SLOAN AUTOMOTIVE LABORATORY

Fundamental Processes Controlling Ash Accumulation in Diesel Particulate Filters and Impacts on DPF Performance

2012 DOE Crosscut Workshop

on Lean Emissions Reduction Simulation

May 2, 2012

Alexander Sappok

V. Wong, C. Kamp, S. Munnis, I. Dimou, C. Chiou, Y. Wang, I Govani, M. Bahr, E. Cross, J. Kroll

Massachusetts Institute of Technology

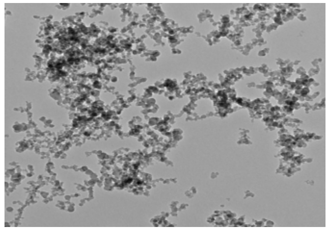
Sloan Automotive Laboratory

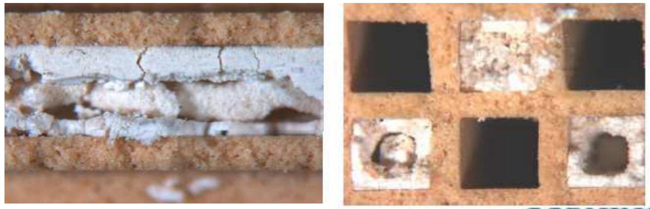
Cambridge, MA

Ash Accumulation Reduces DPF Life and Engine Efficiency

SLOAN AUTOMOTIVE LABORATORY

Lube/ Fuel → Engine-Out Emissions → DPF Ash Accumulation → DPF ΔP Catalyst → Efficiency & DPF Life





Source: K. Aravelli

More Ash than Soot in DPF!

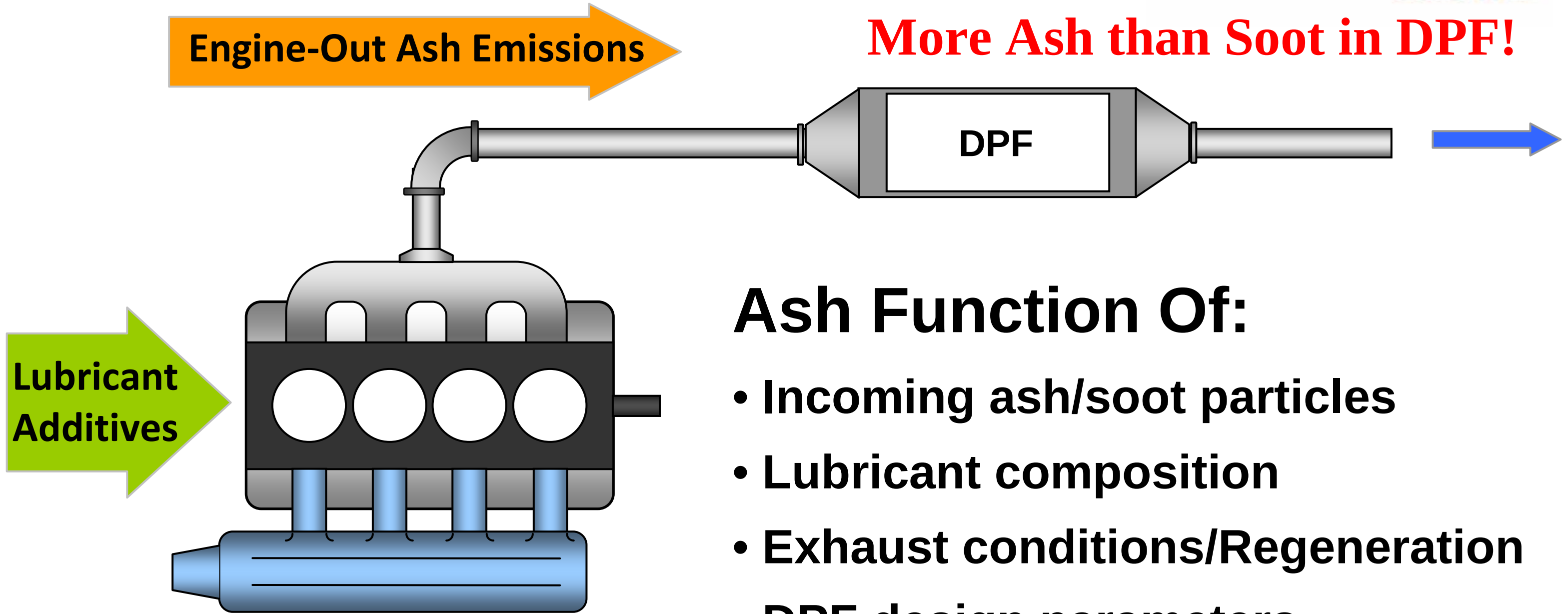
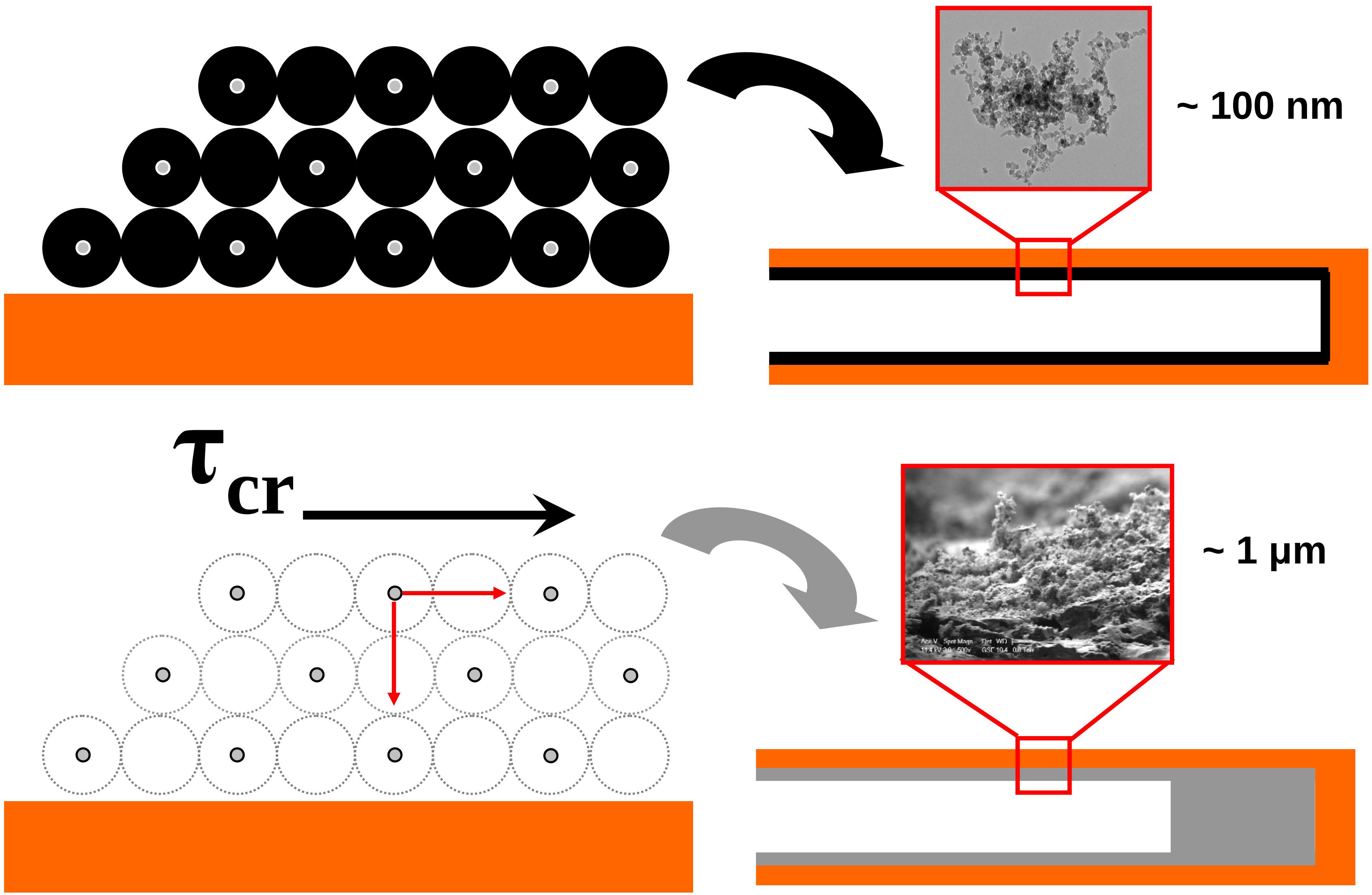


Image: Adapted from ORNL

Ash Function Of:

- Incoming ash/soot particles
- Lubricant composition
- Exhaust conditions/Regeneration
- DPF design parameters
- DPF operating history

Ash Accumulation and Deposit Formation Differs from PM!



