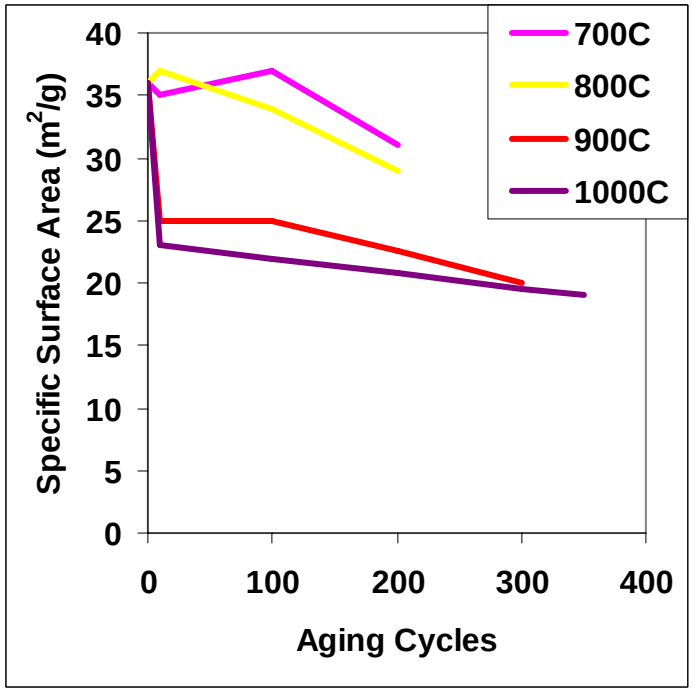
Both Step Changes and Gradual Deactivation Observed when aging at 900 and 1000C

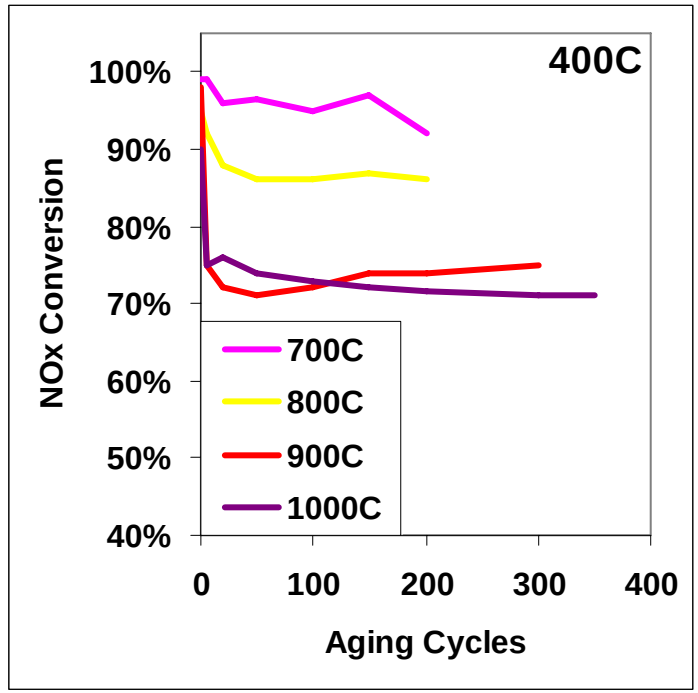




- **Evaluations at 400C show immediate step change in activity after only 5 cycles**
- **Evaluations at 200 and 300C demonstrate a more gradual deactivation**

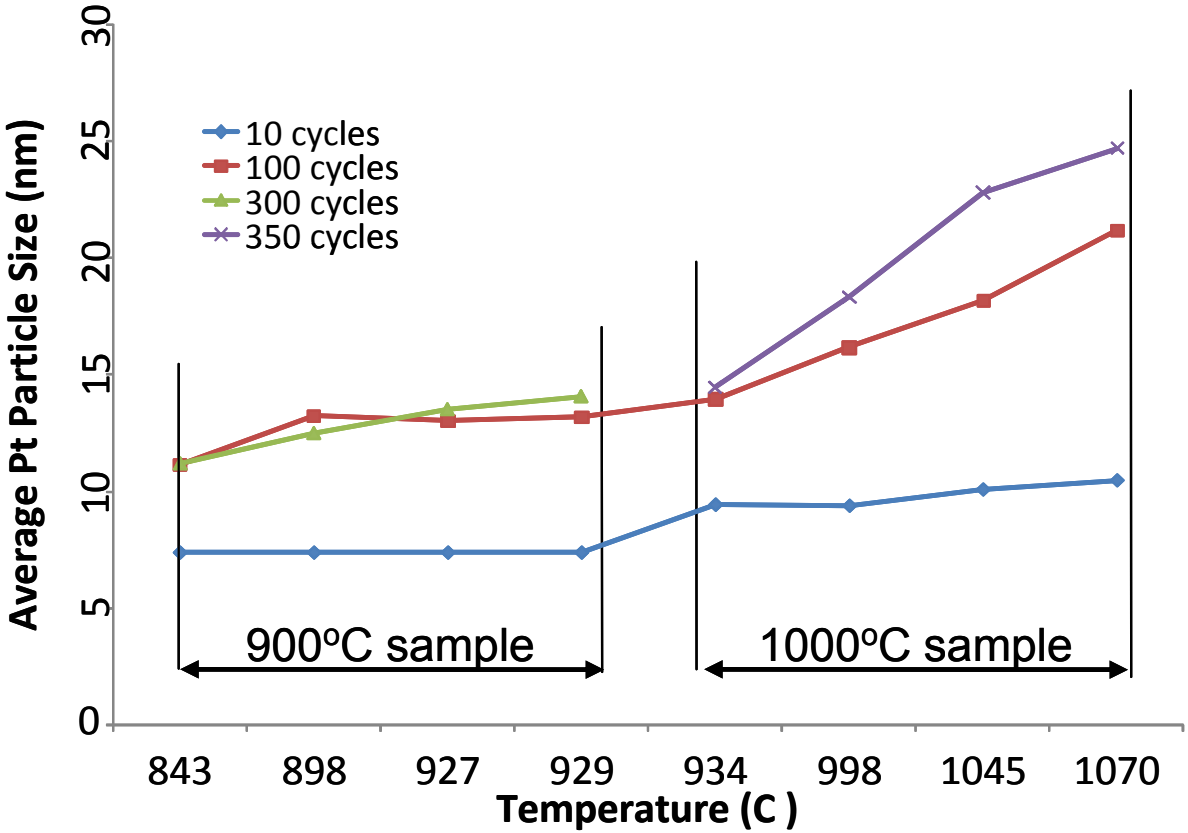
Specific Surface Area Correlates well to NOx Performance Losses at 400C



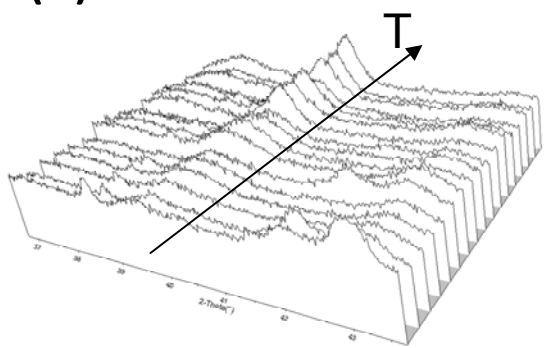


- Surface area decreases as aging temperature and aging time increase
  - Consistent with earlier study on model LNT and high temperature LNT
- Remaining materials characterization is incomplete, so other correlations incomplete
  - Probably very intertwined and modeling necessary to accurately capture materials/performance effects

XRD Can Measure Average PGM Size of Highly Sintered Particles

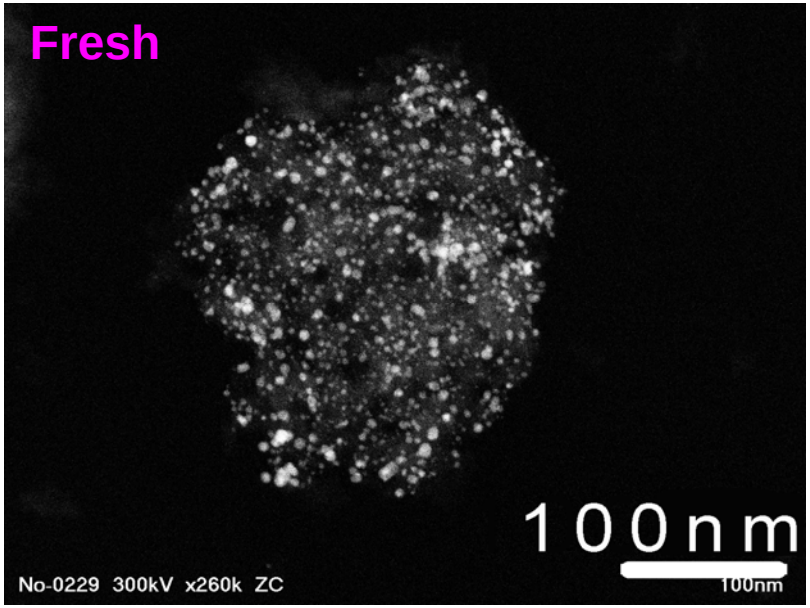


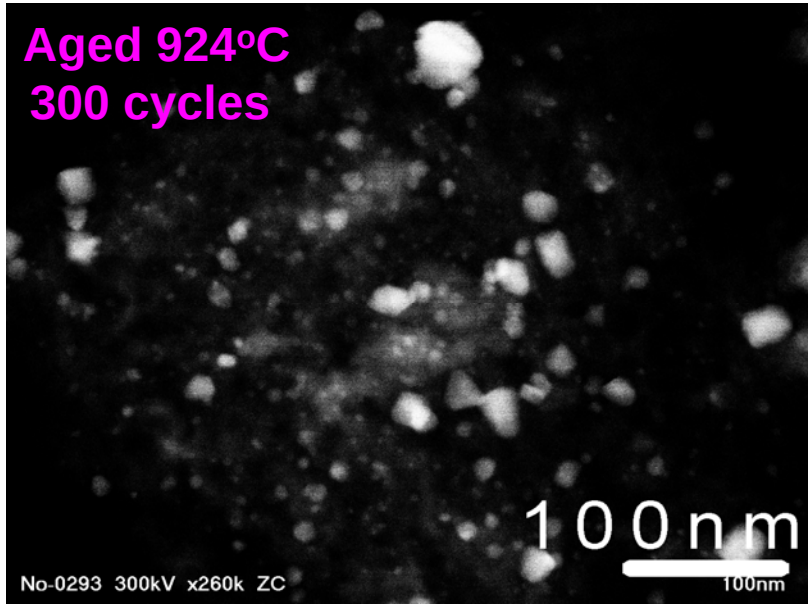
3D plot of all samples analyzed after aging 100 cycles

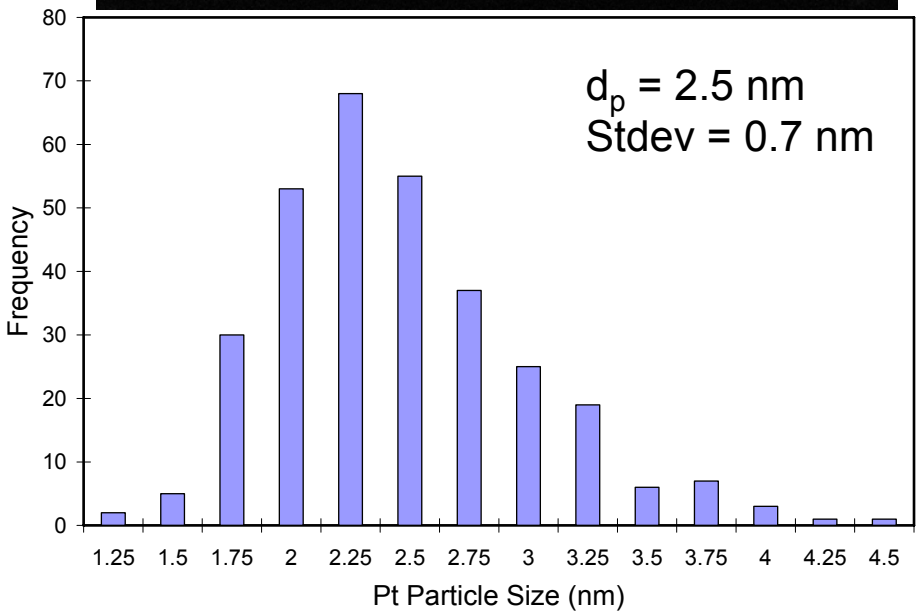


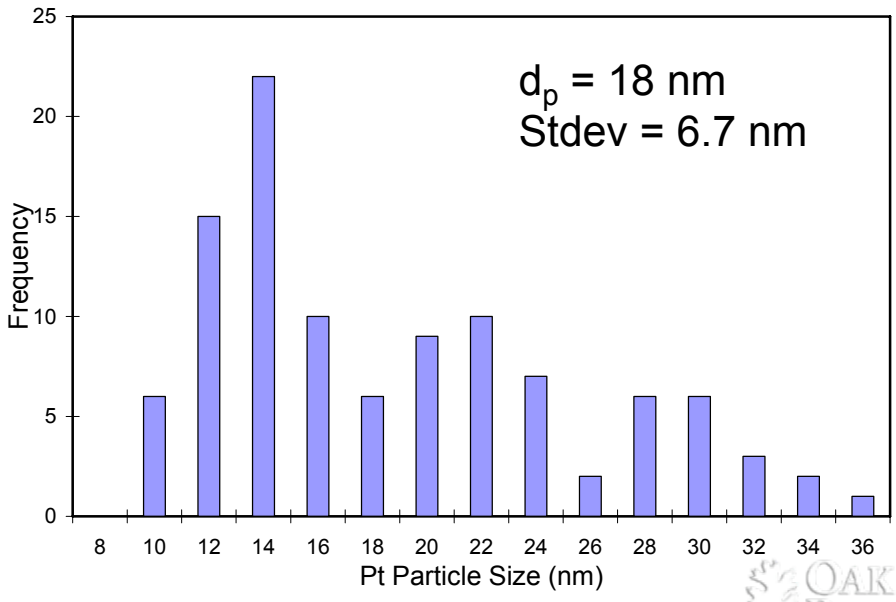
- Pt aged at 700 and 800C too small to measure w/ XRD
- Maximum particle size of ~24 nm occurs after aging at 1070ºC for 350 cycles
- Thermocouple location and sectioning of LNT allows precise measurements with known T history
- Some $BaAl_2O_4$ formation also apparent

Specialized TEM measurements detect size distribution...and eventually PGM size after 700 & 800C

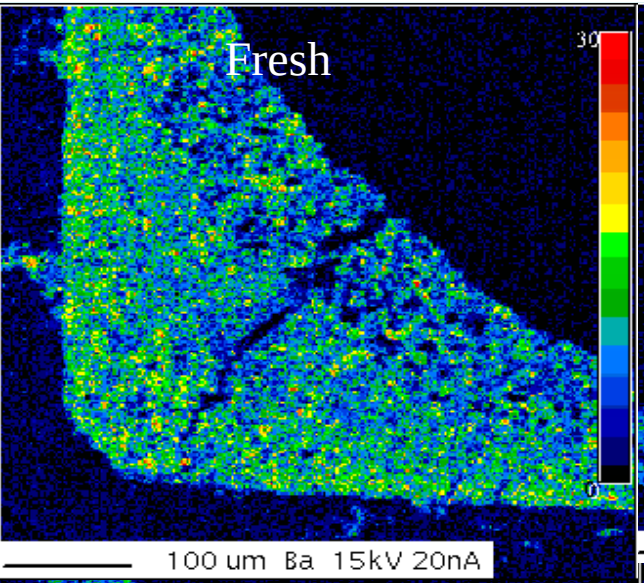


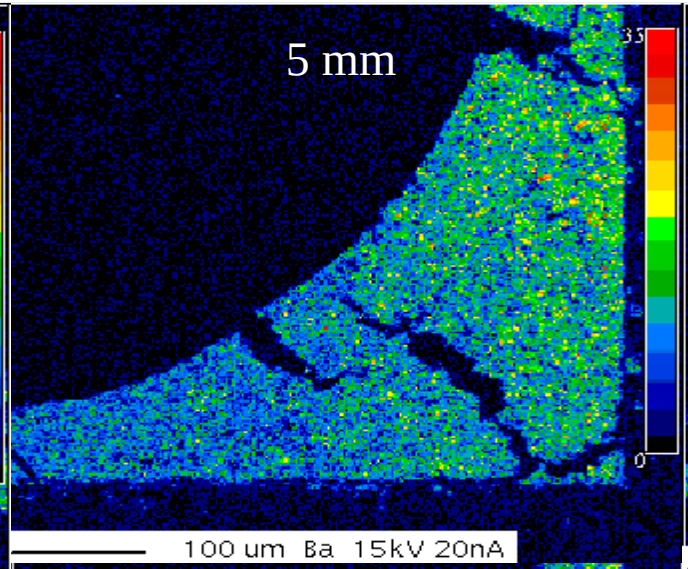


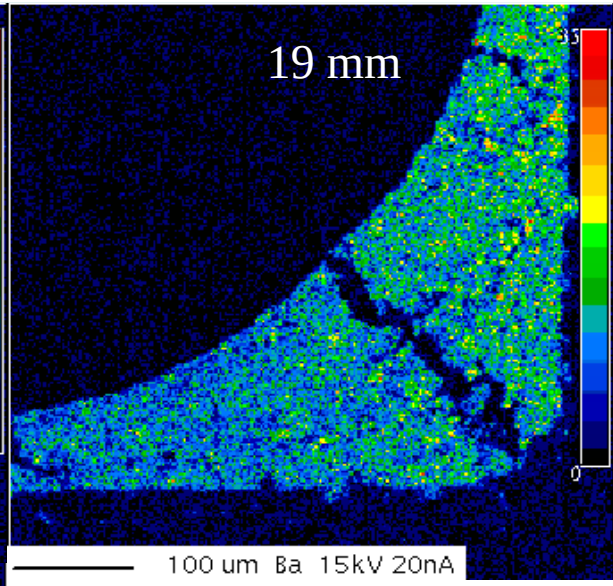


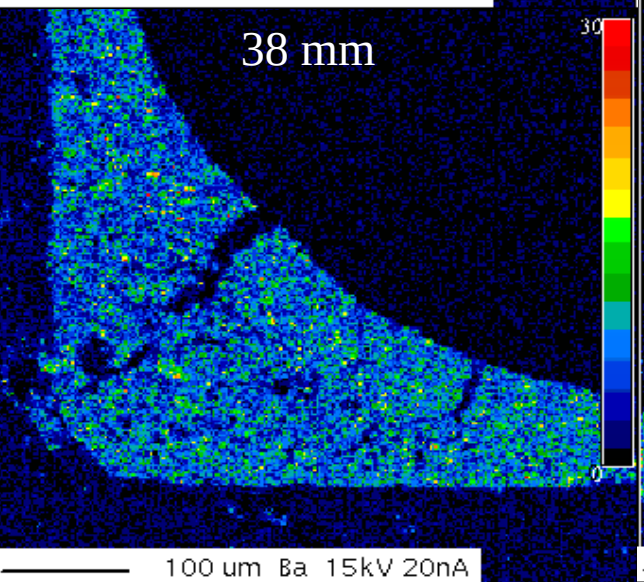


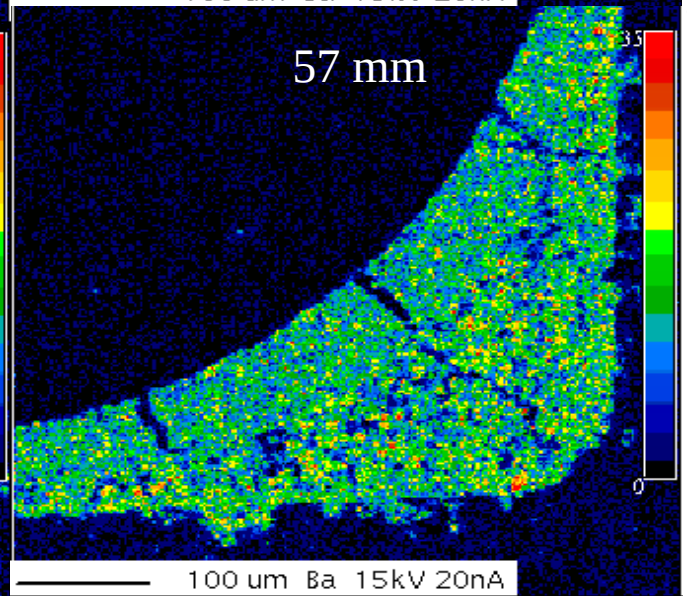
EPMA Ba Elemental Maps of LNTs Aged at 1000ºC for 350 Cycles