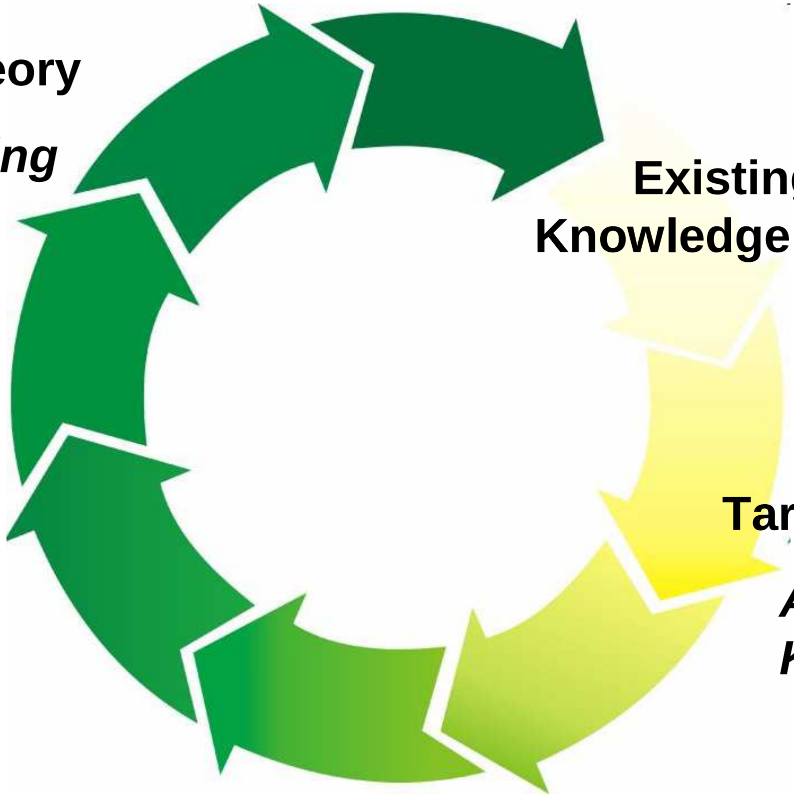
Program Approach & Consortium Activities

SLOAN AUTOMOTIVE LABORATORY

"Holistic approach considering lubricant chemistry, engine operation, and aftertreatment design through combination of focused experiments and theoretical models."

Models and Theory

Build on Existing Framework



Existing Knowledge Base

Targeted Experiments

Address Specific Knowledge Gaps

Ash Properties Analysis

Lab <u>and</u> Field

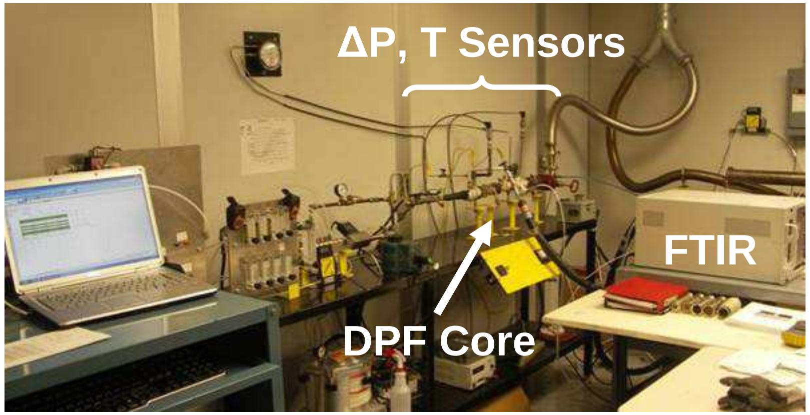
Enhance fundamental understanding of key parameters controlling ash properties and impact on aftertreatment performance.

Experimental Facilities

Cummins ISB 300

- Variable geometry turbocharger
- Cooled EGR
- Common rail fuel injection
- Fully electronically controlled
- Gaseous and PM emissions measurement systems

DPF Bench Reactors

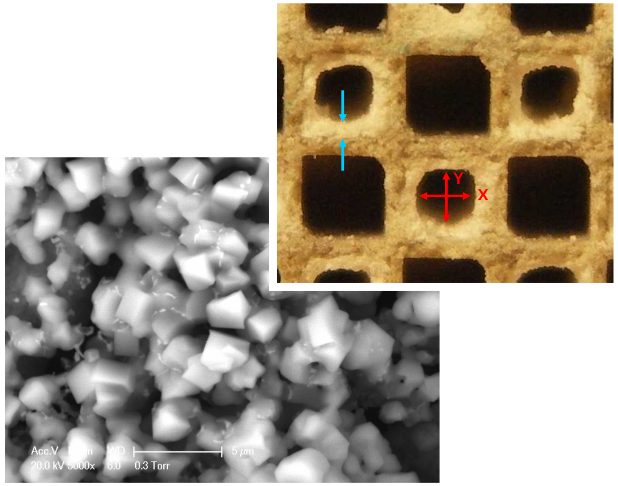


Accelerated Ash Loading

Analytical Test Facilities

Center for Materials Science (CMSE)

- **Materials Analysis**
  - FTIR, Raman, XPS, Optical Microscopes
- **Thermal Analysis**
  - TGA, ICP-OES
- **Electron Microscopy**
  - SEM – EDX, TEM, FIB
- **X-Ray Diffraction**



Ash Exposed to Elevated Temperatures

Extensive and increasing use as part of DPF post-mortem analysis and ash characterization

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash Accumulation

- *Substrate materials, pore size & distribution, porosity*

Role of Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

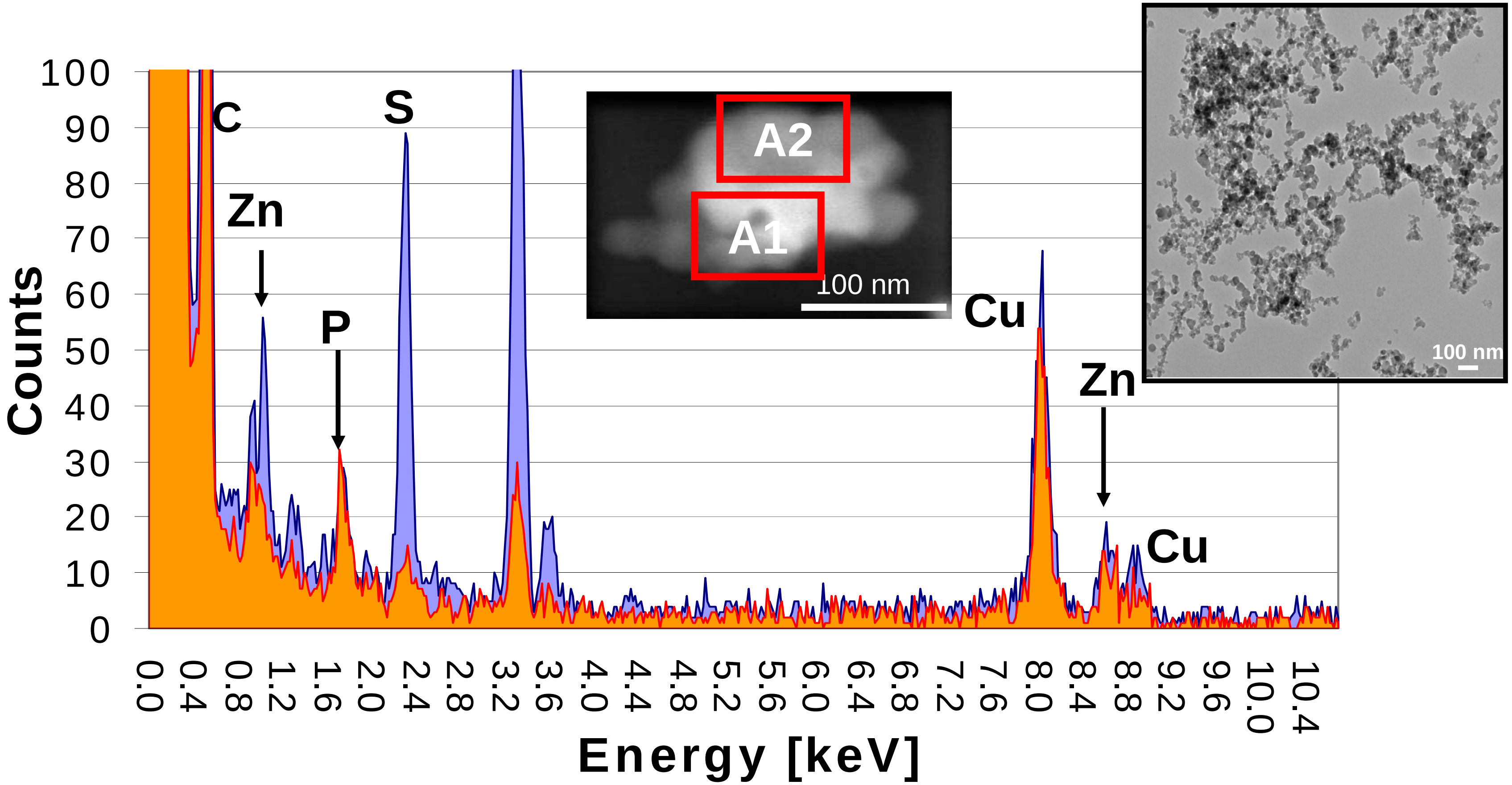
Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

Lubricant-Derived Ash Precursors Bound to PM

SLOAN AUTOMOTIVE LABORATORY

SAE 2007-01-0318

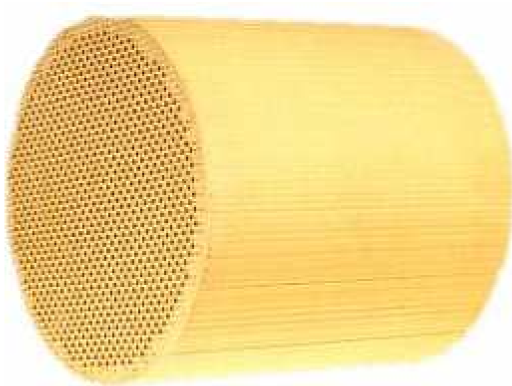


- **Lubricant-derived ash transported to DPF bound to carbonaceous PM**
  - Size of ash precursors of same order or smaller than PM agglomerates
  - No lubricant-derived ash particles found separate from PM
  - Cu peaks due to background from copper TEM grid

Nearly All Metallic Ash Components Trapped in DPF

SLOAN AUTOMOTIVE LABORATORY

1682 rpm, 25% load
(Steady-State)