No agglomeration or sintering of Ba at an aging temperature of 1000C

Comparisons to Field Aged Catalysts…

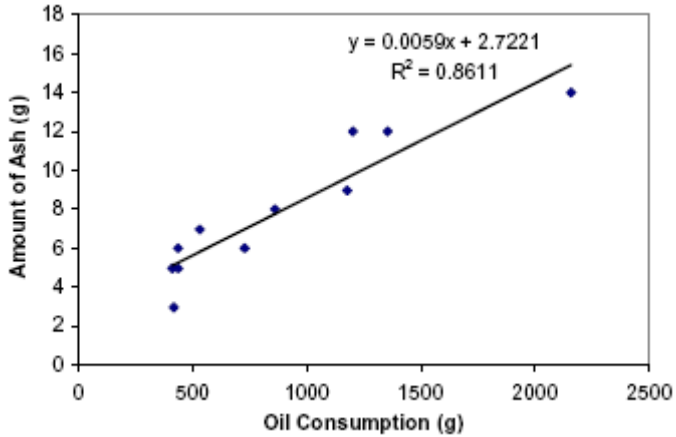
- **Have had difficulty obtaining field aged LNTs, therefore difficult to compare**
  - **General trends seem to fall in line with reported effects**
- **Have geared NOx performance measurements to allow modeling of results**
  - **Implemented CLEERS protocol portions when possible**
  - **Have focused on extensive materials characterization to allow performance correlations and modeling**
    - **Hopefully…allows modeling of both material effects and performance while accounting for material effects**

DPF

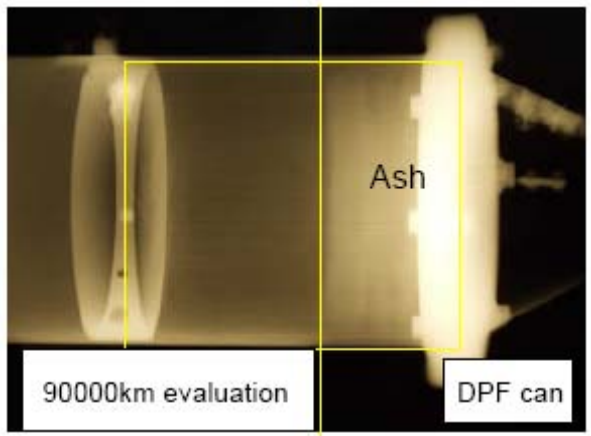
Engine-based Rapid Ash Loading of series of diesel particulate filters

DPF Durability Issues

- **Durability of DPF systems is affected by accumulation of residual ash**
- **Excellent correlation has been demonstrated between lube-oil consumption and ash formation**
- **As the ash forms on the channel walls, some breaks loose and deposits in the rear of the DPF**



DPF ash accumulation as a function of oil consumption*



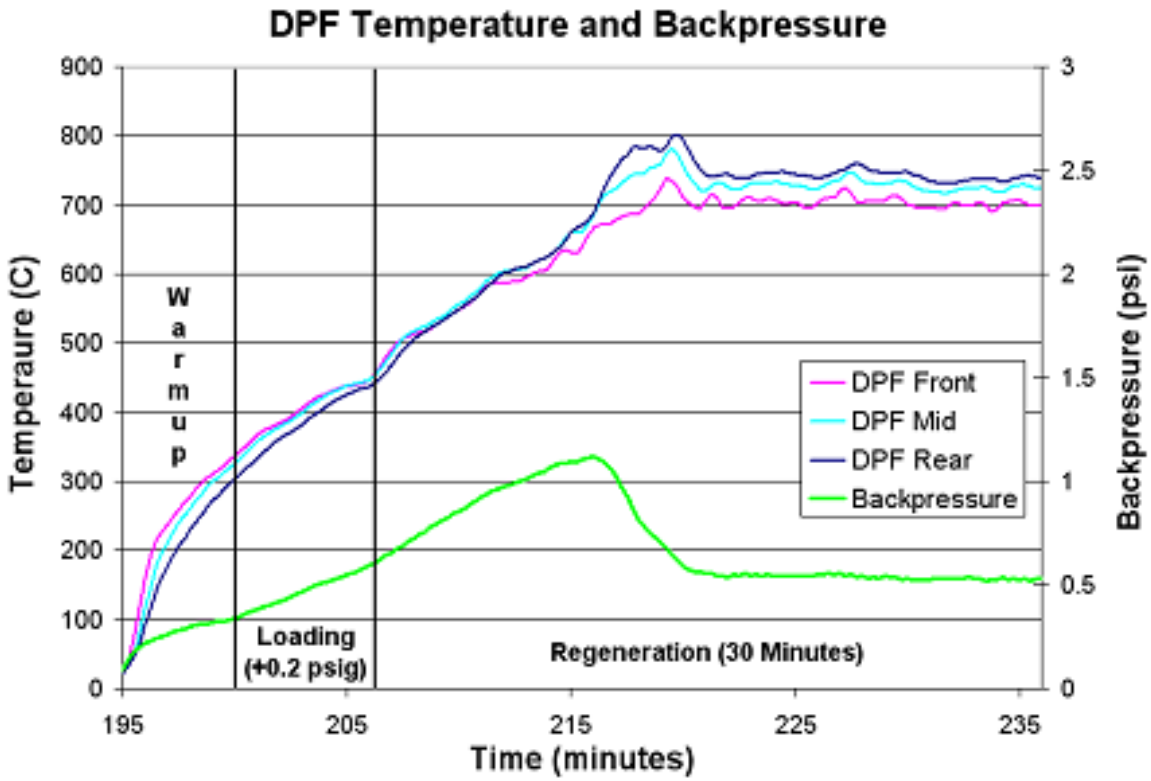
X-Ray analysis of DPF after 90,000 km of operation#

* - Bardasz, E., Cowling, S., Panesar, A., Durham, J., & Tadrous, T., SAE Tech. 2005-01-2168.

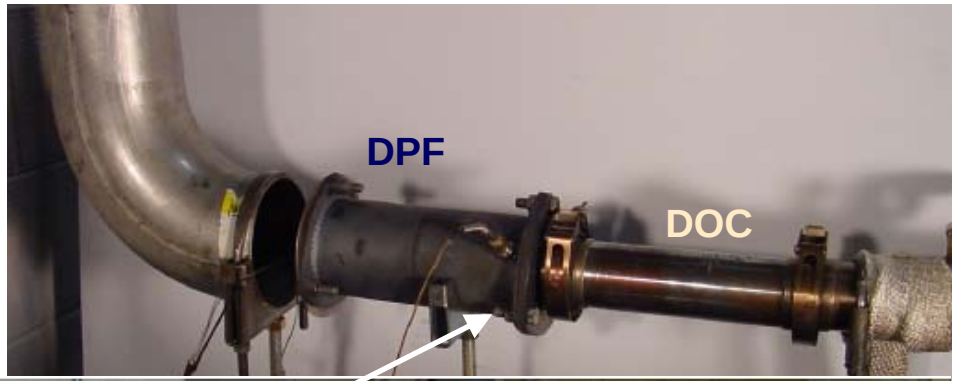
- Blanchard, G., Seguelong, T., Michelin, J., Schuerholz, S., & Terres, F., SAE Tech. 2003-01-0378.

Test Protocol

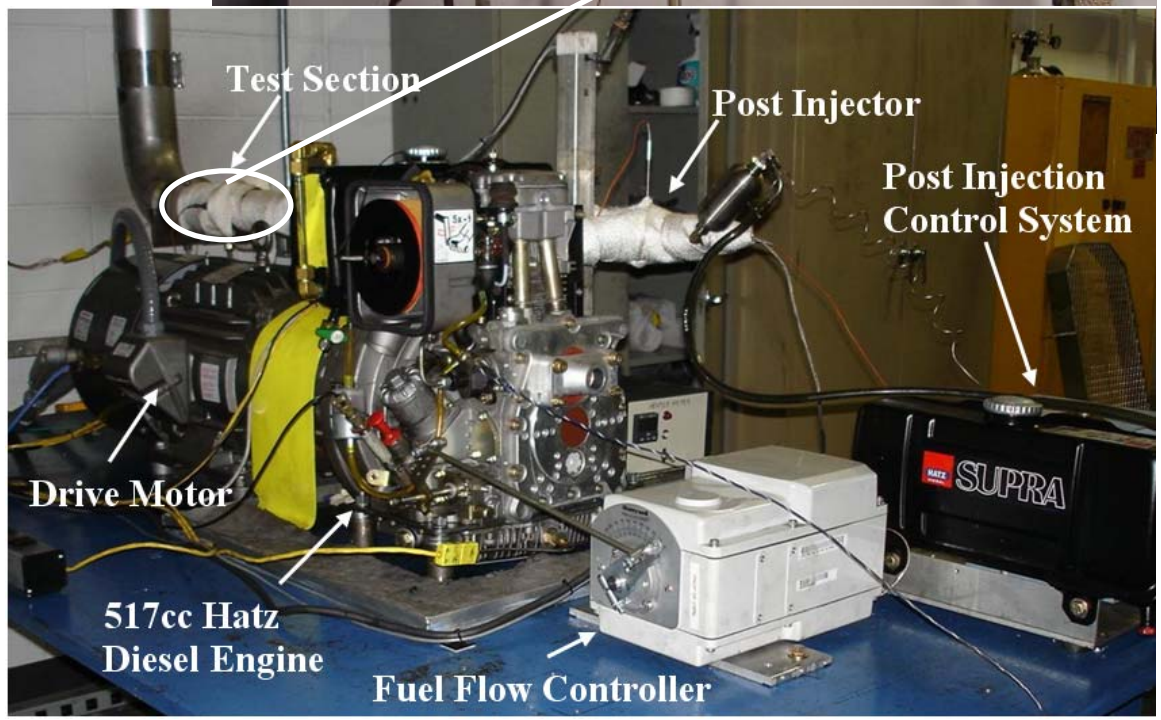
- **5% Lube oil mixed with ULSD fuel**
- **Backpressure threshold for each cycle**
  - **Loading Cycle**
    - **Baseline back-pressure recorded after stabilization**
    - **Active regeneration when 0.2 psi above the baseline**
    - **Target soot loading of 2 grams (~3 grams per liter)**
  - **Regeneration**
    - **Initiated with fuel injection into engine exhaust**
    - **Initial set point to keep DPF front below 600°C**
      - **to avoid uncontrolled regeneration**
    - **Adjust set point such that DPF exit gas temperature to ~725°C**
    - **All regeneration cycles last 30 minutes**

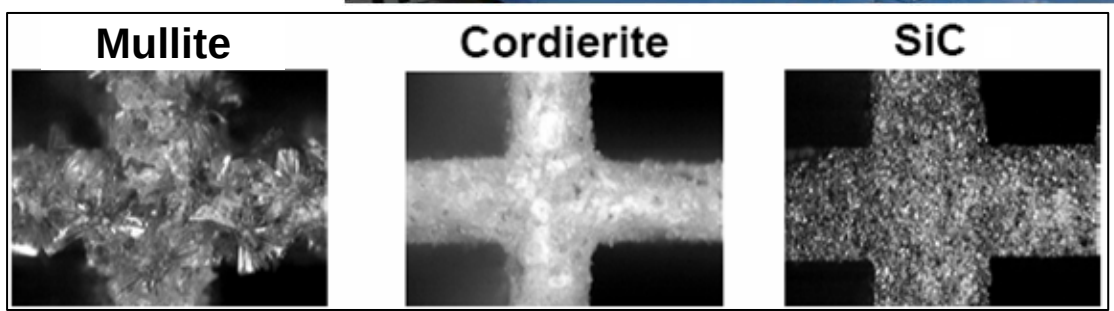


Experimental Setup



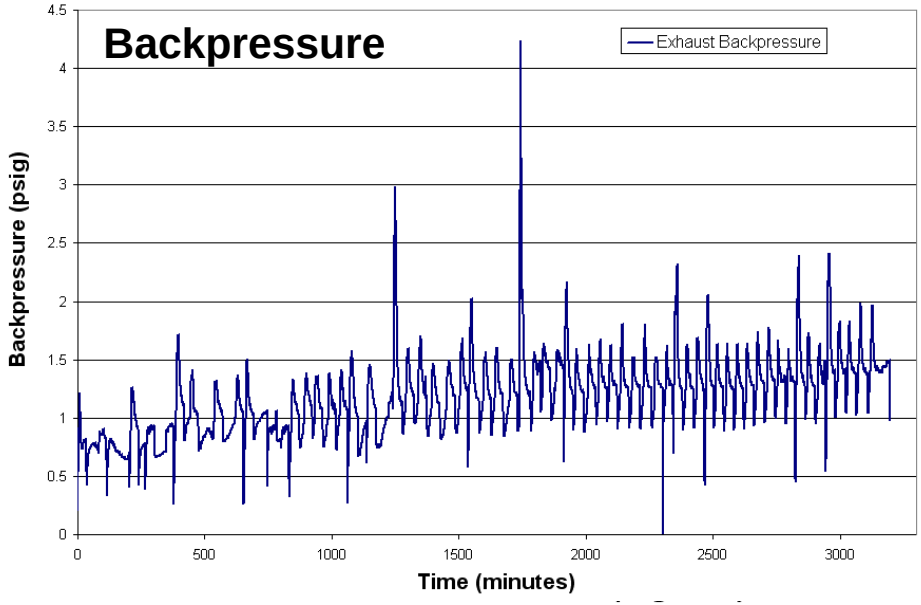
- **517cc Hatz Engine is operated at 1500 RPM continuously**
- **DPF easily removed for periodic weighing**
- **700cc DPFs evaluated**
  - **Cordierite, SiC, mullite**
  - **High PGM, Low PGM, and uncoated filters**

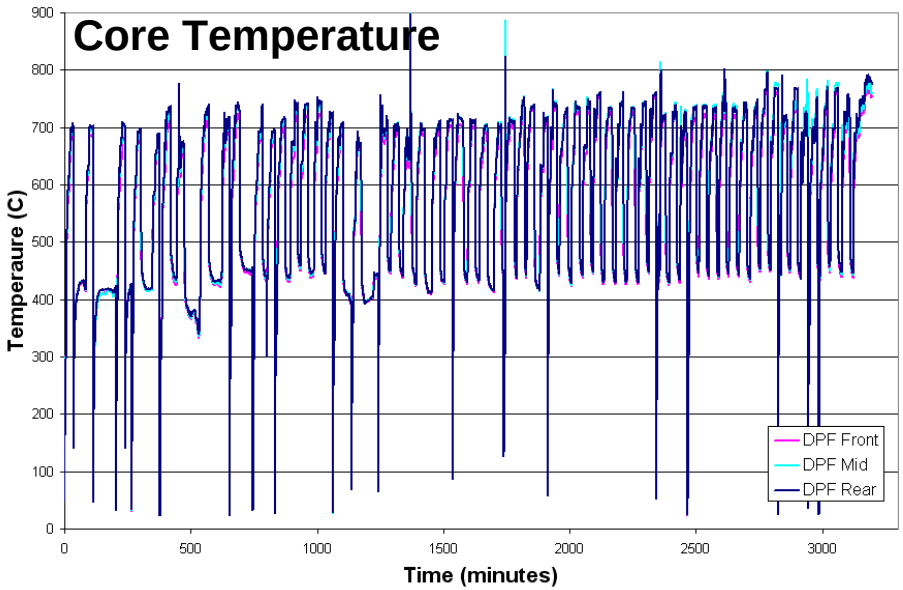


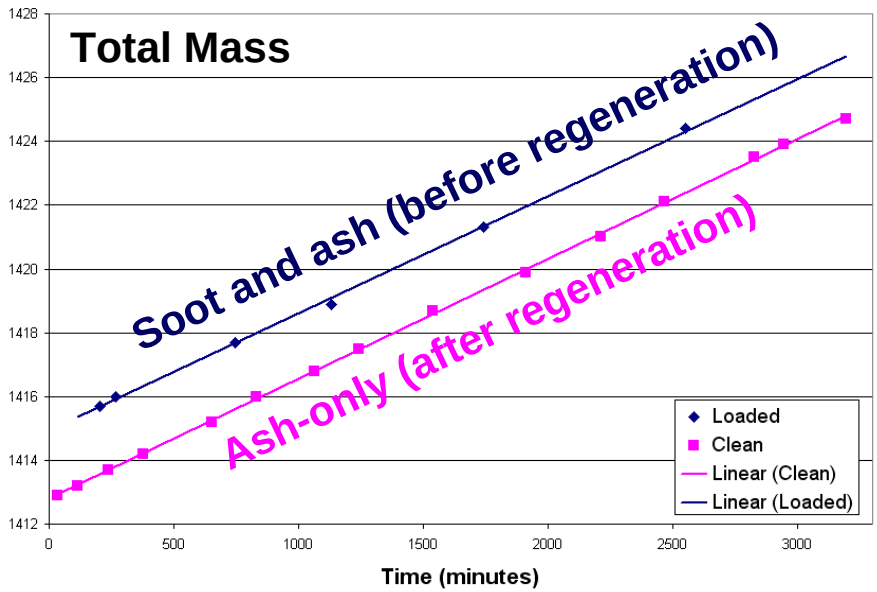


Typical Temperature, Pressure and Mass Profiles During Loading and Regeneration

- **Results for Cordierite (high PGM)**
- **Steady increase in backpressure**
  - **High backpressures resulted in higher soot accumulation rate**
- **Rate of soot accumulation is consistent and repeatable**
  - Loading cycle consistently achieves soot loading of 2 grams
  - Regeneration strategy effectively removes soot from the DPF

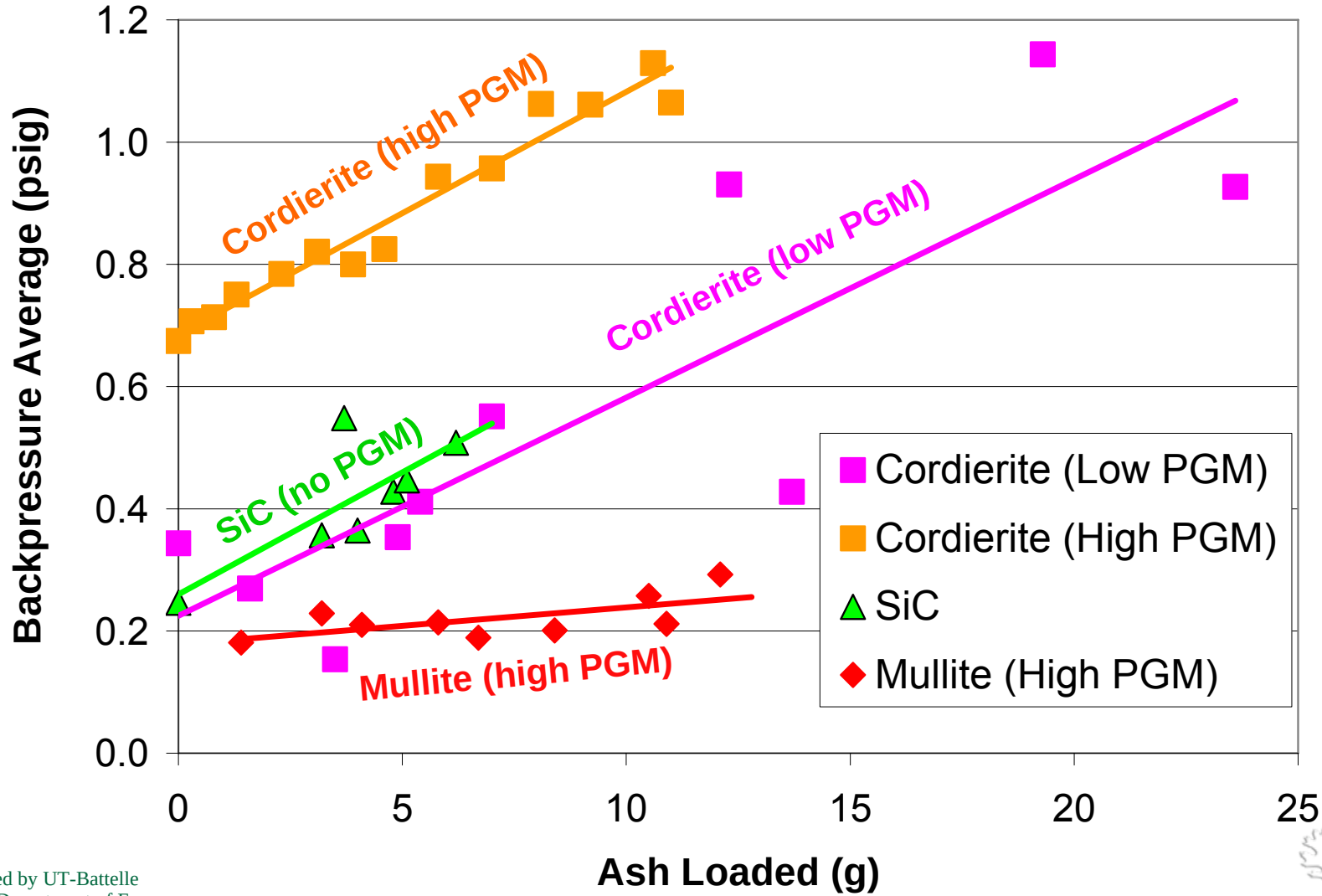






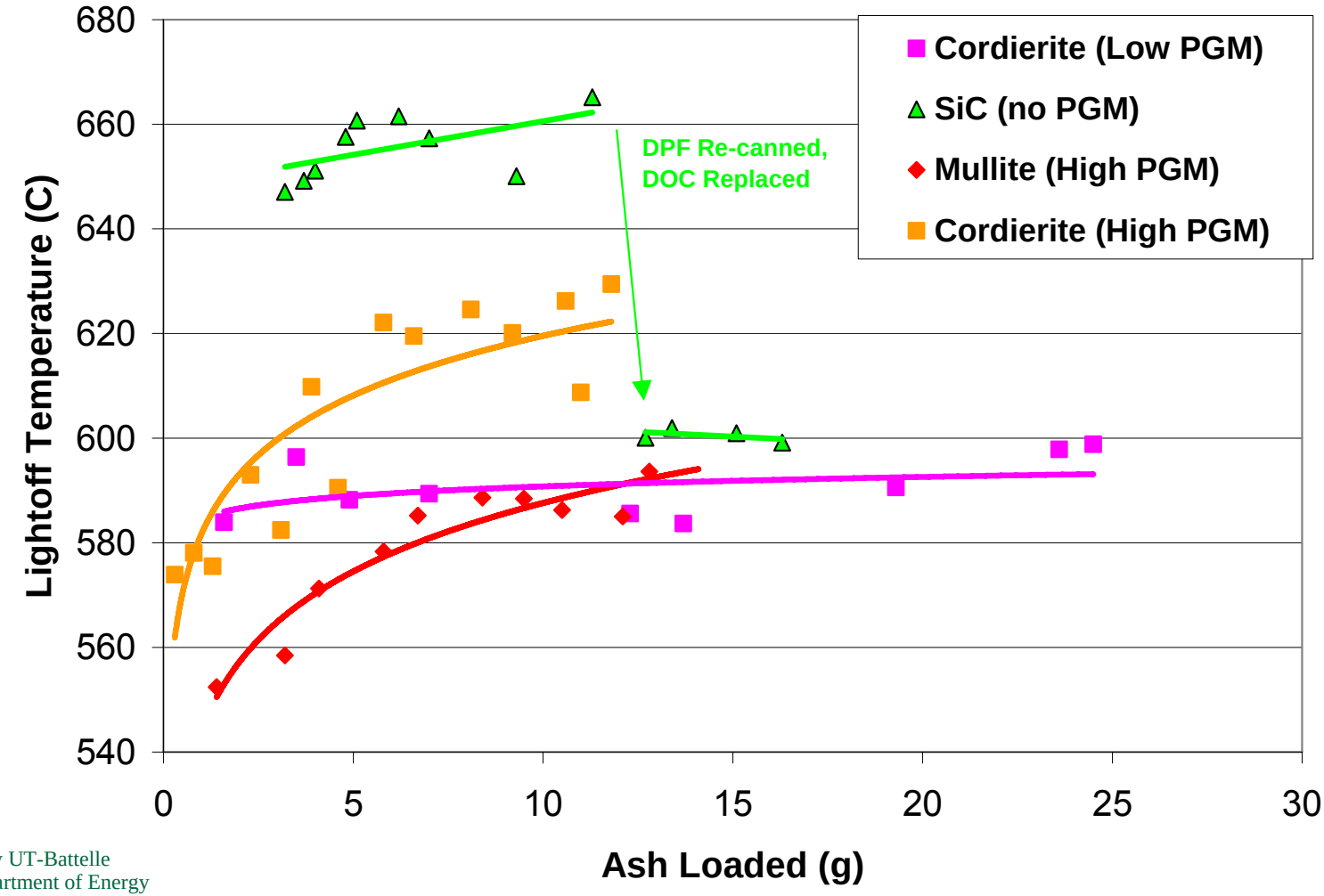
Backpressure Increases with Ash but Varies with DPF Material

- Cordierite and SiC are ~parallel
  - Rate is 0.036-0.040 psi/g_{ash}
- Mullite increase is 6x slower
  - Rate is 0.006 psi/g_{ash}

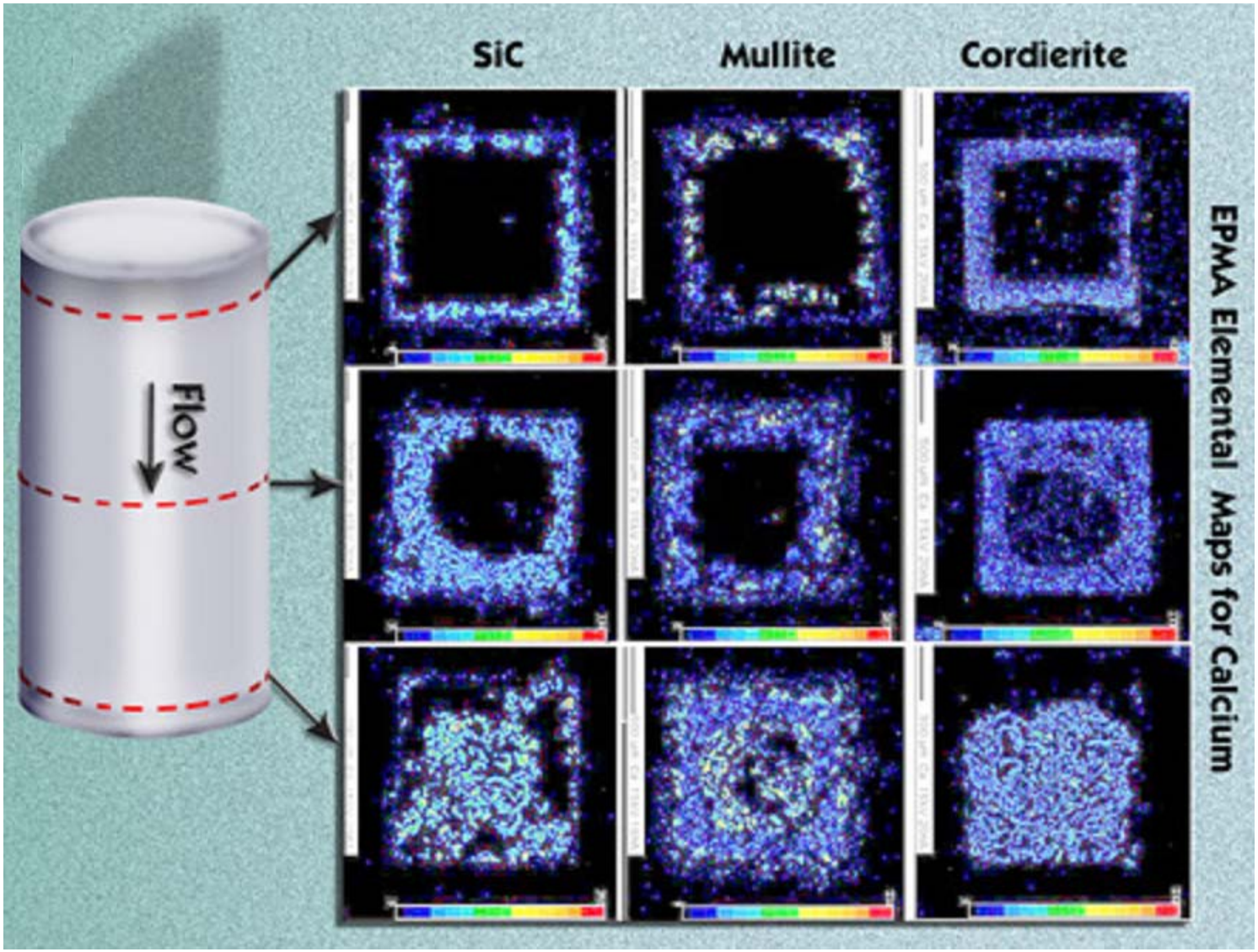


Lightoff Temperature Increases w/ash on C-DPFs

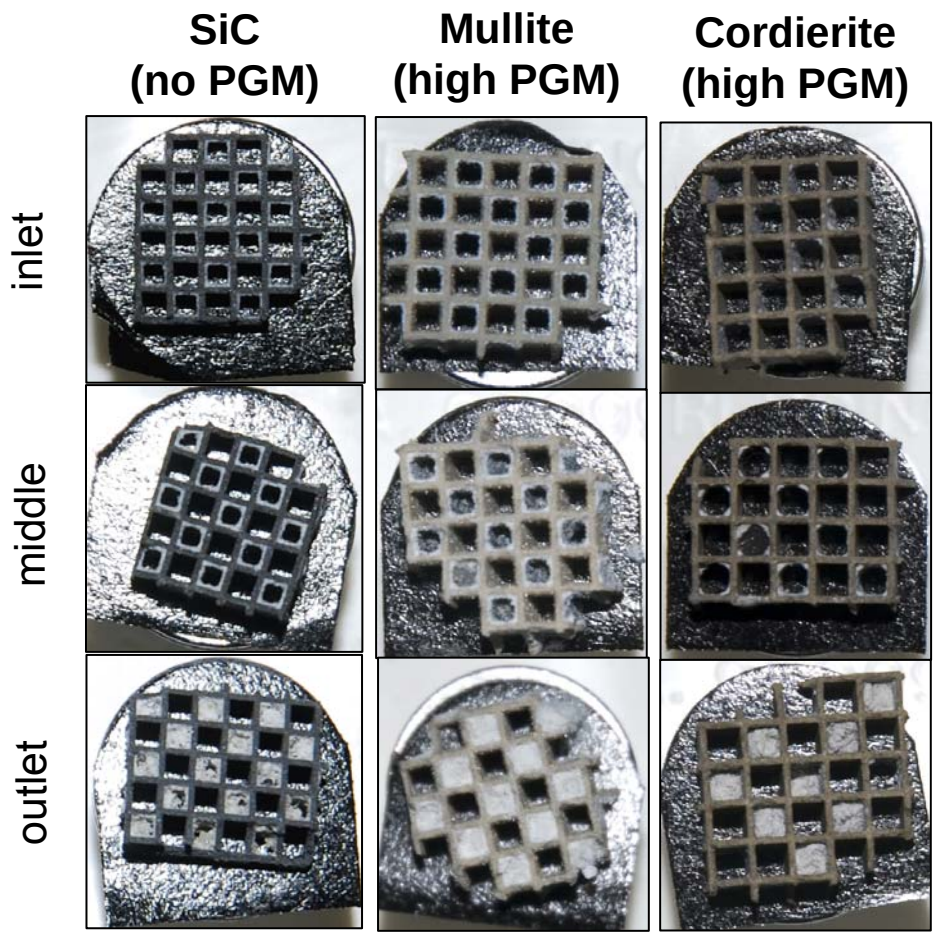
- **Lightoff temperature recorded when backpressure begins to decrease**
- **Highly-catalyzed substrates initially demonstrate lower lightoff temperature**
  - **After ~5 grams of ash accumulation, comparable to other substrates**
- **Ash has minimal effect on lightly-catalyzed and non-catalyzed substrates**



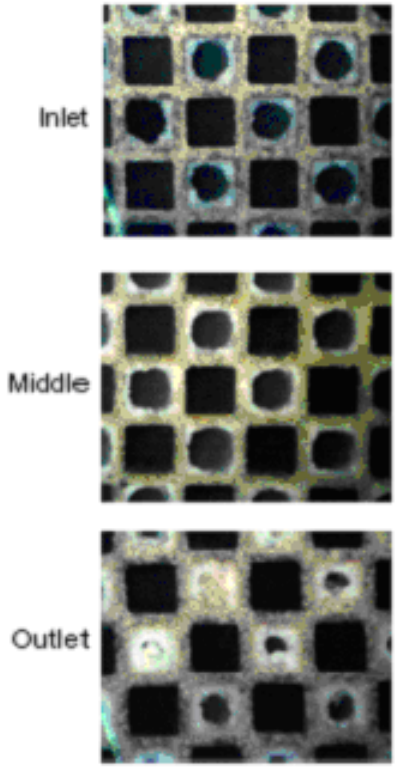
SEM and Elemental maps of Calcium demonstrate ash gradient along DPF channels



50-h Ash Deposits Similar to 600h Engine-aged DPF



Nemoto et al. ash layers in DPFs after 600 hrs*



Test No.1
DH-1 class

- **Compares well with ash deposits in extended engine dynomometer tests**

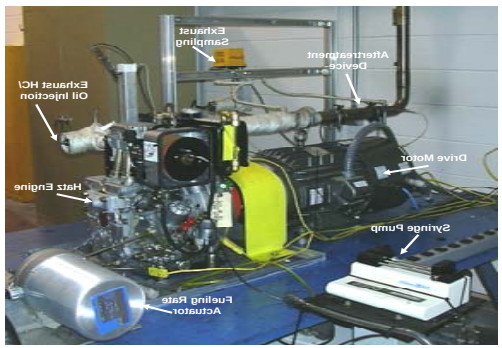
* - Nemoto, S., Togawa, S., Kishi, Y., Ishikawa, T., Matsuura, K., Hashimoto, T., Miura, M., & Yamazaki, T., SAE Technical Paper Series 2004-01-1887.