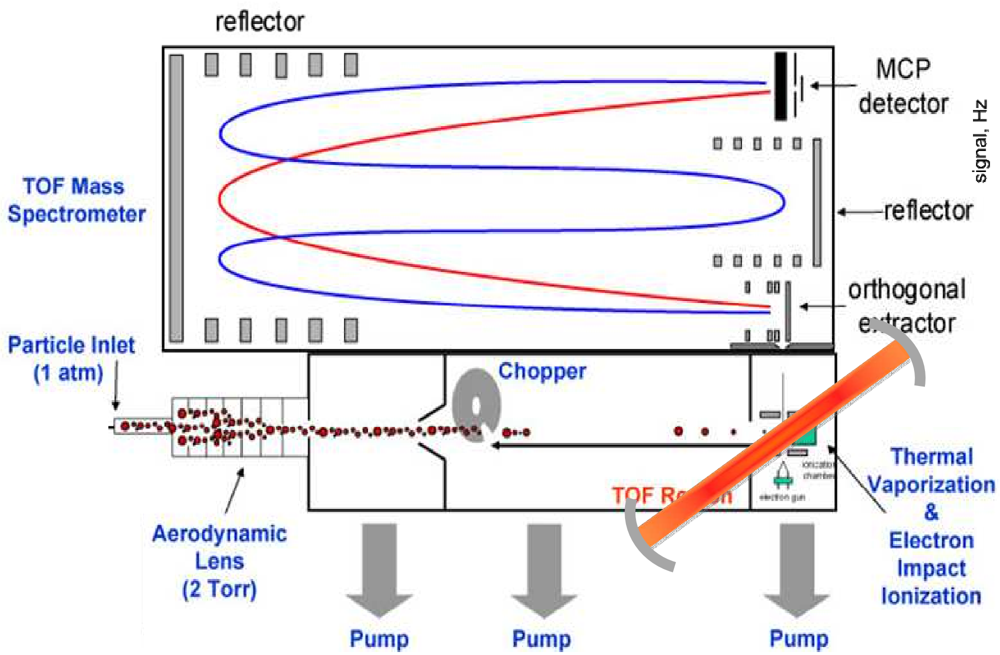
Measured elemental trapping efficiency in DPF

	Ca	Fe	Mg	P	S	Zn
Trapping Efficiency	99.87%	92.43%	98.01%	85.09%	64.89%	99.67%

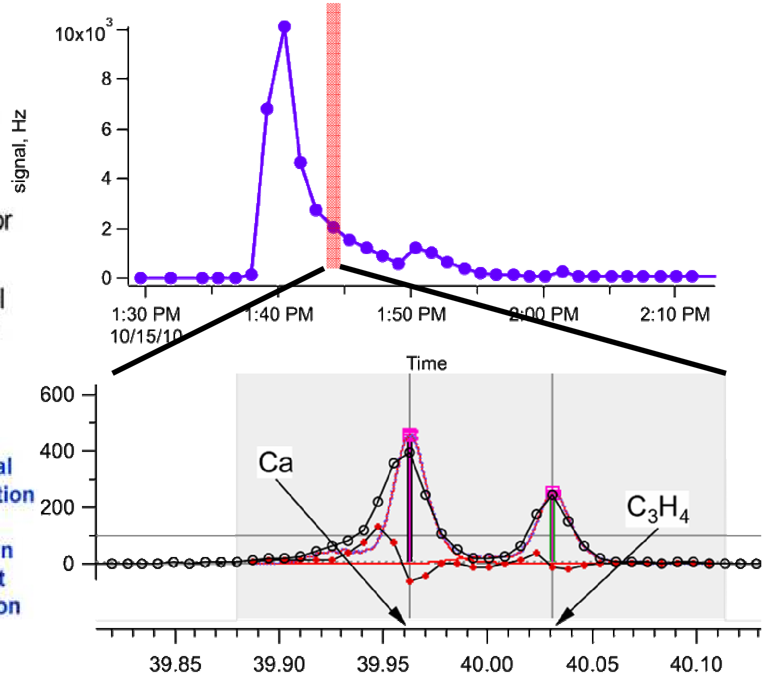
- **Elemental emission rates determined from ICP analysis**
- **Post-DPF PM sampling 20 hours for sample size of 2-3 mg**

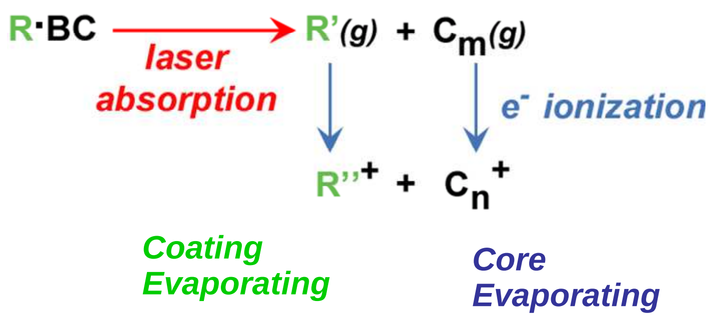
Particle Mass Spectrometer for Ash Measurements

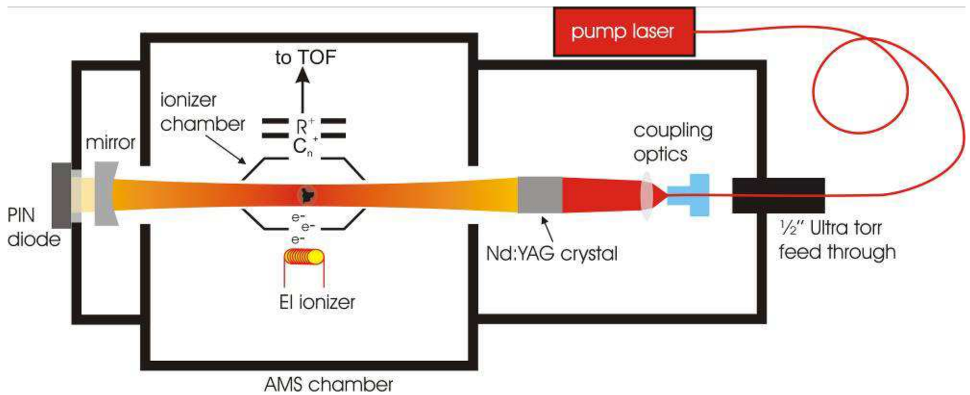
ASME ICEF2011-60100



Time-Resolved Mass-Spec



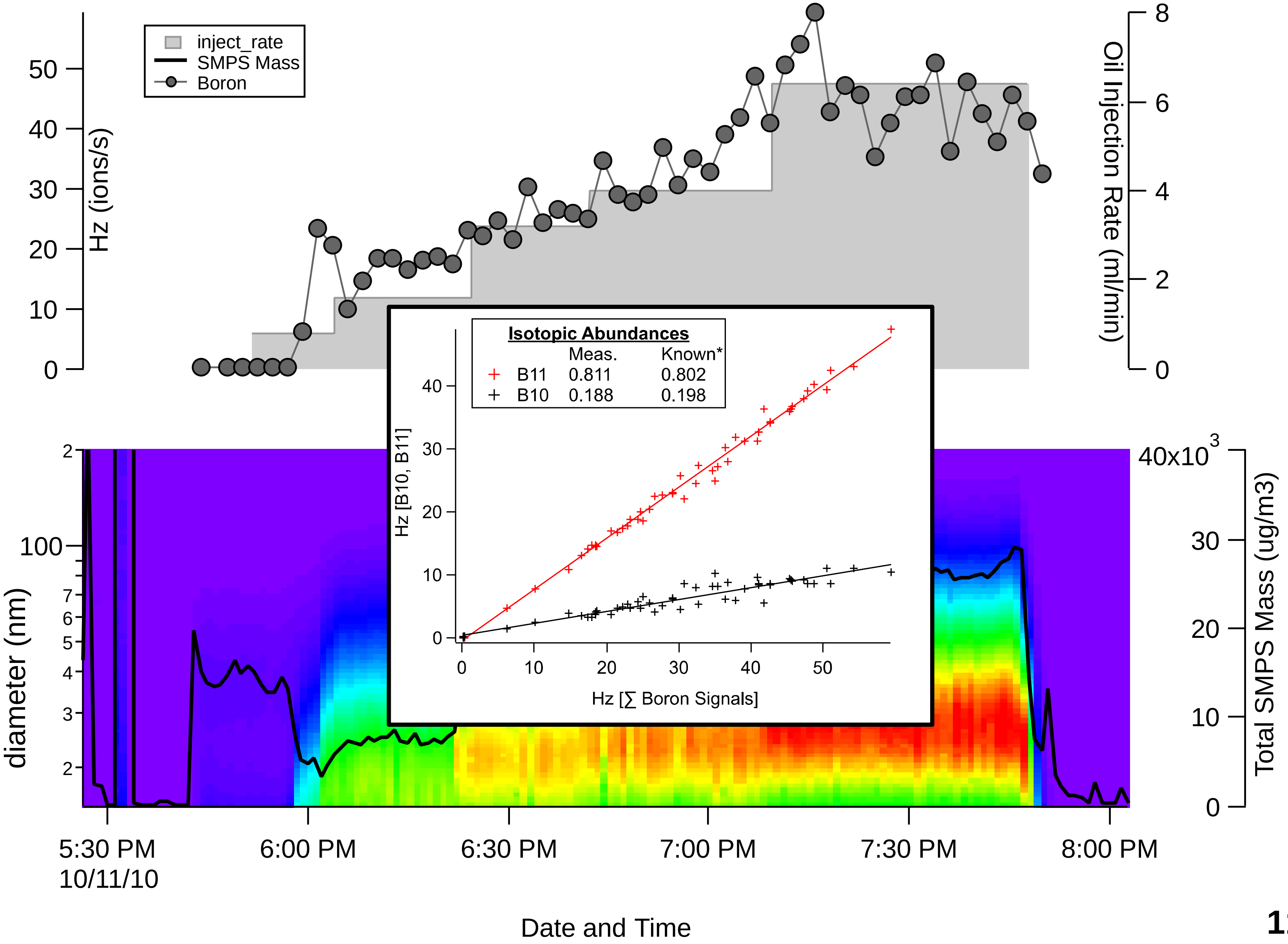




Real-Time Measurement of Exhaust Ash Emissions (I)