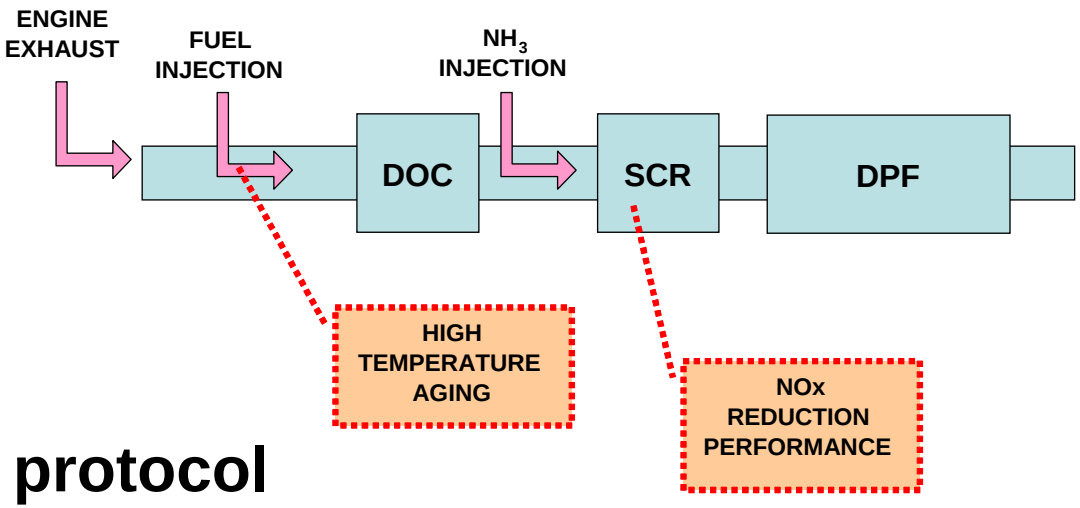
SCR

Engine-based Thermal-aging of DOC-SCR-DPF Emissions Control “System”

SCR: Thermal Aging using System Approach

- **Focus on zeolite-based SCR**
  - **Fe-based zeolites from Catalytic Solutions**
- **Thermal Aging Approach**
  - **Engine-based: active DPF regeneration**
    - **Engine aging → engine and bench evaluation**

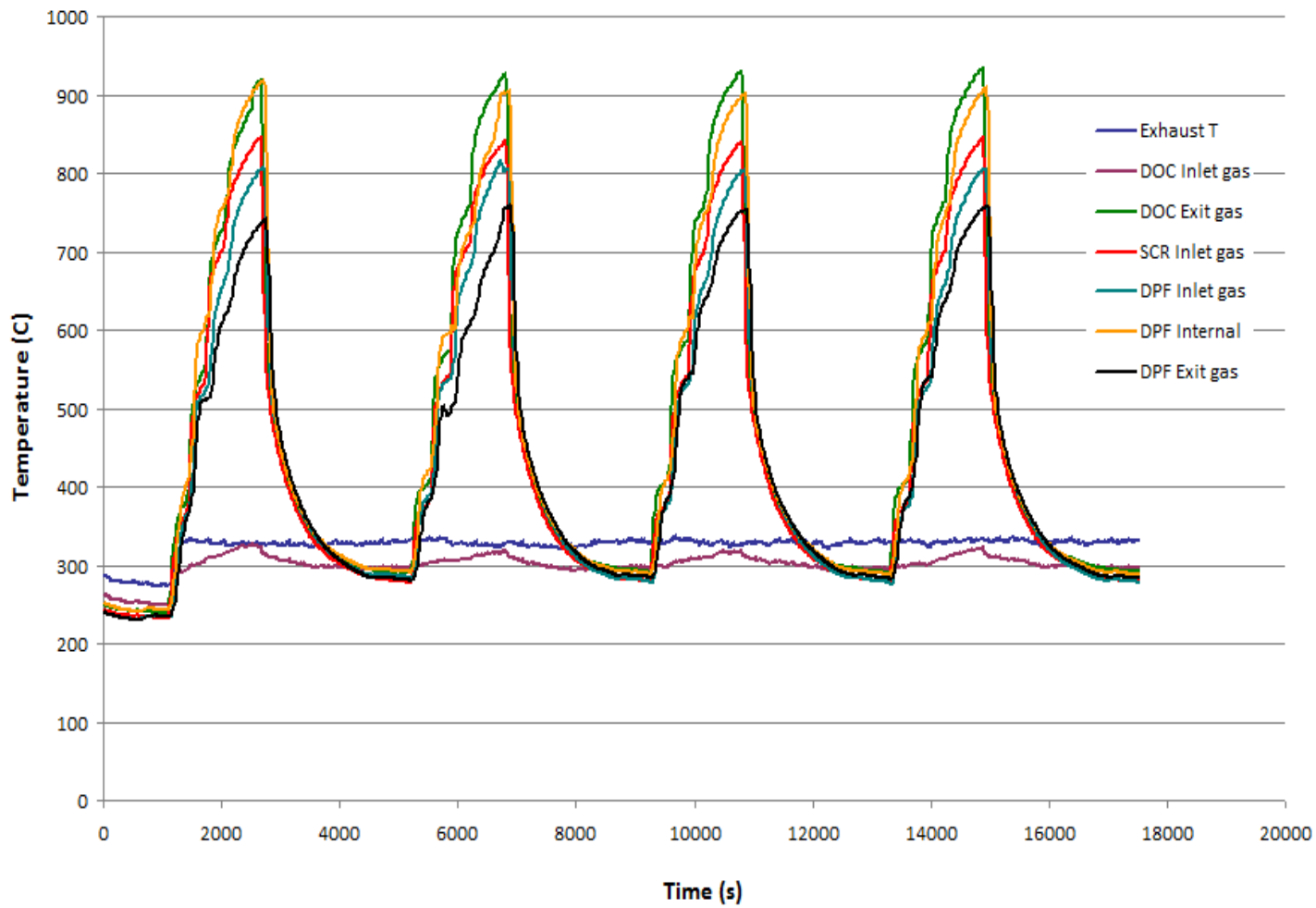




  - **Bench Aging: using CLEERS protocol**
    - **670ºC with 28ppm SO_2 for 64 hrs**
- **Field-aged catalysts already received (Euro bus)**

Typical Temperatures Profile in the engine bench at 850ºC

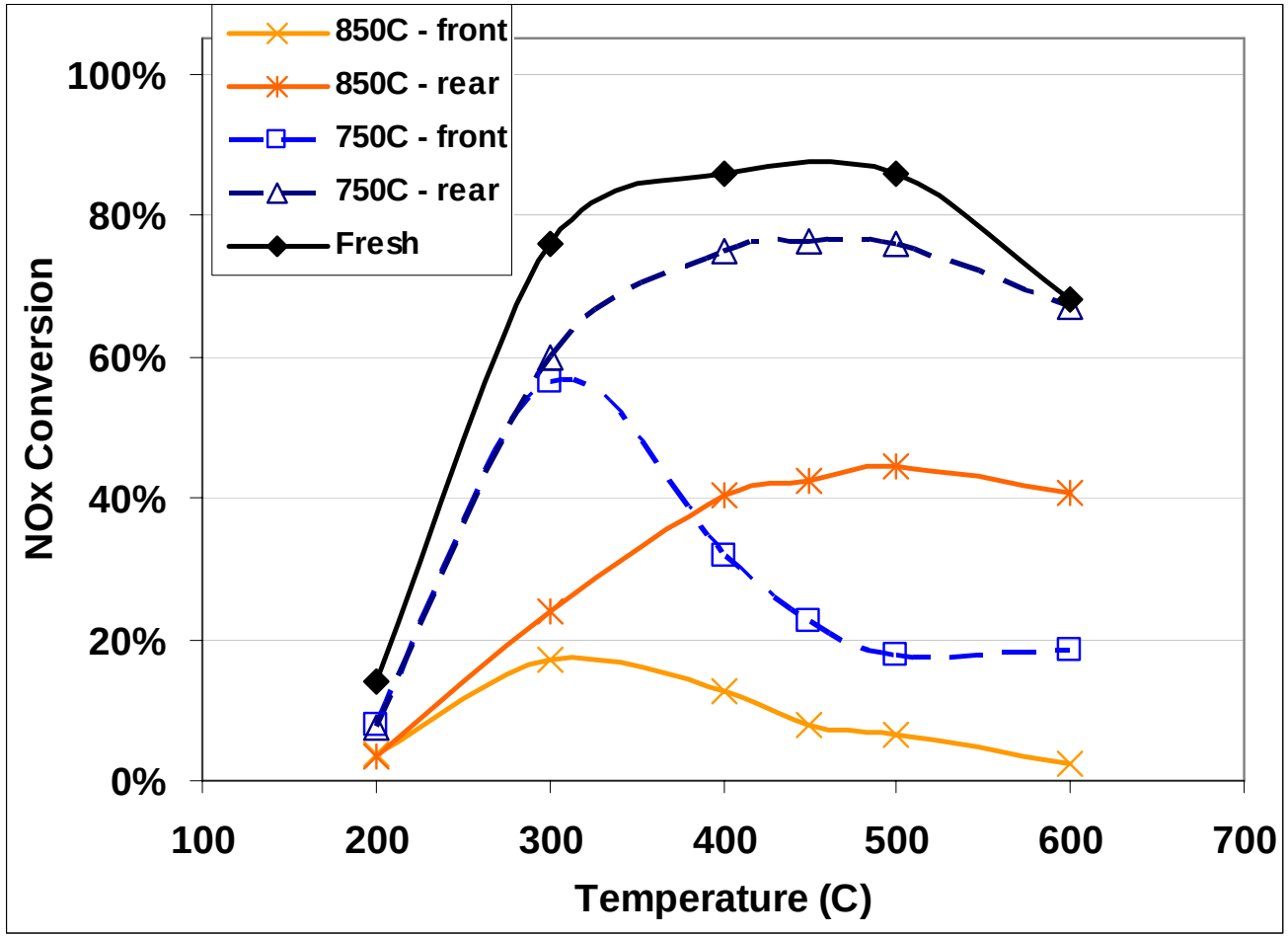
- **Temperature profile is repeatable**
- **Axial temperature variation along SCR catalyst**



Exhaust temperatures during SCR aging on the engine bench, using configuration 1: DOC, SCR, DPF, with 30% actuator setting, performed 02/08/08

Deactivation Occurs more Significantly in Front

- **Front section of aged catalysts deactivated severely**
- **Maximum NO_x conversion of catalyst aged at 850°C is 45%**
- **Maximum NO_x conversion of catalyst aged at 750°C is 76%**
- **Engine Aging at 650°C coming soon**



Catalytic Solutions Fe-SCR-2; NO_x conversion as a function of temperature; evaluated with 14% O_2, 5% H_2O, 5% CO_2, 350ppm NO, 350ppm NH_3 and N_2 balance at 30,000 h^{-1}; Catalyst aged on the engine bench

Composition of simulated exhaust gases

- Evaluations and hydrothermal aging performed at 30,000 h^{-1}

NO_x conversion evaluation

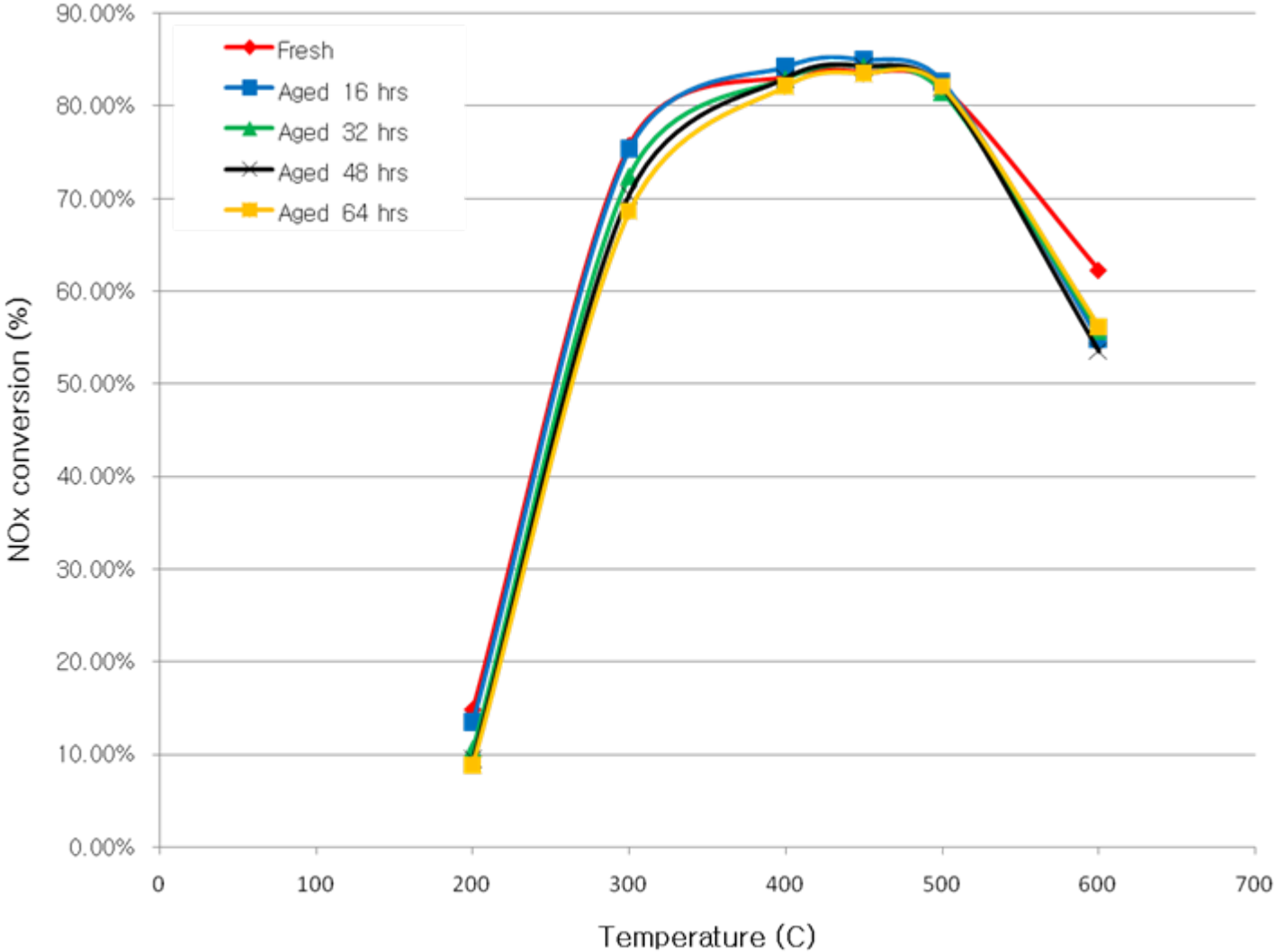
Gas Species	Concentration
H_2O (g)	5%
O_2	14%
CO_2	5%
NO	350ppm
NH_3	350ppm
N_2	balance

Hydrothermal Aging

Gas Species	Concentration
H_2O	5%
O_2	14%
CO_2	5%
SO_2	28ppm
N_2	balance

NO_x conversion of Furnace-aged Fe-Zeolite SCR catalyst at 670°C

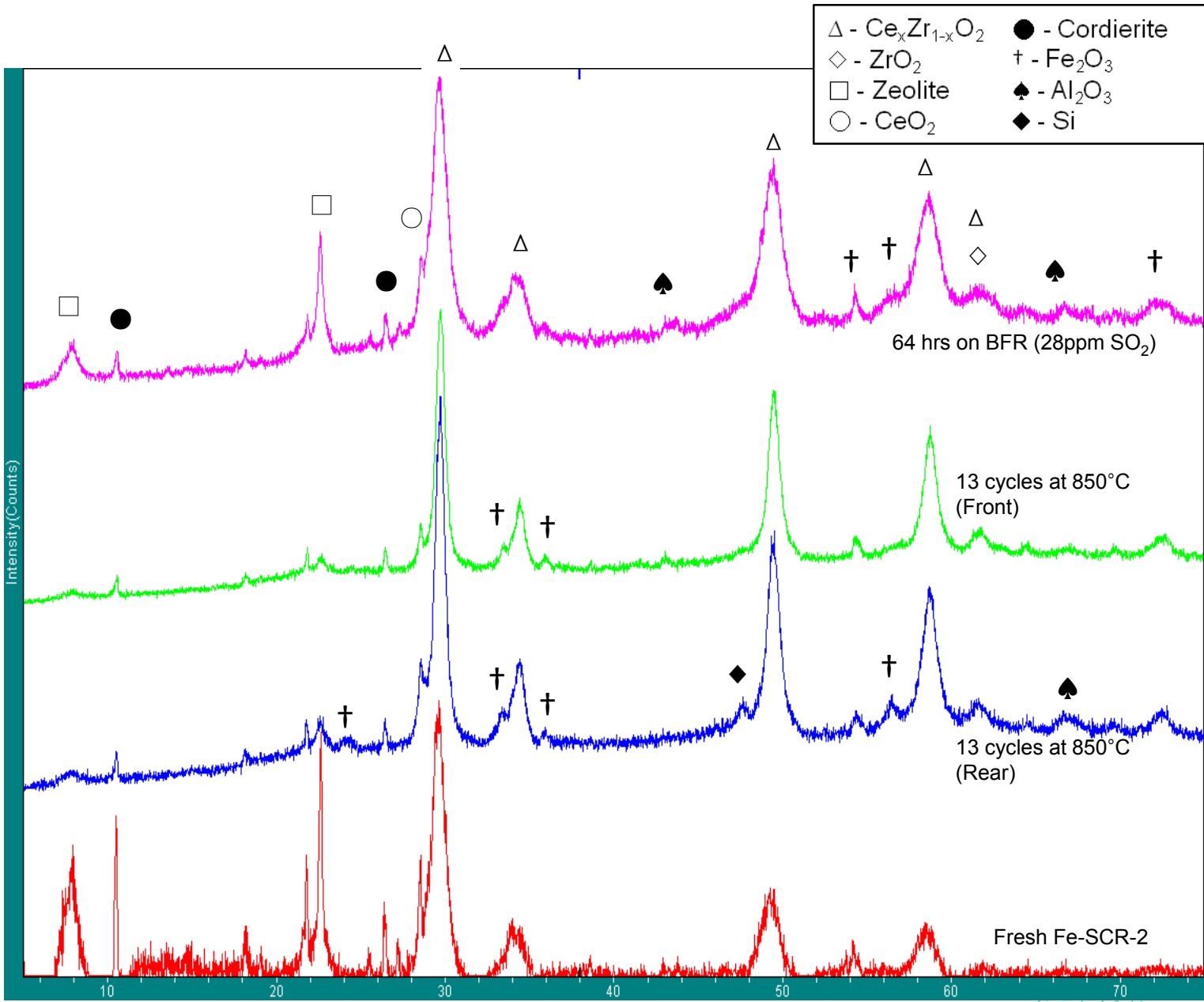
- Aging has not significantly affected NO_x conversion
- Aging performed with 28ppm SO_2
- Middle of catalyst maintained at 670°C during aging