SLOAN AUTOMOTIVE LABORATORY

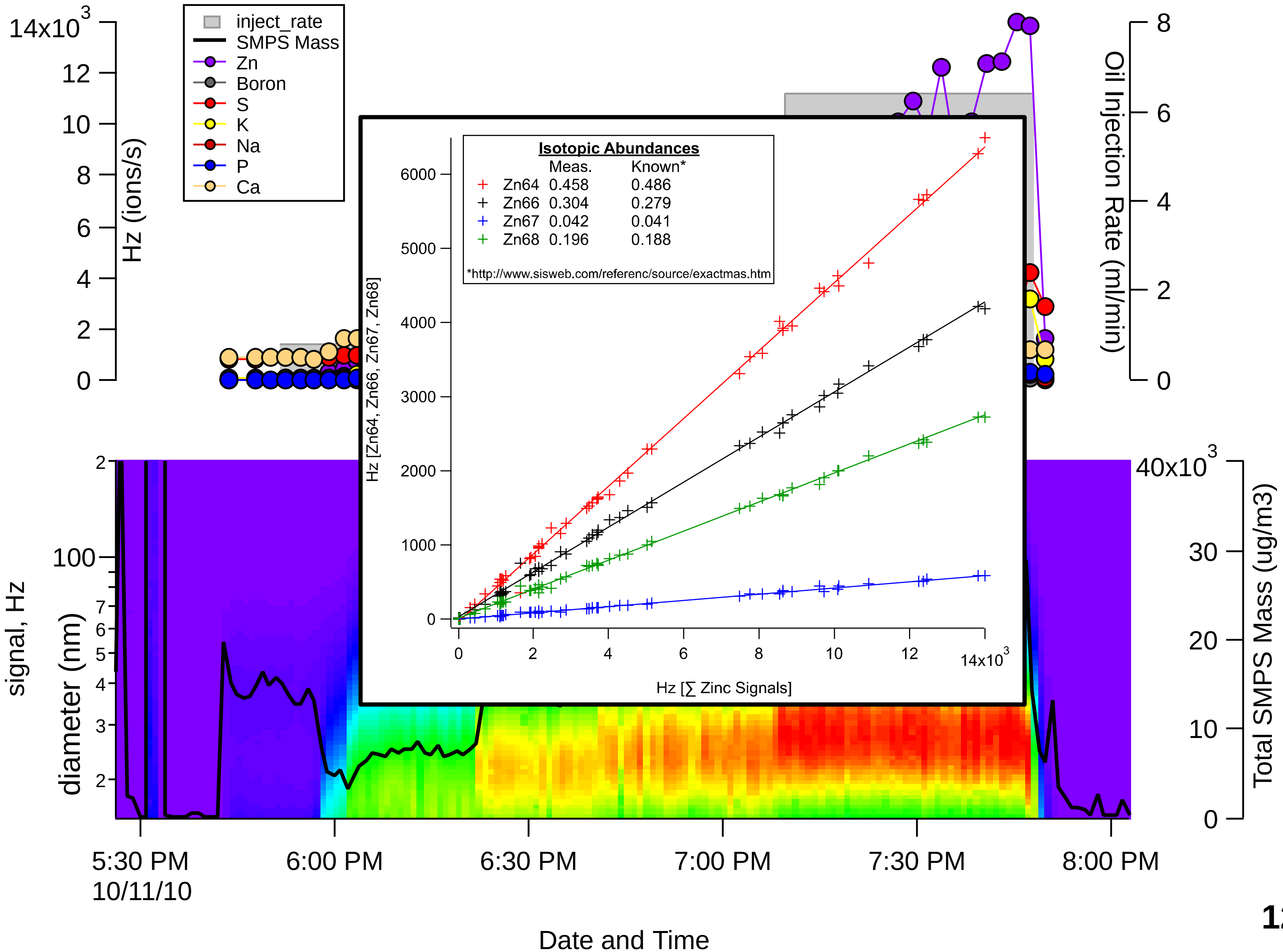
ASME ICEF2011-60100



Real-Time Measurement of Exhaust Ash Emissions (II)

SLOAN AUTOMOTIVE LABORATORY

ASME ICEF2011-60100



Key Parameters Controlling Ash Deposits and DPF Impacts

SLOAN AUTOMOTIVE LABORATORY

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash Accumulation

- *Substrate materials, pore size & distribution, porosity*

Role of Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

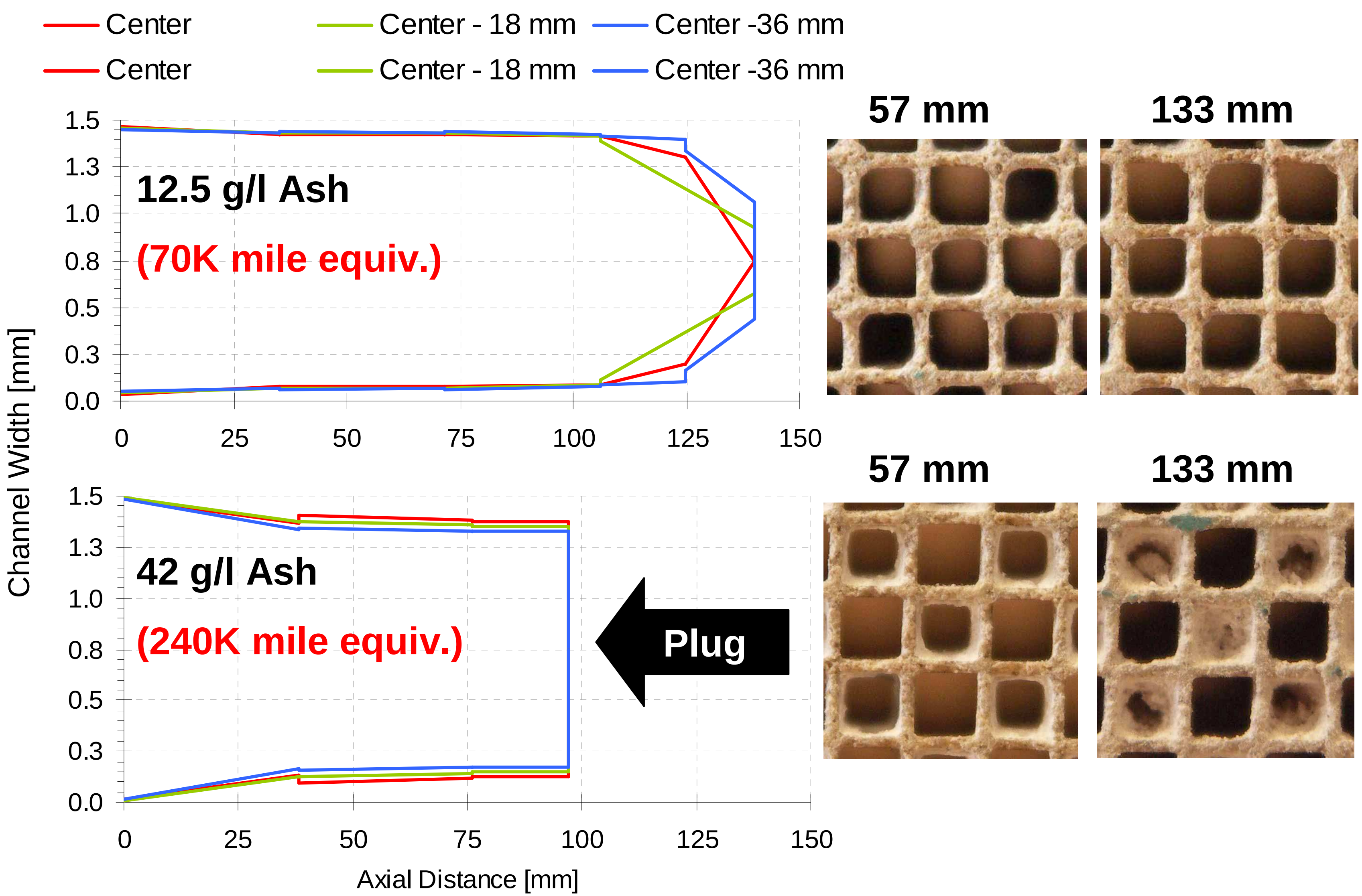
Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

Ash First Accumulates Along DPF Channel Walls

SLOAN AUTOMOTIVE LABORATORY

ASME ICEF2009-14080

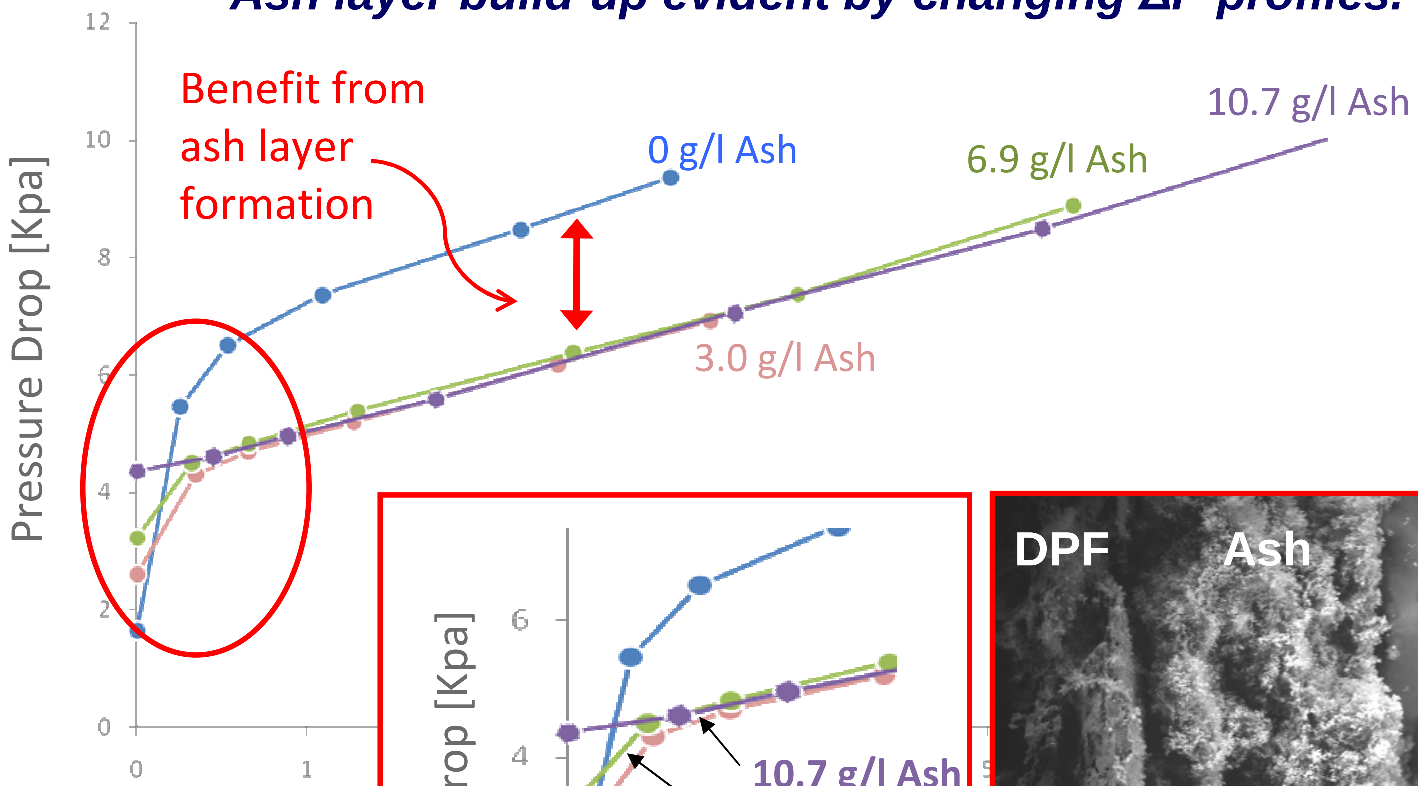


- **Ash accumulation reduces DPF volume and affects pressure drop**

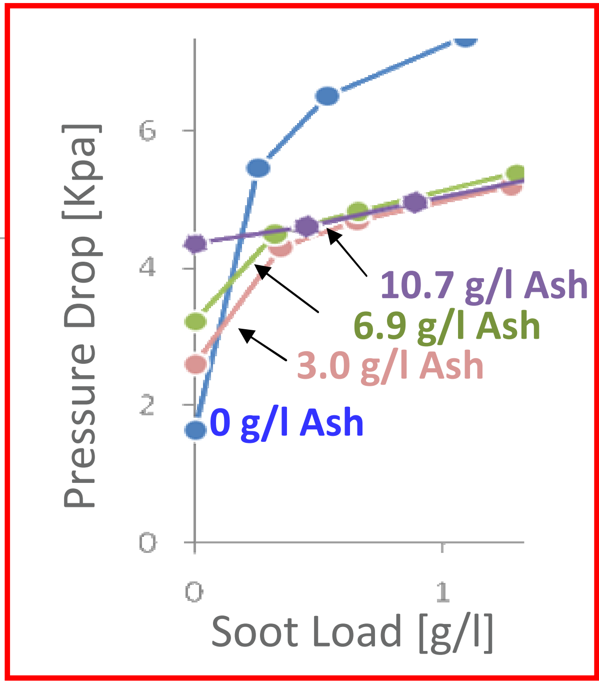
Initial Ash Deposition and Layer Formation

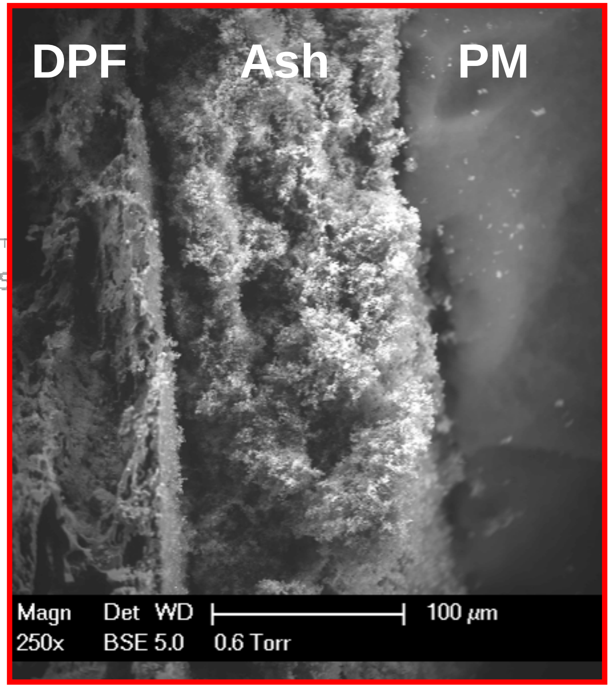
SLOAN AUTOMOTIVE LABORATORY

Ash layer build-up evident by changing ΔP profiles.



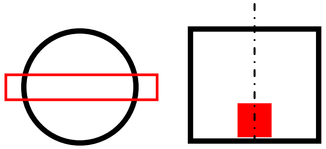
Ash layer not fully established until 10 g/L or ~ 50,000 miles