Catalytic Solutions Fe-SCR-2: NO_x conversion as a function of temperature: evaluated with 14% O_2, 5% H_2O, 5% CO_2, 350ppm NO, 350ppm NH_3 and N_2 balance at 30,000 h^{-1}; Catalyst aged on BFR

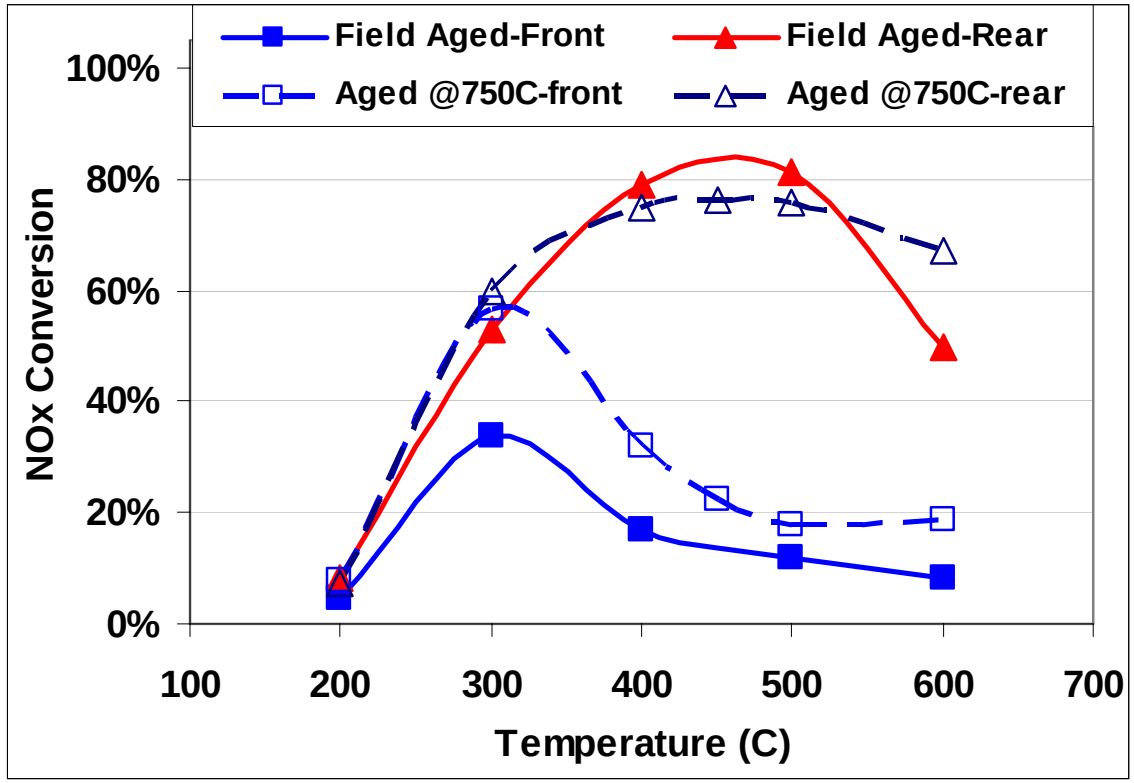
XRD patterns of fresh and aged Fe-Zeolite (Fe-SCR-2) SCR CATALYSTS

- Significantly less zeolite detected in aged samples
- Fe_2O_3 and Al_2O_3 peaks are discernable in aged samples
- Zeolite lattice begins to breakdown around 800°C for many high-silica zeolites
  - Zhdanov
- Surface area impact also being measured



Field-aged Fe-SCR shows similar Deactivation Characteristics of Engine Aging at 750C

- Front section of field-aged catalyst severely degraded
- Field-aged catalyst performance slightly worse
  - Suggests actual field conditions exceeded 750C
    - But less than 850C
- Overall vehicle performance was maintained in field



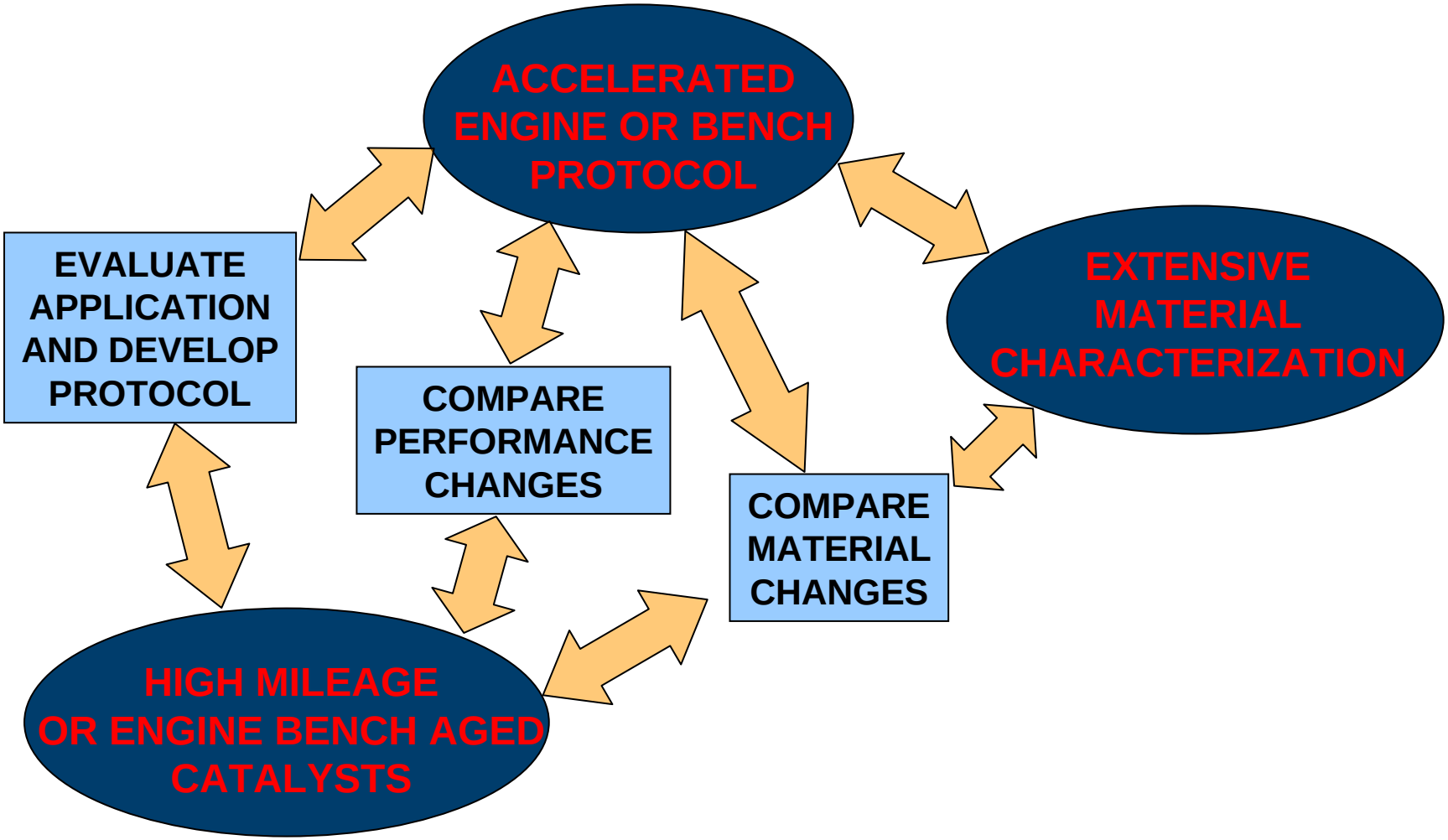
NOx Conversion characteristics of field-aged and fresh SCR catalysts; evaluated at varying temperatures, 5% H2O, 5% CO2, 14% O2, 350ppm NO, 350ppm NH3, N2 balance, GHSV=30,000

Summary and Future Directions

- **Project has laid groundwork for diesel emissions control accelerated aging/poisoning protocol development**
  - **Phosphorous poisoning**
  - **Bench and engine-based thermal aging**
  - **Ash loading**
- **Results have been incorporated into models**
  - **PSAT aging impact on LNTs**
  - **MIT starting modeling effort on DOC**
  - **More incorporation desired and needed**
- **Future plans**
  - **Biodiesel constituent effects (Na/K) on emissions control devices…performance and materials characterization study**
  - **Collaboration with EPA for possible certification of protocols to allow industry implementation**
    - **Similar to existing gasoline-based accelerated aging protocols**

Supplemental Slides

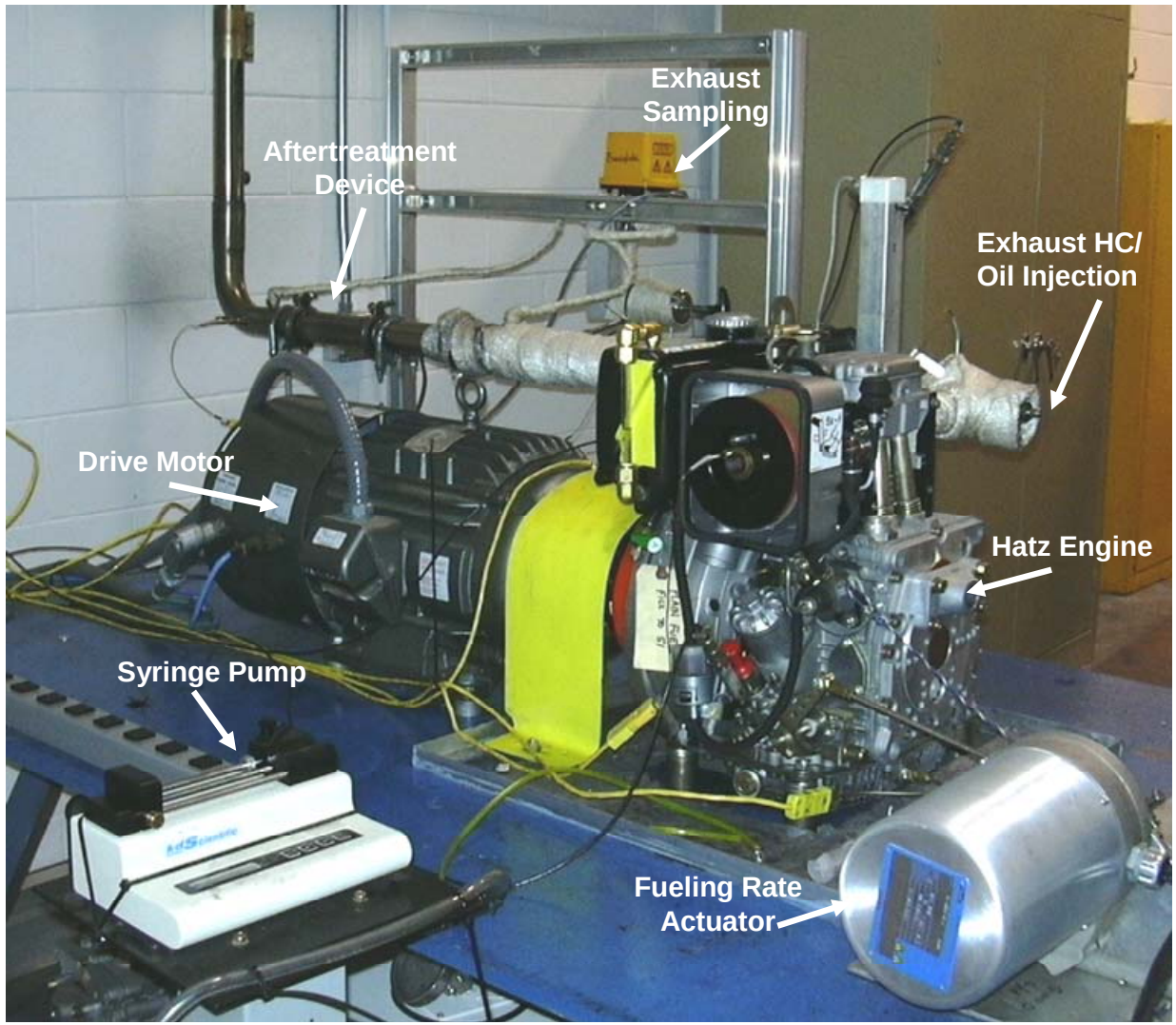
Development of Rapid Protocols



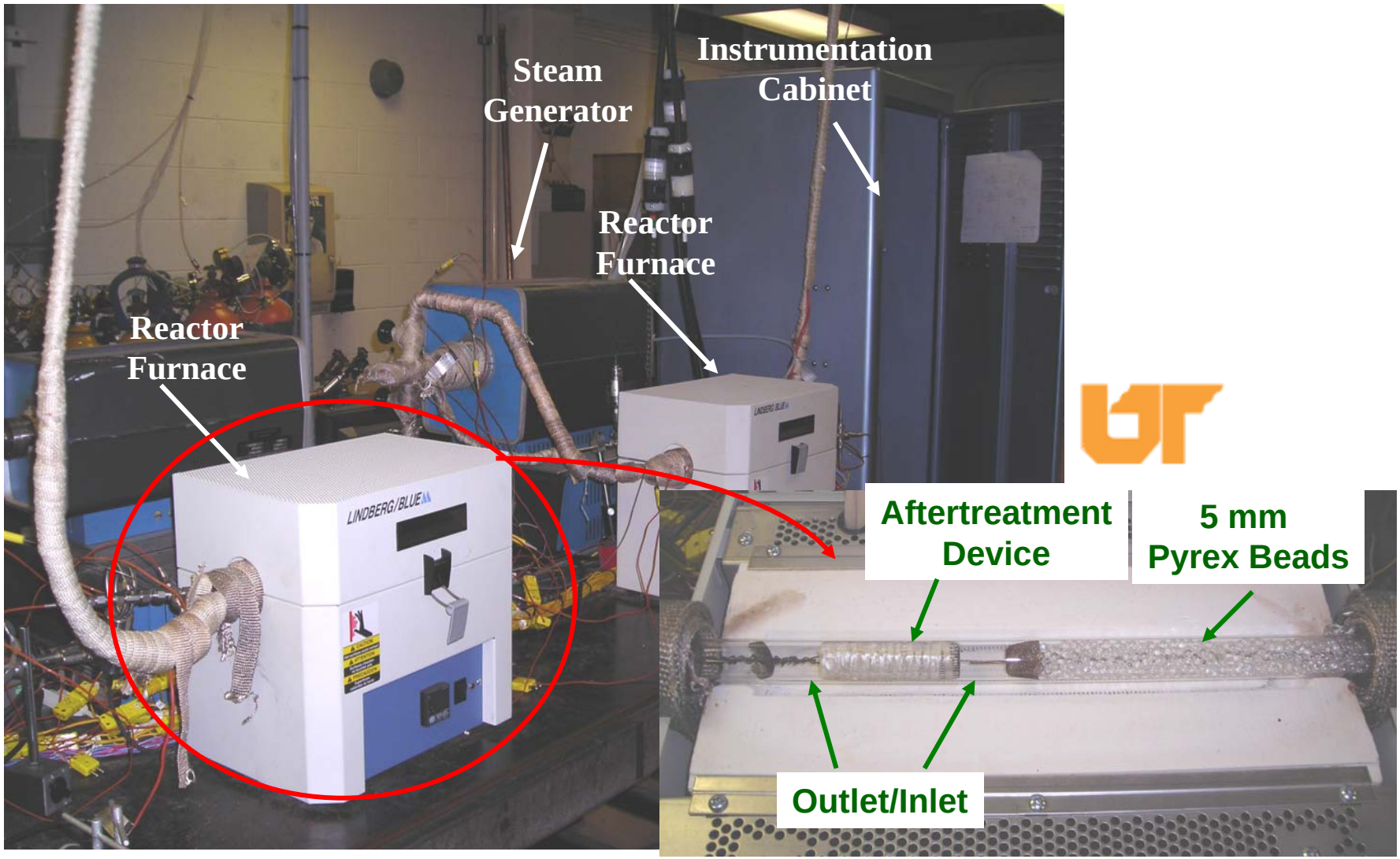
Experimental equipment

- **Small diesel engine (ORNL)**
- **Bench reactor (UTK)**
- **Catalytic micro-reactor (ORNL)**
- **Materials characterization (UTK and ORNL)**
- **Catalysts**
  - **BASF, Delphi, Catalytic Solutions, Cummins Filtration**
  - **Some model catalysts, most fully formulated**
- **Substrates**
  - **NGK, Dow**
- **Thanks again to the catalyst and substrate companies who helped us in this research**