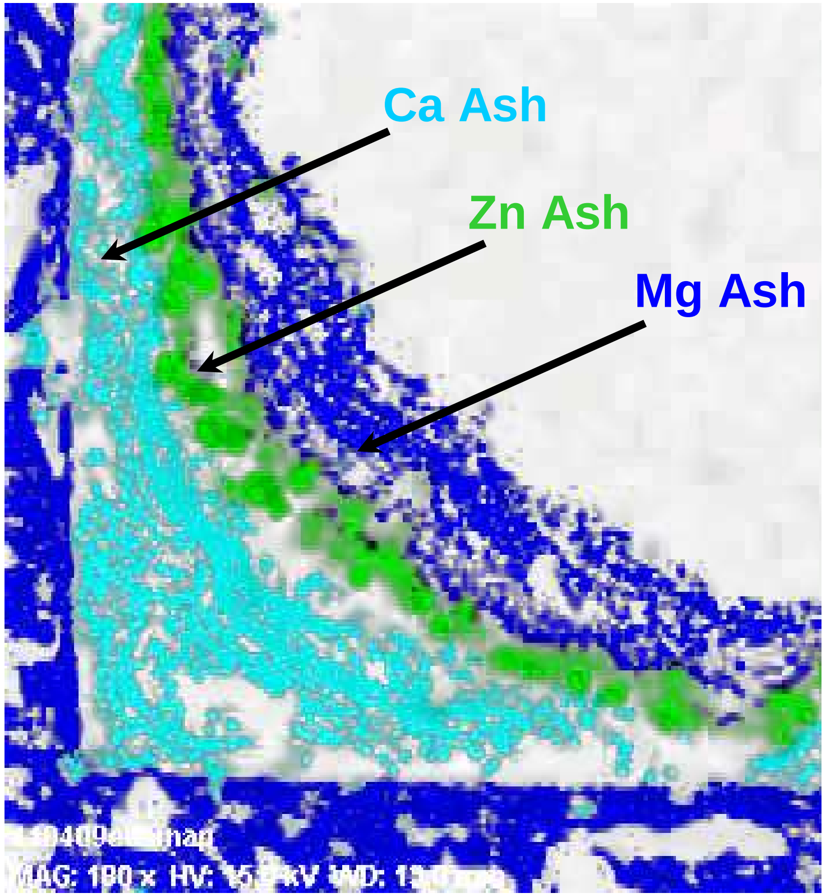




Application of Tracer Produces Stratified Ash Layers

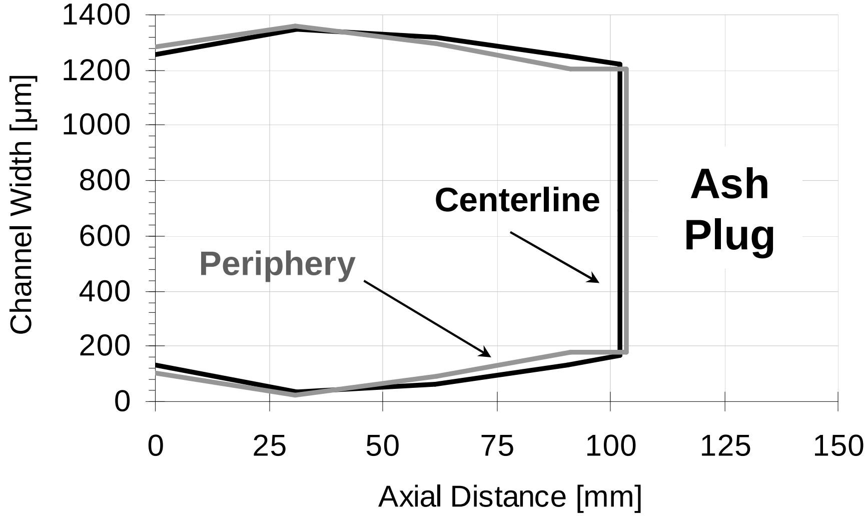
ASME ICEF2011-60072

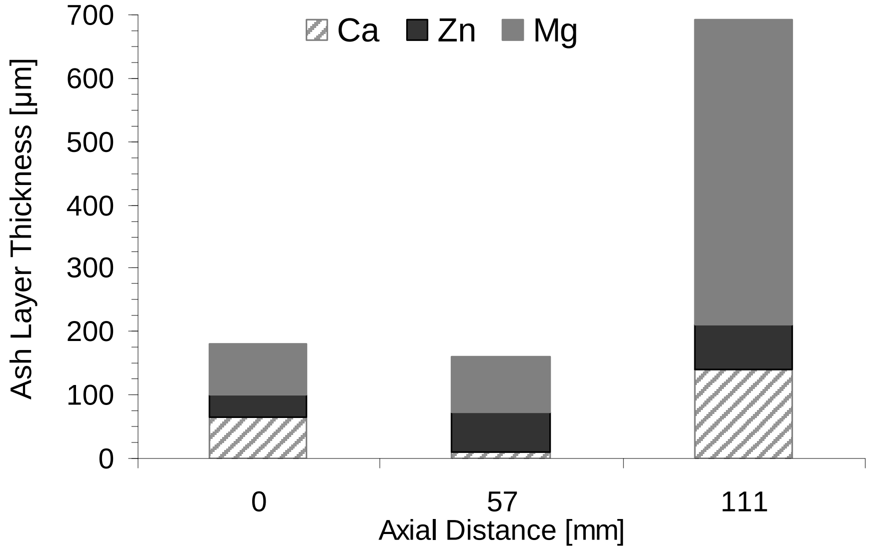




DPF Substrate

Ash Thickness and Distribution





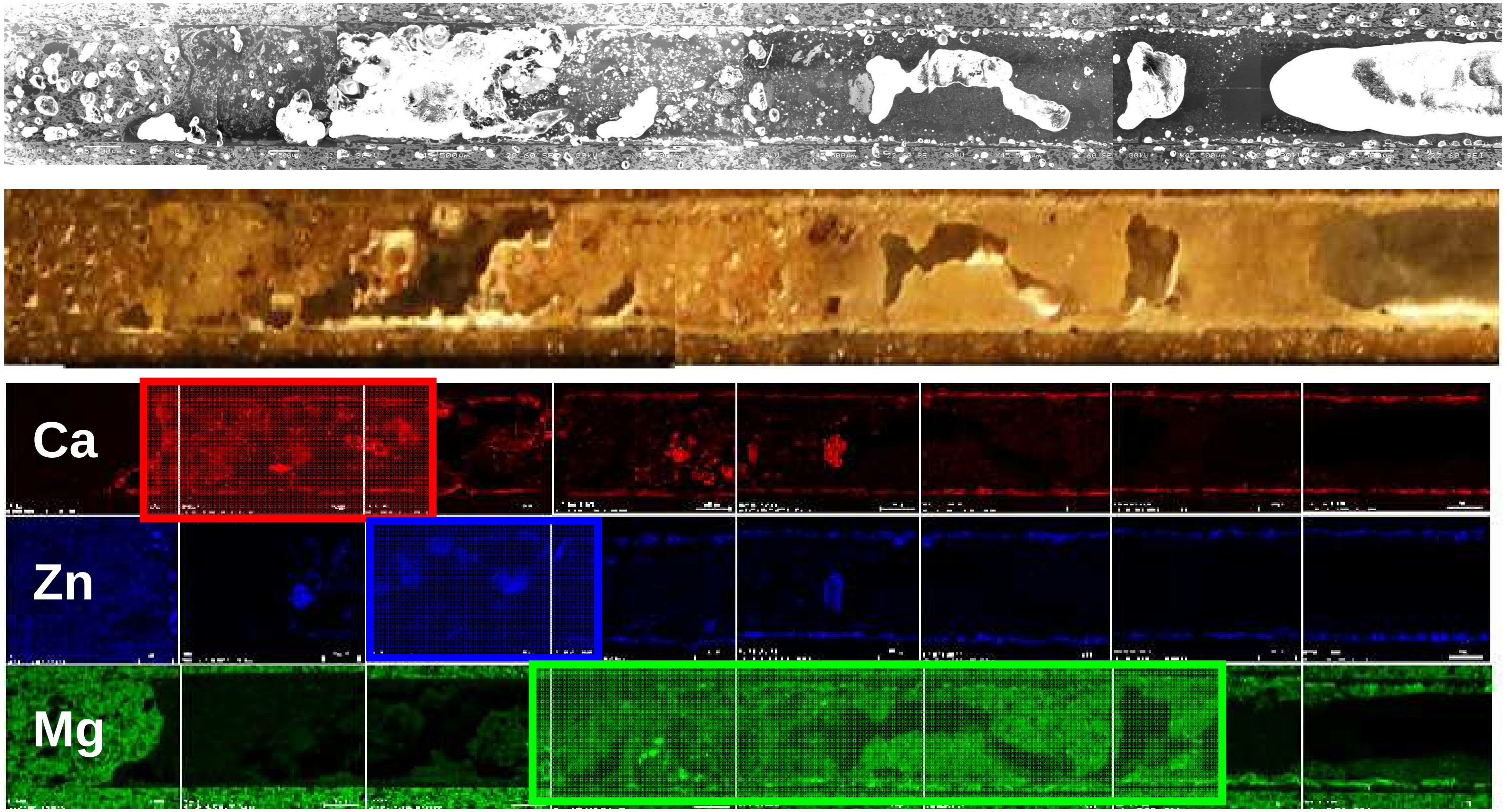
Voids in Ash Plug – Opportunities to Improve Packing

ASME ICEF2011-60072

Voids may explain low ash packing density…

Large voids throughout ash layer

Start of plug and ash layer



Key Parameters Controlling Ash Deposits and DPF Impacts

SLOAN AUTOMOTIVE LABORATORY

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash Accumulation

- *Substrate materials, pore size & distribution, porosity*

Role of Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

Additive Chemistry Impact on Ash Properties

Lubricant matrix all formulated to 1% sulfated ash, except base oil.

Lubricant	Ca *ppm*	Mg *ppm*	Zn *ppm*	P *ppm*	S *ppm*	B *ppm*	Mo *ppm*
Base	*<1*	*<1*	*<1*	*8*	*60*	*1*	*<1*
Base + Ca	2,928	5	<1	2	609	3	<1
Base + Mg*	<1	2,070	<1	<1	460		<1
Base + ZDDP	<1	<1	2612	2,530	6,901	1	<1
Base, Ca+ZDDP*	2480	<1	1280	1,180	2,750		<1
Base, Mg+ZDDP*	<1	1730	1280	1,180	2,840		<1
Commercial CJ-4	1,388	355	1,226	985	3,200*	586	77

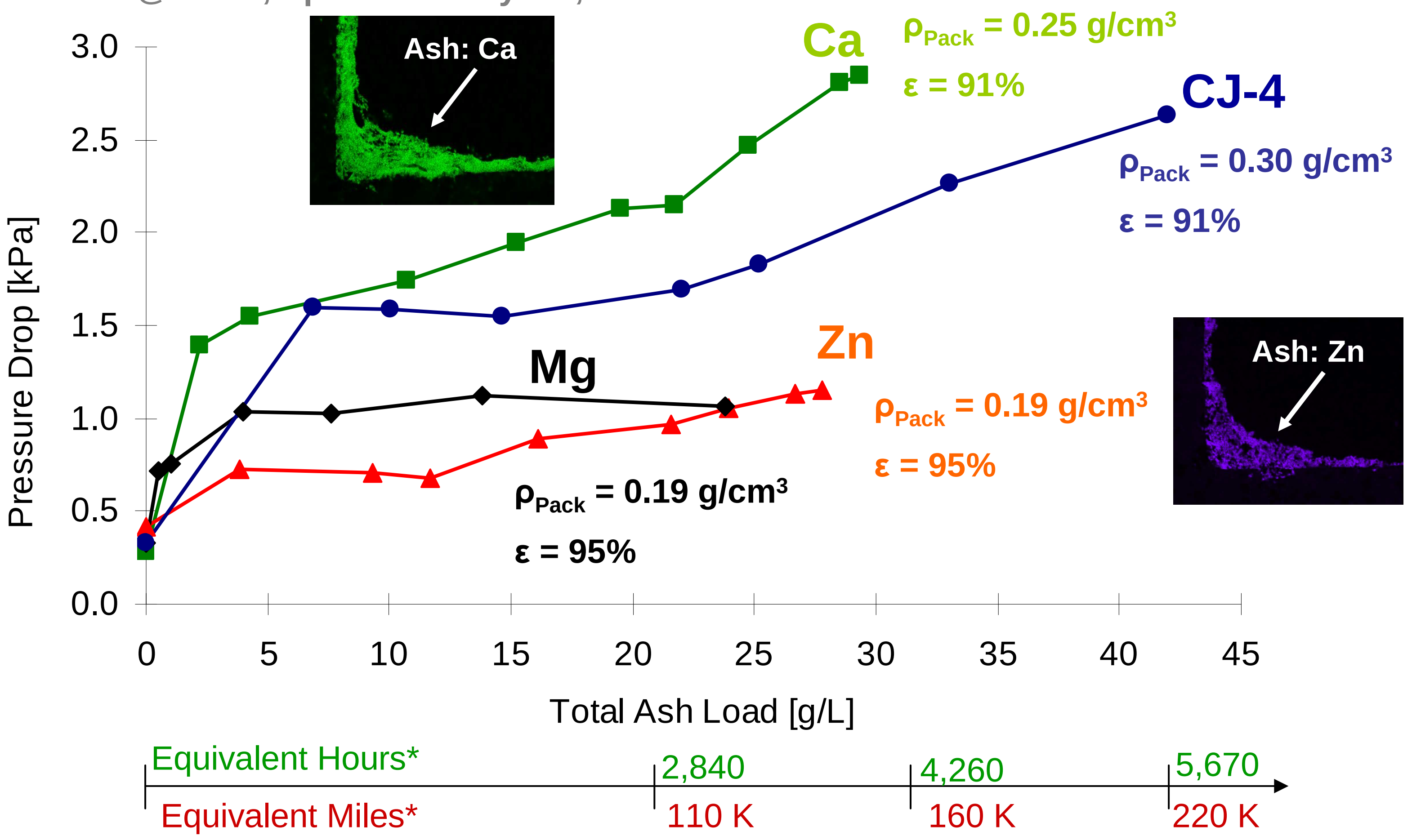
Composition of ash directly related to lubricant additive chemistry.