Engine Bench Setup

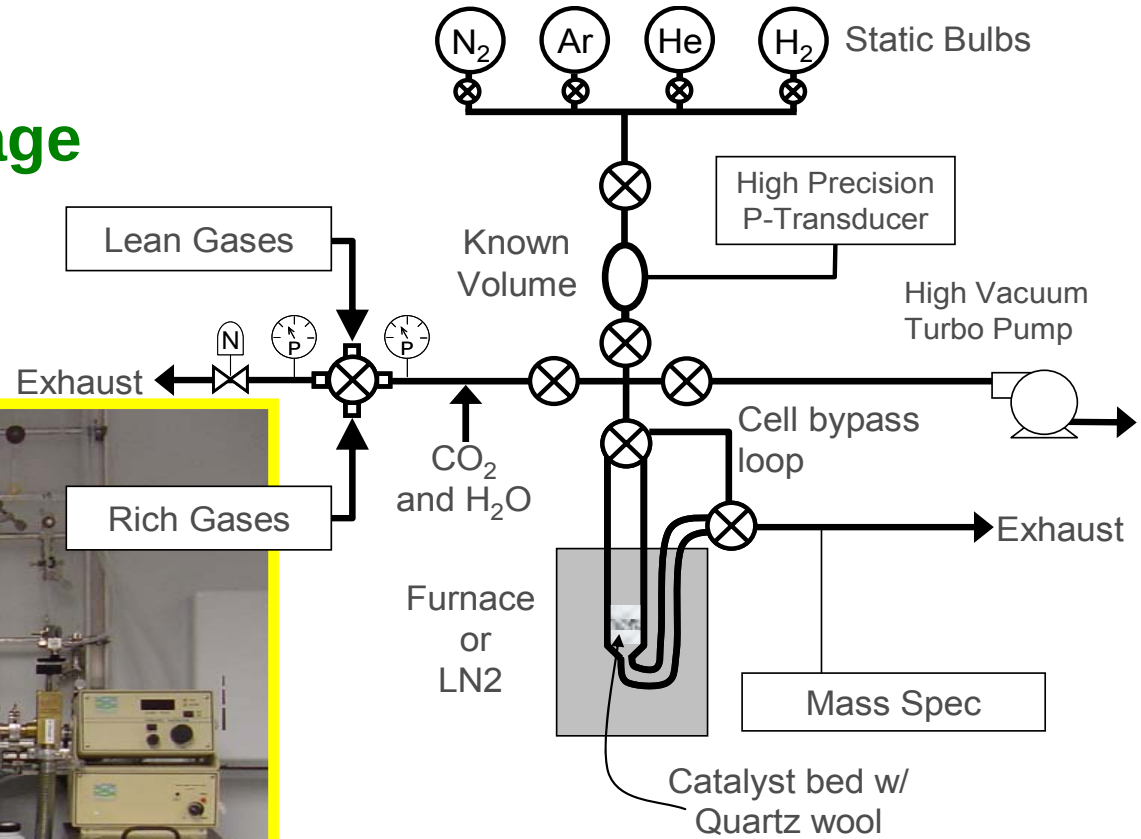


Bench-Flow Reactor

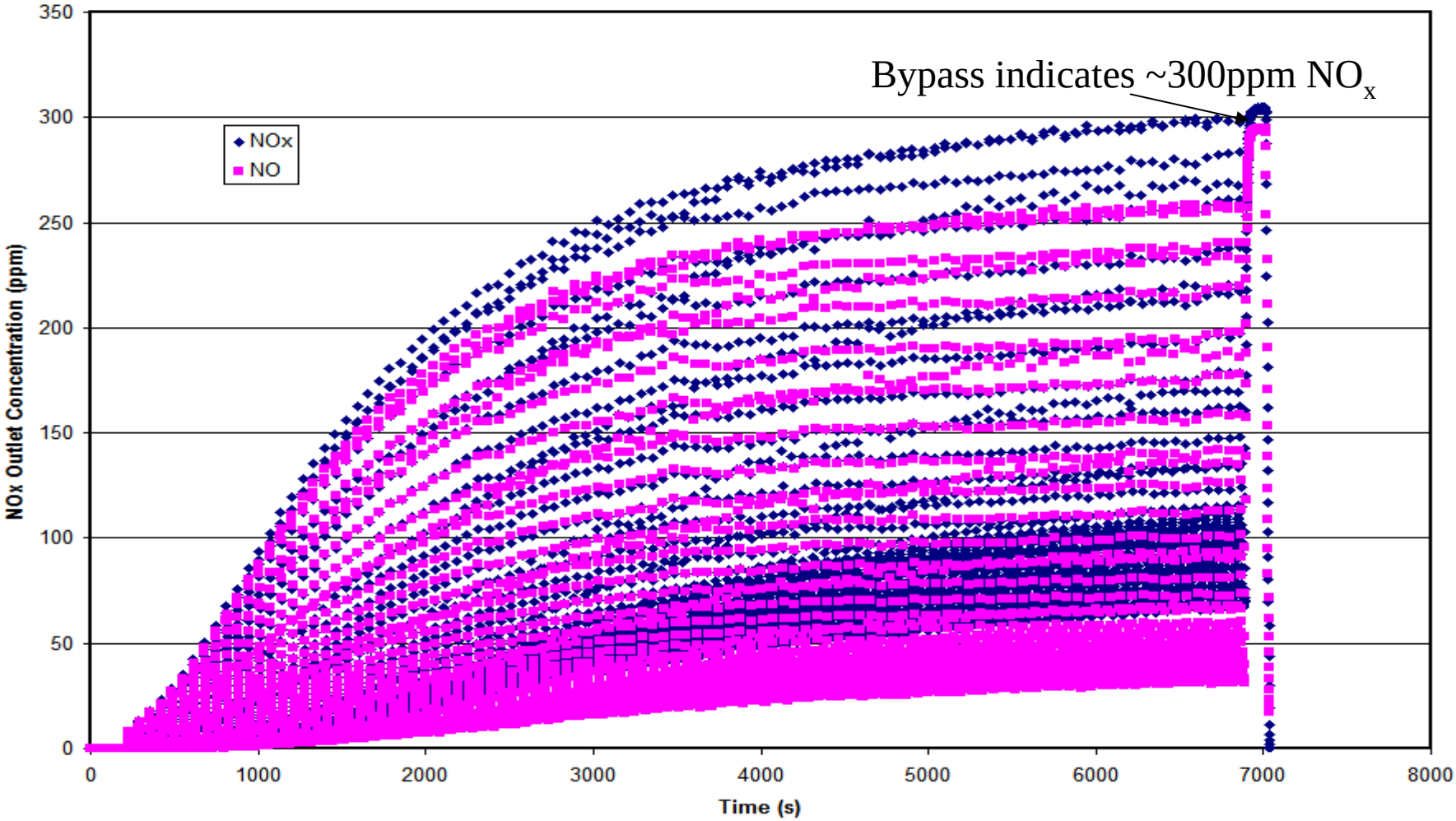


Catalytic Micro-reactor Apparatus

Measurement of storage capacity, conversion, and surface area

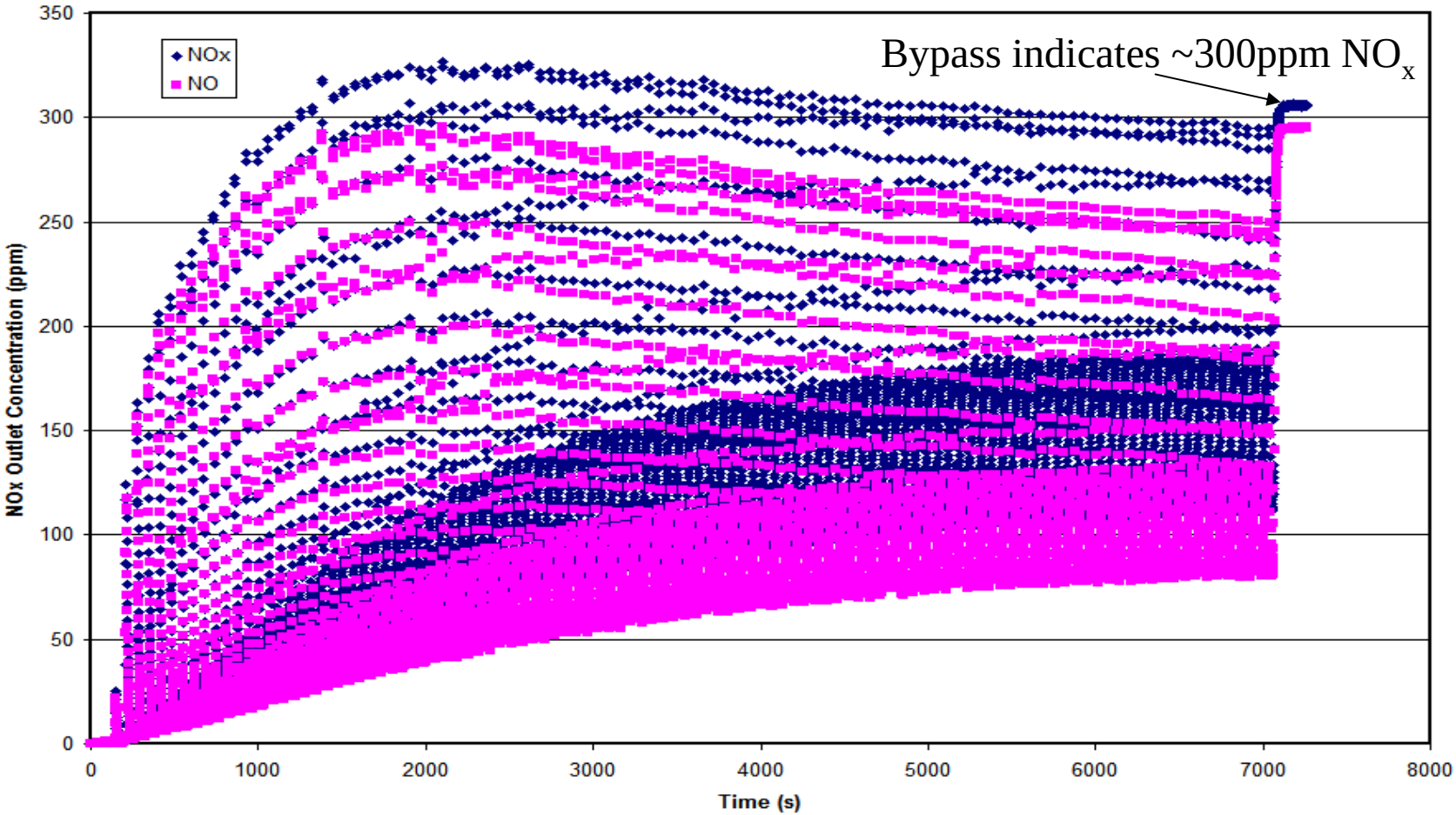


200°C Evaluation of Fresh LNT



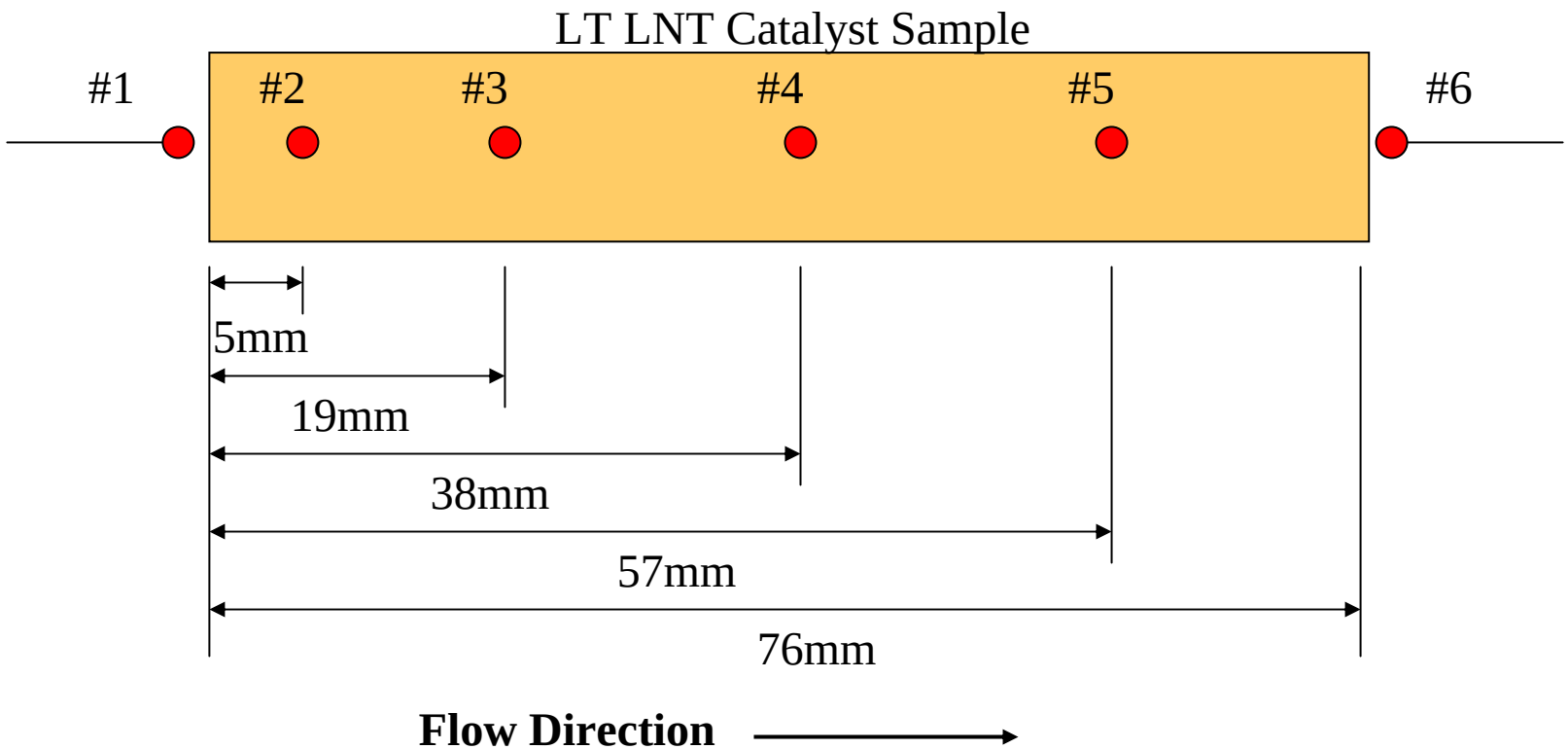
- Steady state NO_x Conversion is not achieved after ~2 hours of evaluation
- NO_x excursion continues to increase for the duration of the experiment
- NO_x storage capacity also continues to fall throughout the experiment

200°C Evaluation of LNT Aged at 1000°C for 5 cycles



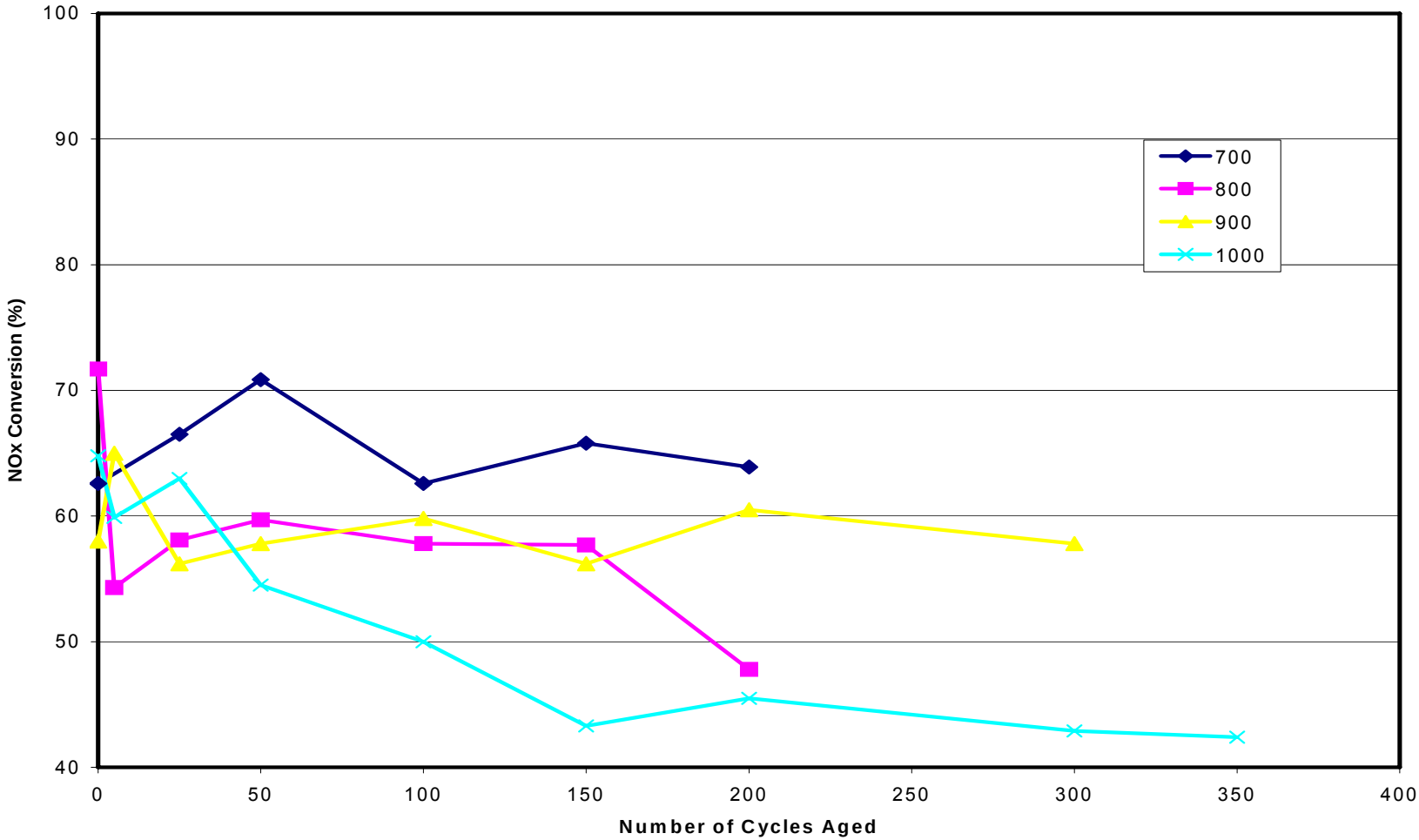
- Steady state NO_x Conversion is not achieved after ~2 hours of evaluation
- NO_x excursion begins to fall after peaking at ~325 ppm
- NO_x storage capacity continues to decrease throughout the experiment

Thermocouple Locations



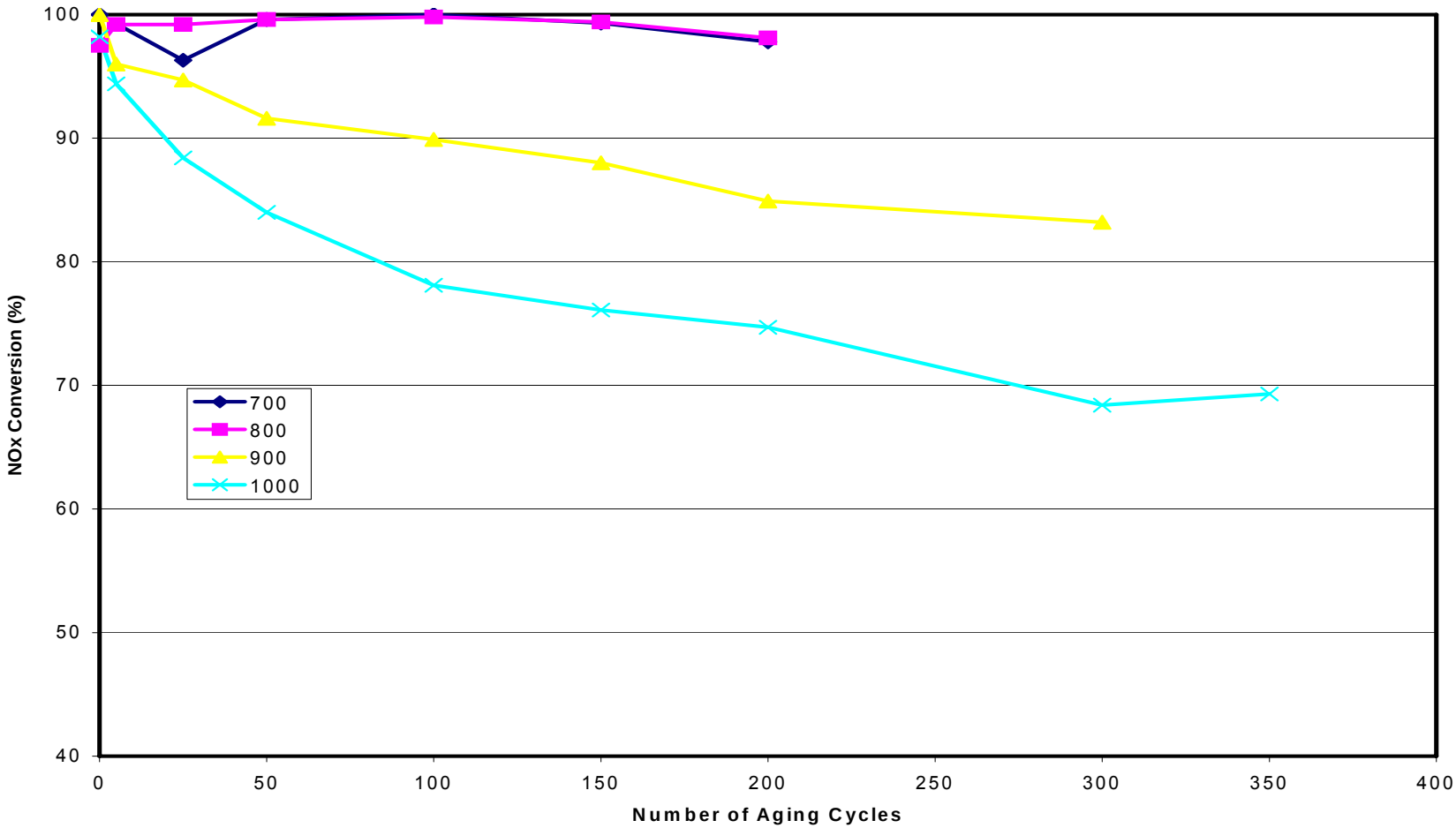
- By measuring the catalyst's temperature at multiple axial locations we are able to obtain the axial temperature profile during aging and evaluation and to determine the effect of aging temperature on the performance of the catalyst

Performance of LNTs Aged at 700, 800, 900, and 1000°C Using 200°C Evaluation Cycle



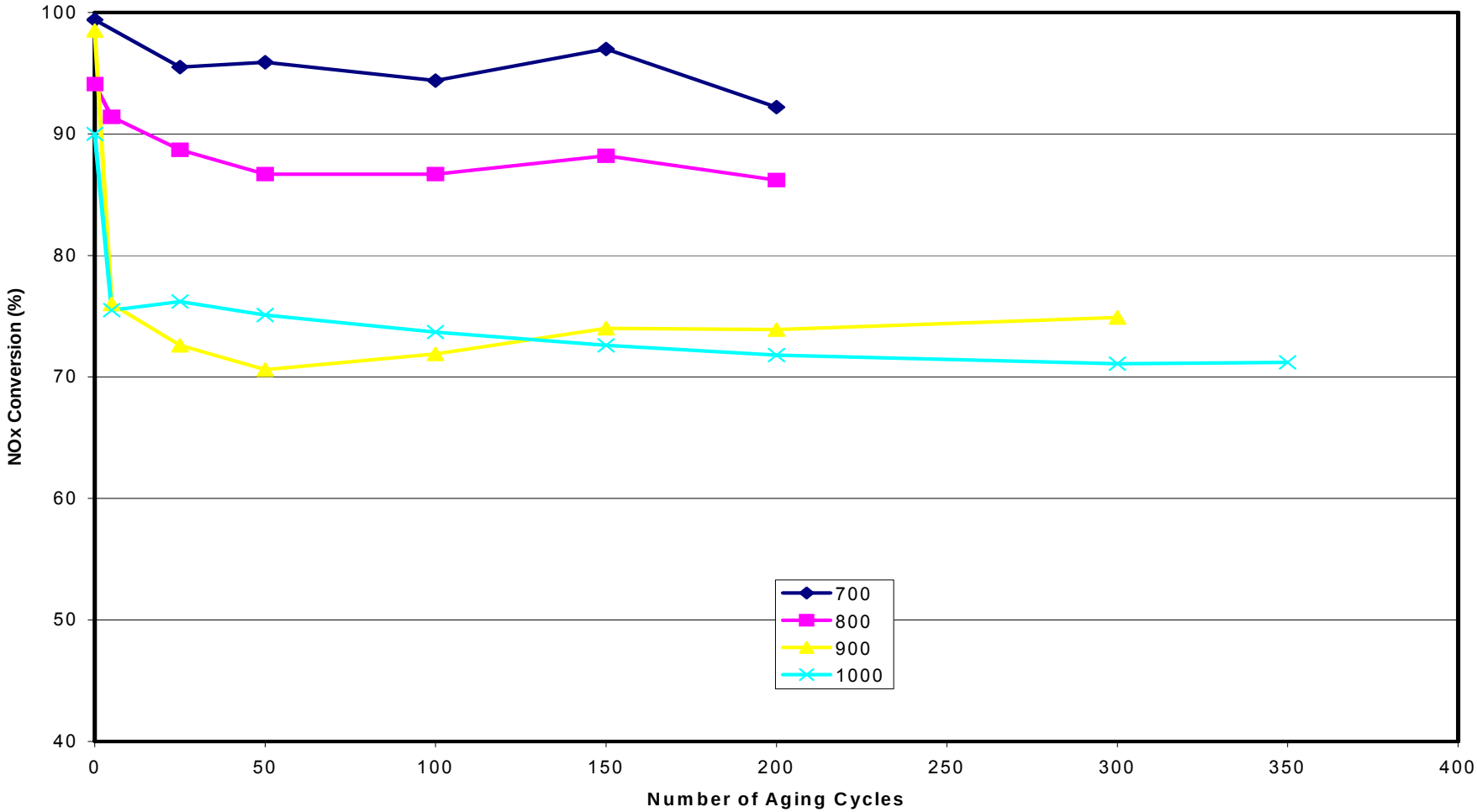
- Conversion is lowest after aging at 1000C
- Results are not consistent

Performance of LNTs Aged at 700, 800, 900, and 1000°C Using 300°C Evaluation Cycle



- Conversion falls with aging temperature as expected

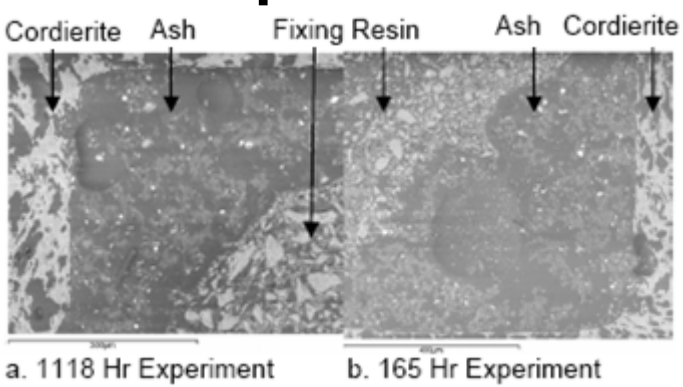
Performance of LNTs Aged at 700, 800, 900, and 1000°C Using 400°C Evaluation Cycle



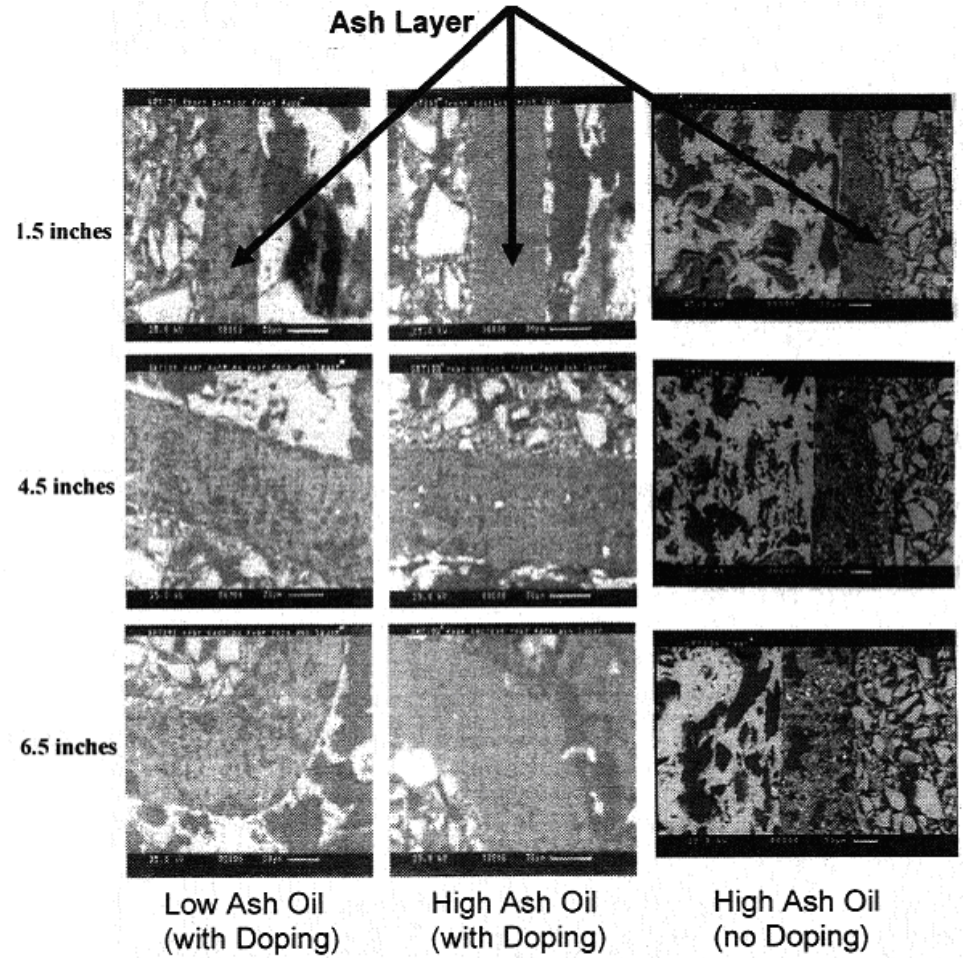
- Conversions after aging at 900°C and 1000°C are very similar

DPF Durability Issues

- **Accelerated lube-oil consumption methods have been shown to produce ash layers that compare favorably with layers formed solely with natural lube-oil consumption**



EPMA images of ash layer formed from natural oil consumption (left) and oil misting (right)[11]



SEM images of ash layers for three oil formulations and consumption mechanisms[15]

[11] Sutton, M., Britton, N., Otterholm, B., Tengström, P., Frennfelt, C., & Murray, I. (2004). Investigations into lubricant blocking of diesel particulate filters. (SAE Technical Paper Series 2004-01-3013).
[15] Bardasz, E., Mackney, D., Britton, N., Kleinschek, G., Olofsson, K., Murray, I., & Walker, A. (2003). Investigation of the interactions between lubricant-derived species and aftertreatment systems on a state-of-the-art heavy duty diesel engine. (SAE Technical Paper Series 2003-01-1963).

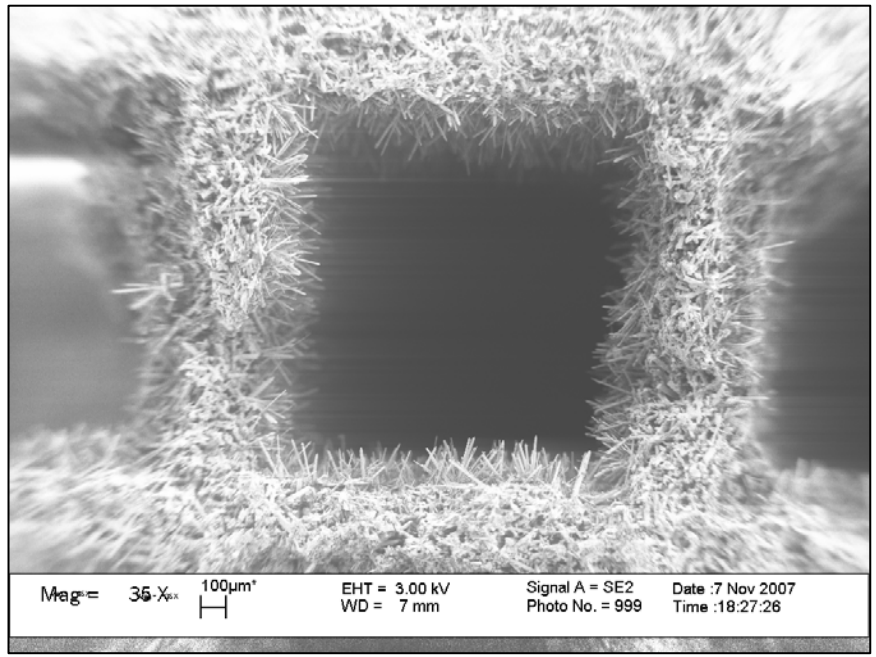
Characterization of ash with ICP

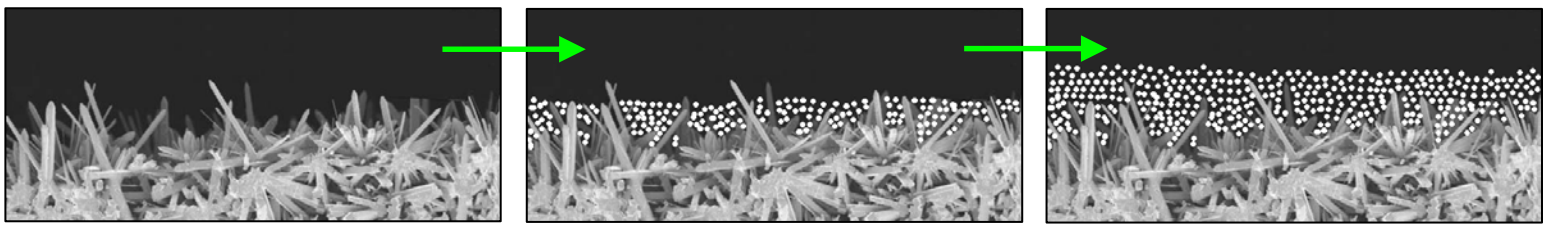
- **Identify and quantify (?) ash constituents in oil and fuel**
- **Quantify (?) recovery of ash constituents in filter**

- **Results indicate a varying degree of recovery rate**
  - **up to ~90% for both Calcium and Zinc, but varies from sample to sample**
  - **May be difficult to completely rely on this technique for quantification**
- **Distribution within filter corresponds to ash layer gradient along axis**
  - **Layer thickness is minimal near the inlet**
  - **Thickness increases along the length of the filter**

Mullite Materialistic Details

- **Mullite (High PGM)**
  - **Initial backpressure lowest of all tests**
    - **Most porous material**
  - **Fewest regenerations required**
    - **Extremely effective in continuously regenerating soot**
    - **Still gain ~2 grams of soot between regenerations**
  - **Backpressure slope is roughly horizontal for the first 2/3 of the experiment, then begins to increase**
    - **Textured surface increases filtration surface area and appears to maximize soot-catalyst interaction when catalyst is present**





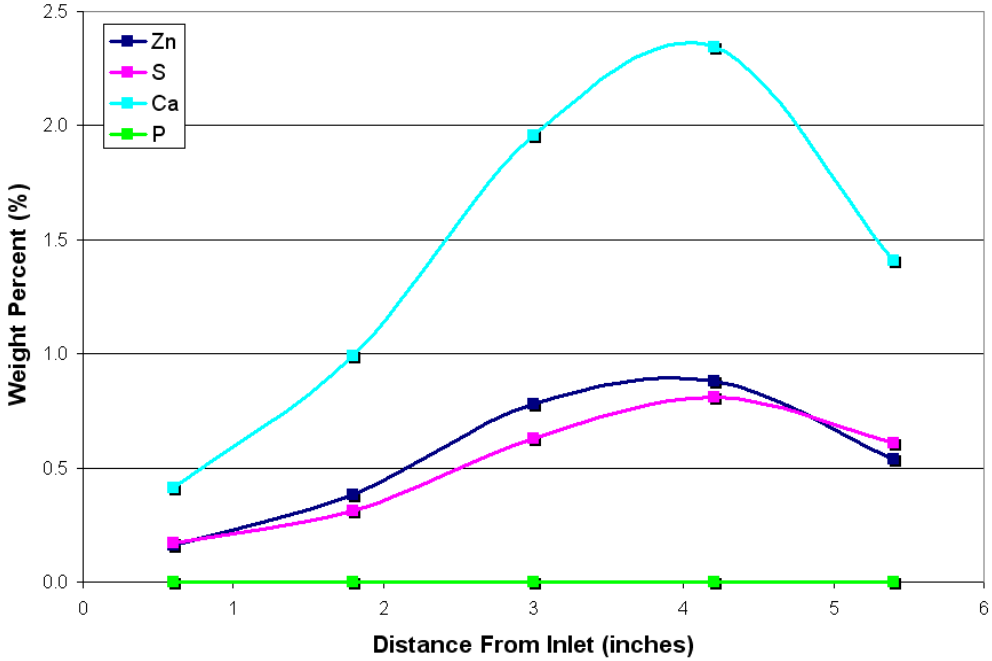
Characterization - ICP

- **Ash recovery is calculated by quantifying the presence of calcium, zinc, phosphorus and sulfur in the fuel, lube-oil and ash-loaded substrate**
- **Recovery efficiencies as high as 91% were calculated for calcium**
- **Lengthwise distribution can be analyzed by cutting the sample into sections for individual analysis**
- **Additional analysis revealed the presence of iron in the ash, accounting for up to 5% of the DPF mass increase**