Major Ash Components		Density *g/cm³*	Melting Point *°C*	Description
$CaSO_4$	Calcium Sulfate	2.96	1,460	Sinters/Decomposes ~1,250 °C
$CaZn_2(PO_4)_2$	Calcium Zinc Phosphate	3.65		
$Zn_2(P_2O_7)$	Zinc Pyrophosphate	3.75		Sintering begins ~ 800 °C
$Zn_3(PO_4)_2$	Zinc Phosphate	4.00	900	Sintering begins ~ 800 °C
$Zn_2Mg(PO_4)_2$	Zinc Magnesium Phosphate	3.60		
MgO	Magnesium Oxide	3.58	2,832	
MgSO4	Magnesium Sulfate	2.66	1,124	Decompostion 900-1,100 °C

Ca Ash Shows 2X Increase in ΔP Over Zn & Mg Ash

ASME ICES2012-81237

Flow Bench @ 25 °C, Space Velocity: 20,000 hr^{-1}



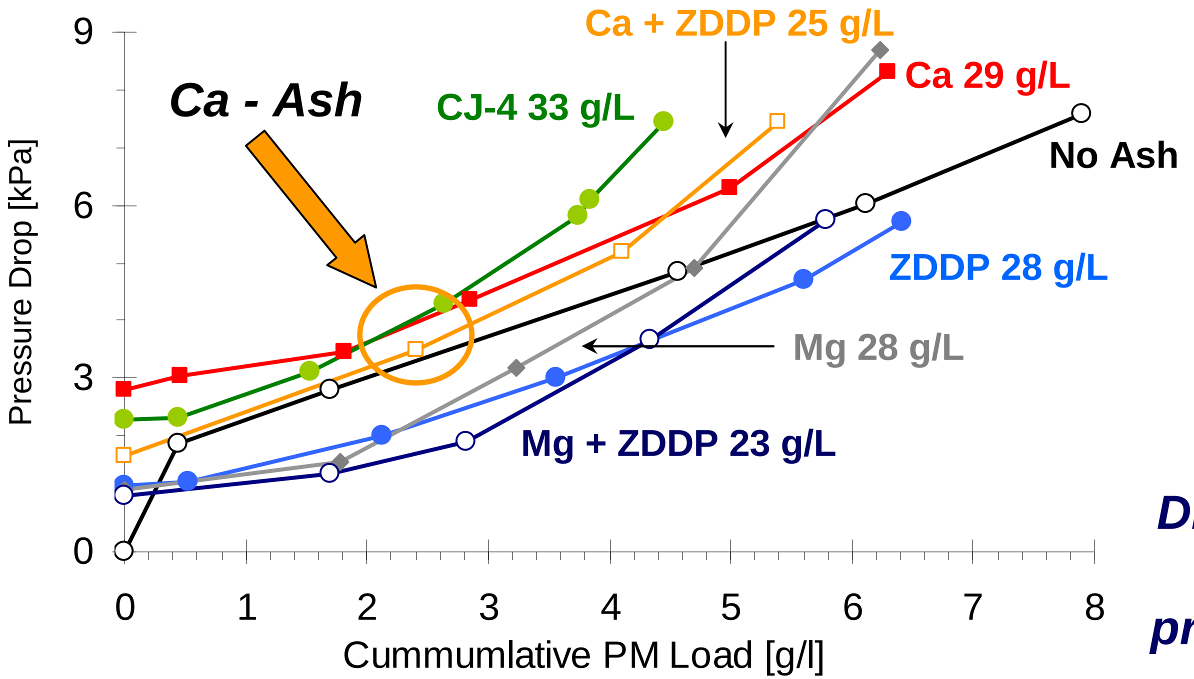
- Lubricant additive chemistry affects ash properties and pressure drop
- Ca-based ash shows much larger effect on pressure drop than Zn ash

* Assumes: 15 g/hr avg. oil consumption, avg. speed of 40 mph, and full size DPF of 12 L volume

Ash Chemistry Impacts Ash Properties and DPF ΔP

SLOAN AUTOMOTIVE LABORATORY

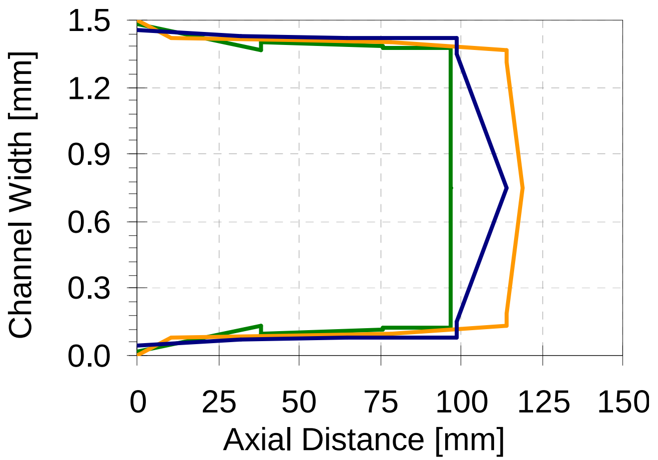
ASME ICES2012-81237

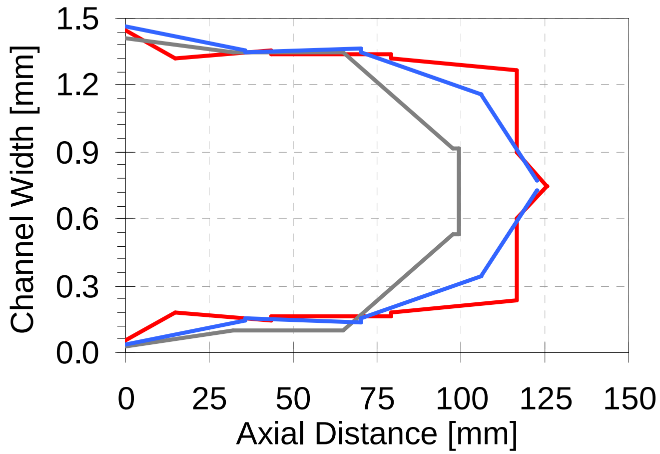


Cordierite 200/12

Differences in DPF ΔP due to ash properties (ρ, ε, D_p)

Ash Distribution Profiles





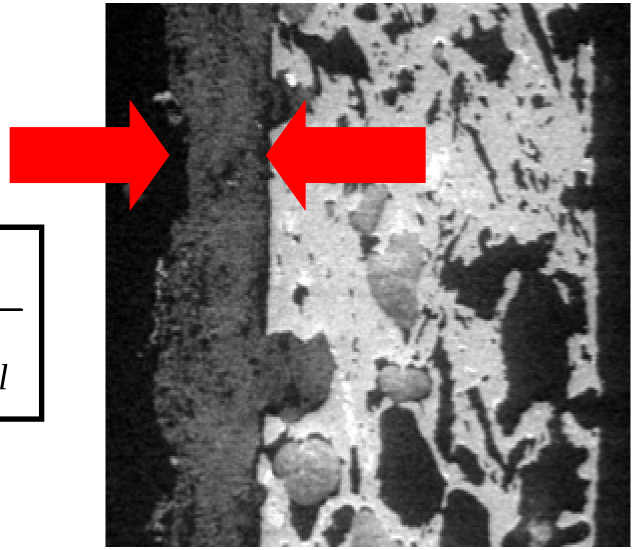
Detailed Understanding of Ash Properties Required

SLOAN AUTOMOTIVE LABORATORY

$$\Delta P_{Wall/Ash/Soot} = \left(\frac{\mu}{K_P}\right) \cdot v_w \cdot w$$

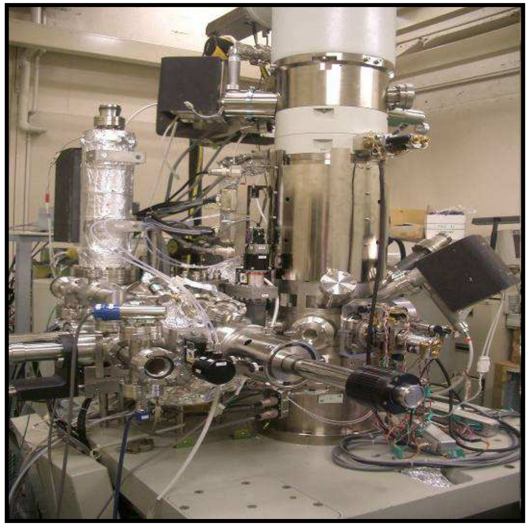
$$K = f\left(\varepsilon, \overline{D}_P\right)$$

$$\varepsilon = 1 - \frac{\rho_{Packing}}{\rho_{Theoretical}}$$



Ash Properties

- Provide critical information to explain fundamental differences in ΔP
- Complex mixture of metal oxides, sulfates, phosphates
- Characterization of particle morphology, physical, chemical properties challenge