		Test 3 - Cordierite (Low PGM)				Test 4 - SiC (No PGM)				Test 5 - Mullite (High PGM)			
		Zn	S	Ca	P	Zn	S	Ca	P	Zn	S	Ca	P
Average Concentration	wt %	0.548	0.506	1.424	0.000	0.279	0.183	0.601	0.115	0.449	0.270	0.712	0.125
Mass in DPF	g	2.290	2.114	5.948	0.000	1.349	0.888	2.908	0.558	1.894	1.139	3.002	0.527
Concentration in Oil	wt%	0.129	0.749	0.351	0.119	0.124	0.380	0.231	0.110	0.124	0.380	0.231	0.110
Mass in Oil	g	3.424	19.898	9.335	3.174	3.296	10.103	6.143	2.932	3.296	10.103	6.143	2.932
Recovery	%	66.88%	10.62%	63.72%	0.00%	40.94%	8.79%	47.34%	19.04%	57.46%	11.27%	48.87%	17.97%
Concentration in Fuel + Oil	wt%	0.005	0.029	0.013	0.004	0.006	0.032	0.011	0.006	0.006	0.032	0.011	0.006
Mass in fuel	g	2.504	14.924	6.721	2.249	3.066	16.457	5.571	2.964	3.066	16.457	5.571	2.964
Recovery	%	91.42%	14.17%	88.50%	0.00%	44.01%	5.39%	52.20%	18.83%	61.76%	6.92%	53.89%	17.77%

Characterization - ICP

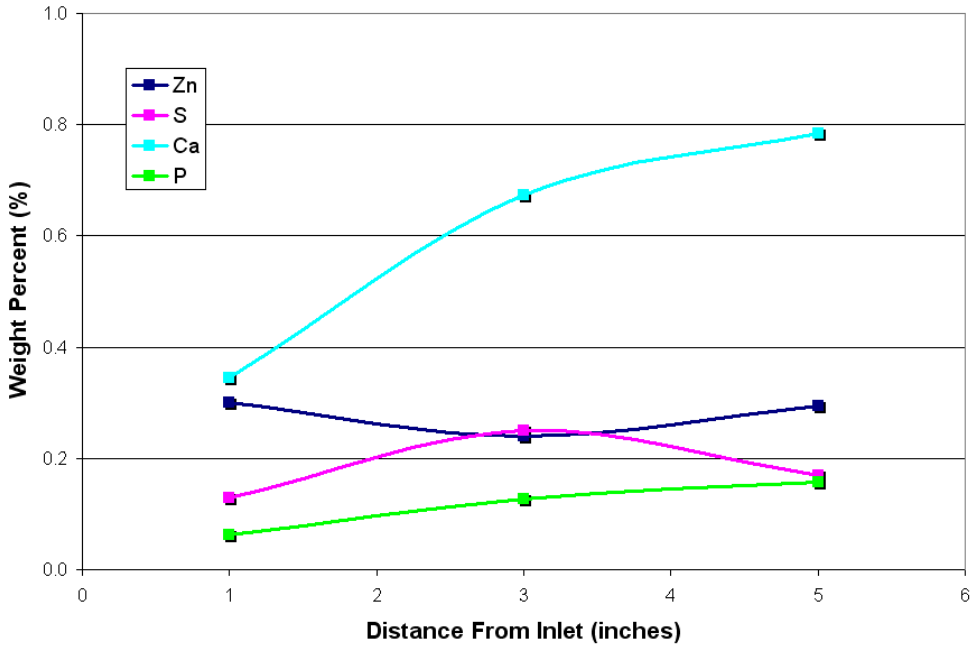
- **Test 3: Cordierite (low PGM)**
  - **Mass of ash increases along the length of the DPF**
  - **Greatest concentrations observed 4” from inlet**
  - **Concentrations in rear decrease due to ash plugging and the presence of cordierite channel plugs**
  - **Presence of phosphorus is negligible**
  - **Highest ash recovery (~90%)**



ICP Results for lightly-catalyzed cordierite DPF

Characterization - ICP

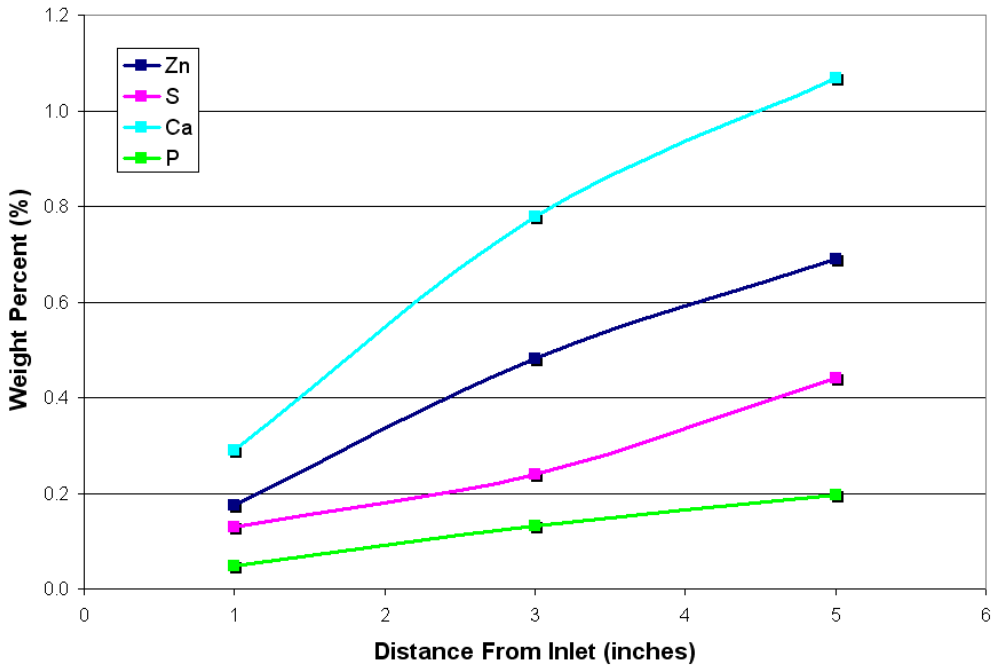
- **Test 4: SiC (no PGM)**
  - **Calcium concentrations increase along the length of the channel**
  - **Phosphorus presence is no longer negligible**
  - **Zinc, calcium and phosphorus appear fairly evenly distributed**
  - **Ash recovery based on these constituents is fairly low (52%)**



ICP Results for non-catalyzed SiC DPF

Characterization - ICP

- **Test 5: Mullite (high PGM)**
  - **Concentration of all four constituents increase along the length of the channels**
  - **Ash recovery based on these constituents slightly higher than that calculated for SiC (~61%)**



ICP Results for highly-catalyzed mullite DPF

Characterization - XRD

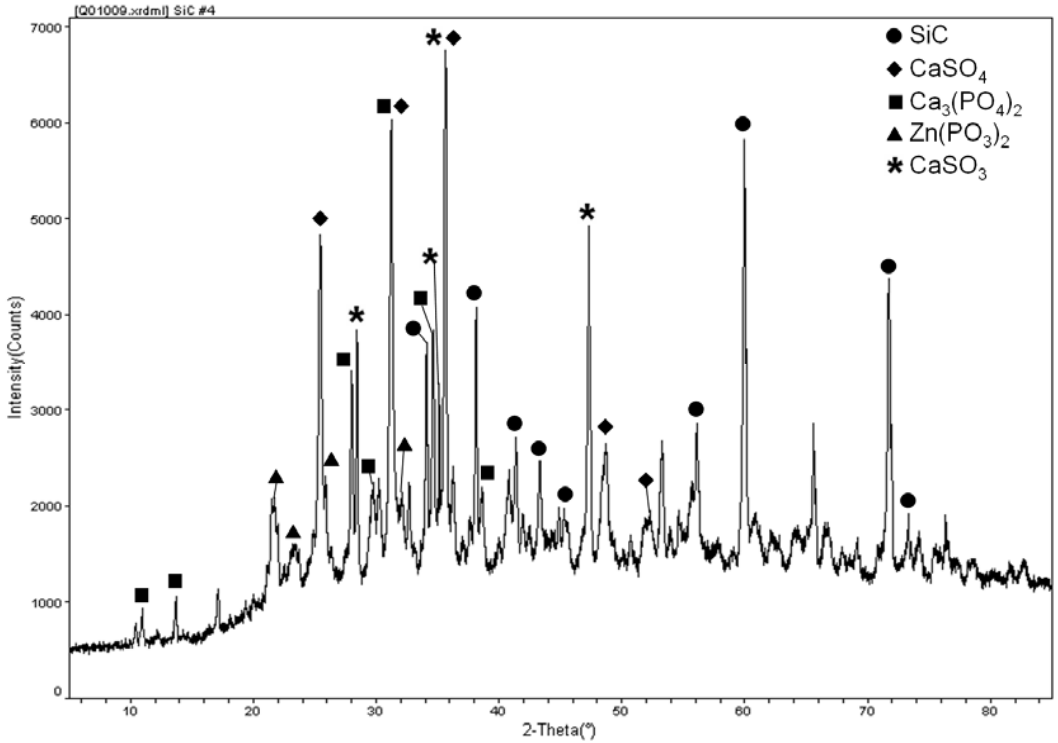
- **Ca, Zn, S and P regarded as primary ash constituents**
- **Compounds identified:**
  - **$CaSO_4$**
    - **Most prevalent in literature (~75%)**
  - **$Ca_3(PO_4)_2$**
  - **$Zn(PO_3)_2$**
    - **Second-most prevalent in literature (~15%)**
  - **ZnO and CaO**
    - **Present in some form in addition to other compounds not easily identifiable**
  - **$CaSO_3$**
    - **Difficult to discern presence as some peaks are masked by other compounds**

Characterization - XRD

- **XRD (X-Ray Diffraction) used to identify compounds in ash**
  - **Ca, Zn, S and P regarded as primary ash constituents**
  - **Compounds identified:**
    - **$CaSO_4$**
      - **Most prevalent in literature (~75%)**
    - **$Ca_3(PO_4)_2$**
    - **$Zn(PO_3)_2$**
      - **Second-most prevalent in literature (~15%)**
    - **ZnO and CaO**
      - **Present in some form in addition to other compounds not easily identifiable**
    - **$CaSO_3$**
      - **Difficult to discern presence as some peaks are masked by other compounds**

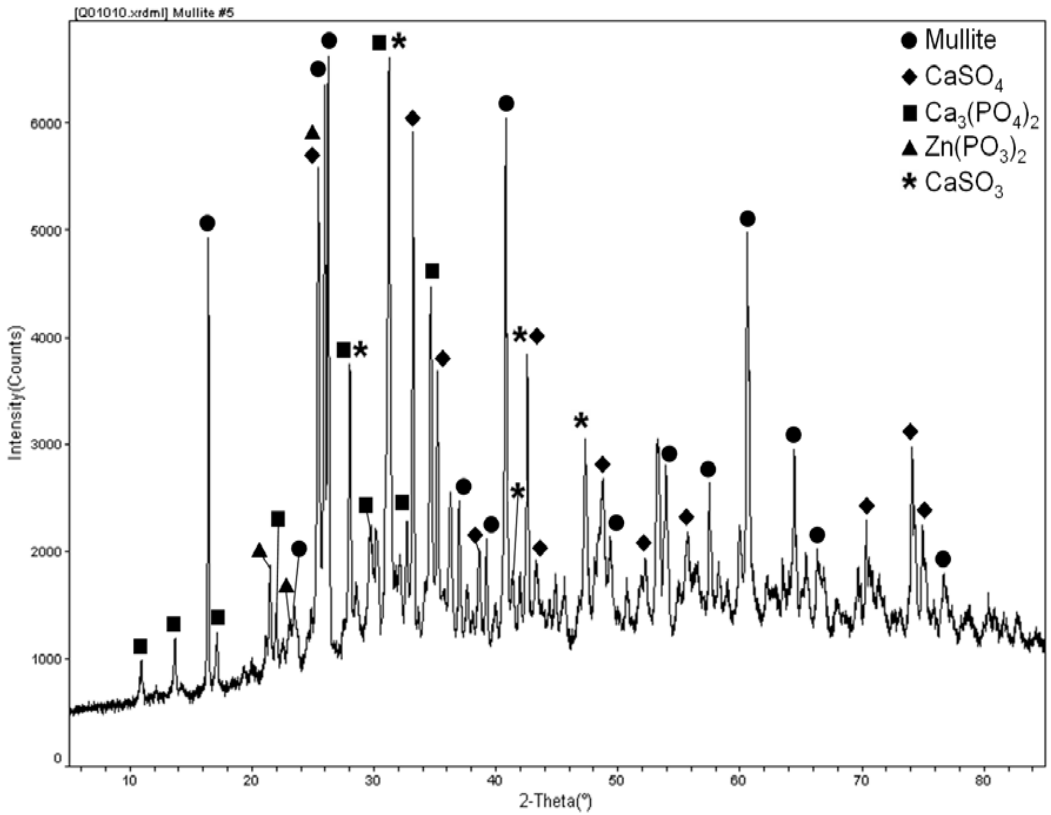
Characterization - XRD

- **Test 4: SiC (no PGM)**
  - **SiC and $CaSO_4$ responsible for the largest peaks**
  - **Remaining elements are likely present, but difficult to identify due to peak overlap**



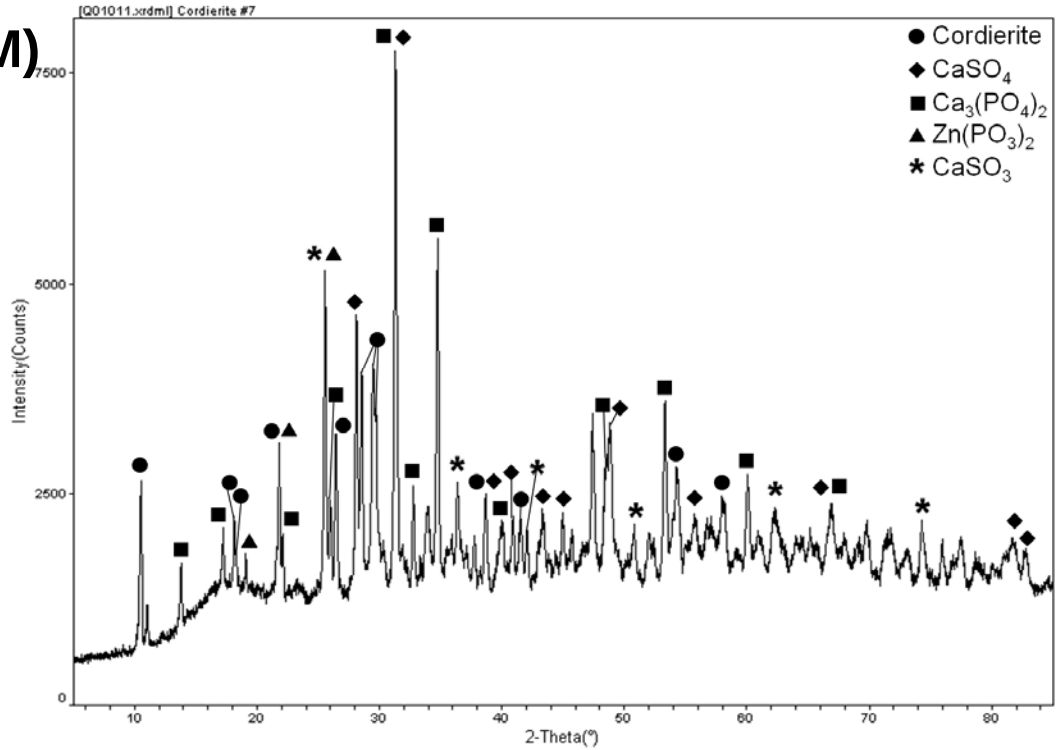
Characterization - XRD

- **Test 5: Mullite (high PGM)**
  - **Mullite and $CaSO_4$ are again readily identified**
  - **$Ca_3(PO_4)_2$ is also identified as a strong candidate**
  - **It is again difficult to confirm the presence of the remaining elements**



Characterization - XRD

- **Test 7: Cordierite (high PGM)**
  - **Cordierite and $CaSO_4$ are the only compounds identified with any certainty**
  - **There are fewer pronounced peaks**
    - **Analysis of the numerous smaller peaks further complicates identification**



Summary of Accelerated DPF Ash Loading

- **Ash loading protocol developed to deposit ash gradient along channel**
  - **Similar to the gradient observe in unaccelerated tests**
- **Backpressure increases with all substrates**
  - **SiC and Cordierite show same rate of increase**
  - **Mullite shows smaller rate of increase**
- **Active regeneration light-off temperature increases with ash loading**
  - **No trend apparent based on substrate material**
  - **PGM does not appear to assist active soot regeneration when significant ash is present**

Application of what we have learned to evaluation of useful life

- **Start from field samples and application data**
- **Evaluate performance in test cell**
- **Cut sections from catalysts**
  - **Cores for bench reactor evaluation**
  - **Materials characterization**
  - **Micro reactor evaluation**
- **Correlate materials changes to application data**
- **Project performance to full useful life**
- **Model rates of change to provide input for vehicle or system models and to help understand and define phenomena**