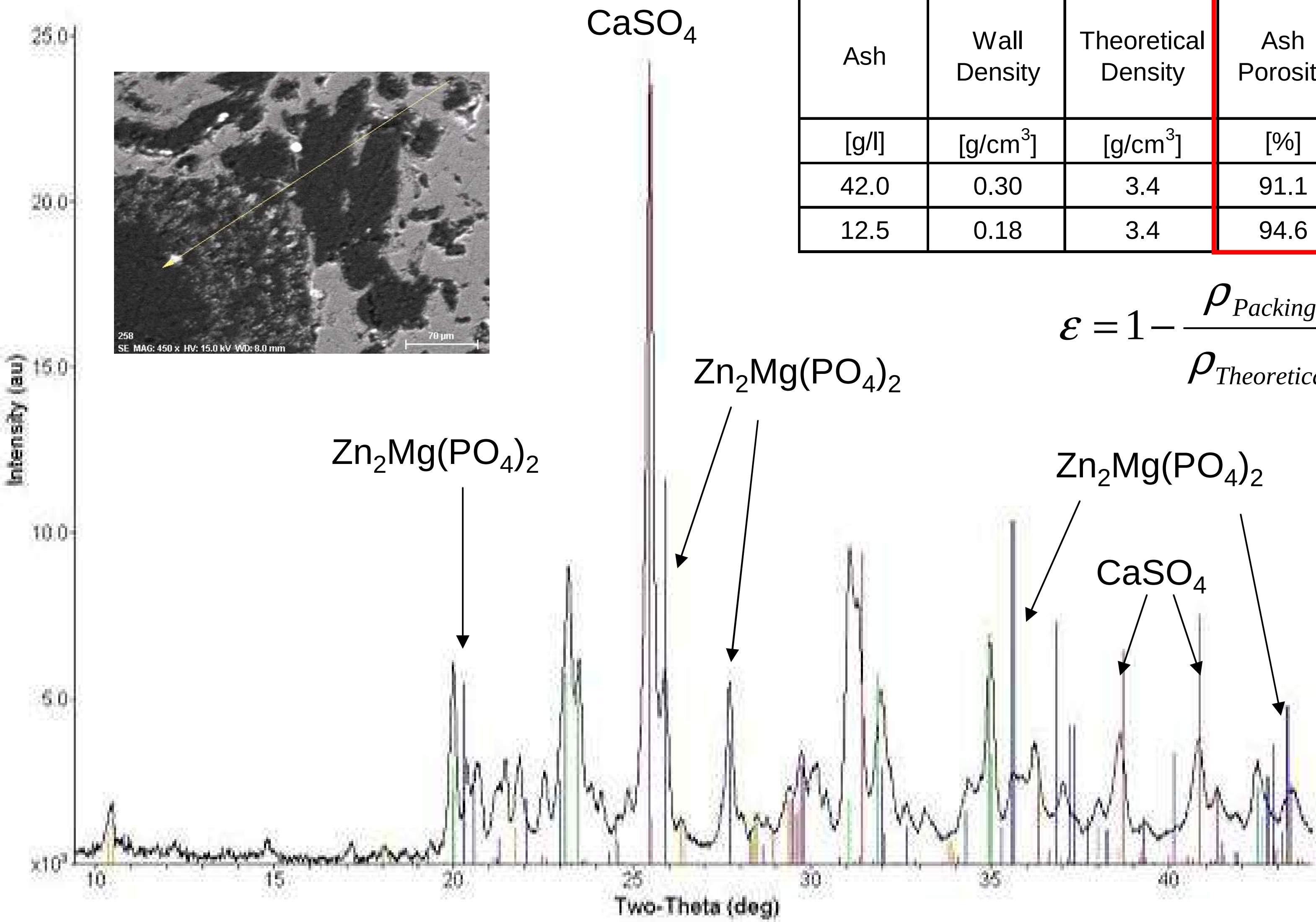
New Techniques and Diagnostics

- C. Kamp Presentation (12/2010)

CJ-4 Ash Composition and Porosity

SLOAN AUTOMOTIVE LABORATORY

SAE 2010-01-1213



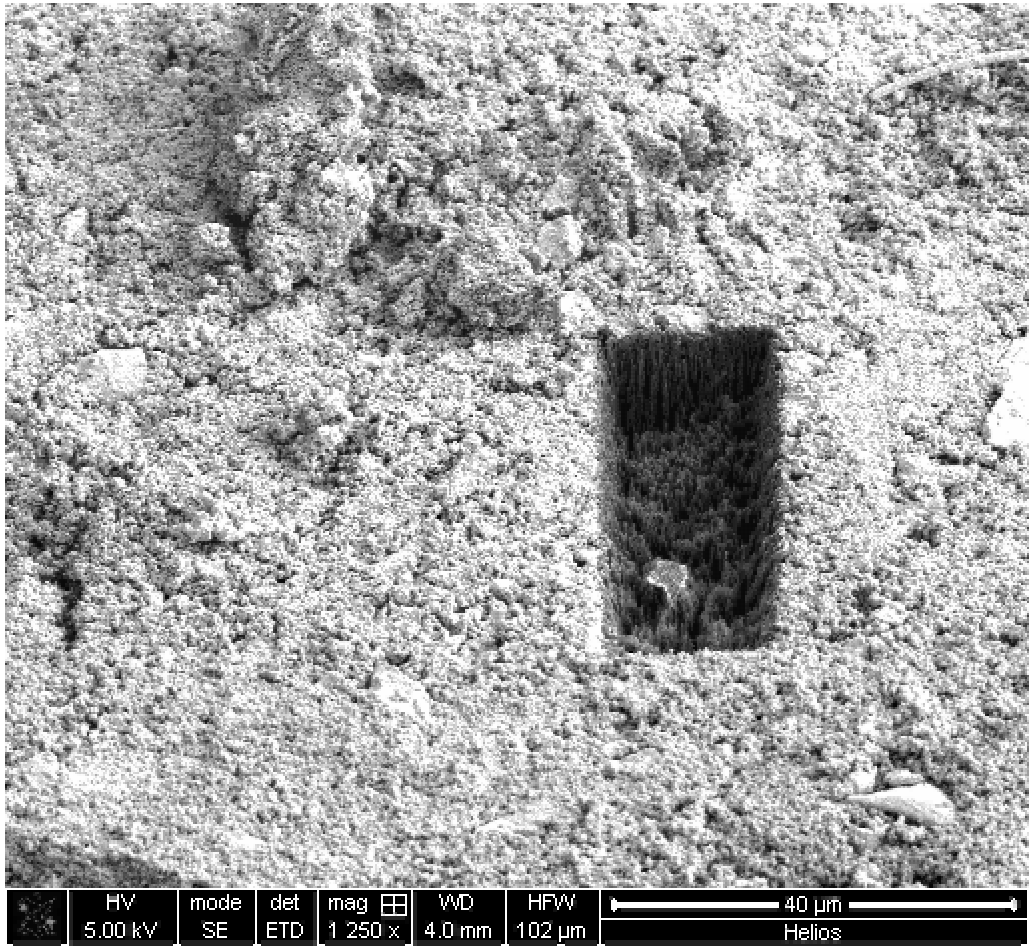
Ash	Wall Density	Theoretical Density	Ash Porosity
[g/l]	[g/cm³]	[g/cm³]	[%]
42.0	0.30	3.4	91.1
12.5	0.18	3.4	94.6

$$\varepsilon = 1 - \frac{\rho_{Packing}}{\rho_{Theoretical}}$$

Ash – PM Layer Interface Clearly Defined

SAE 2012-01-0836

Focused Ion Beam (FIB) Milling Coupled with SEM

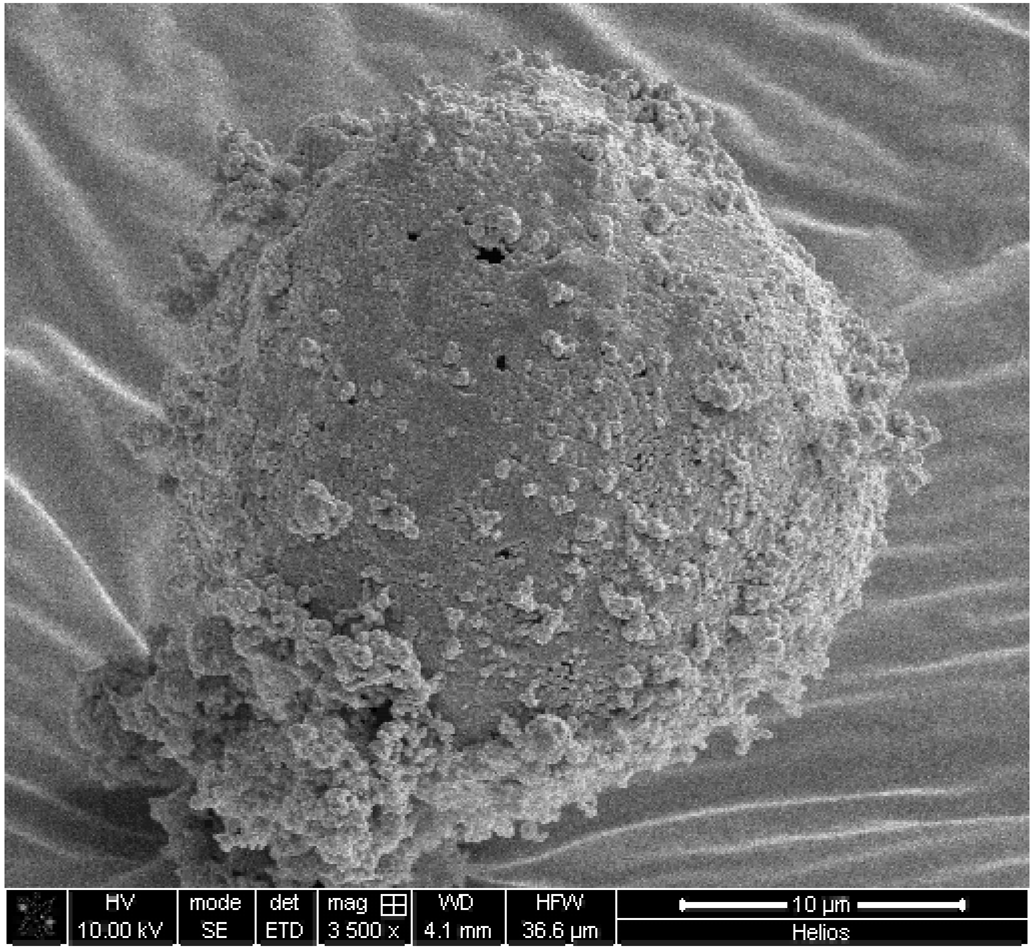


Unlike PM depth filtration in DPF surface pores, very little soot penetrates into ash layer.

Individual Ash Particles Also Porous

SAE 2012-01-0836

Focused Ion Beam (FIB) Milling Coupled with SEM

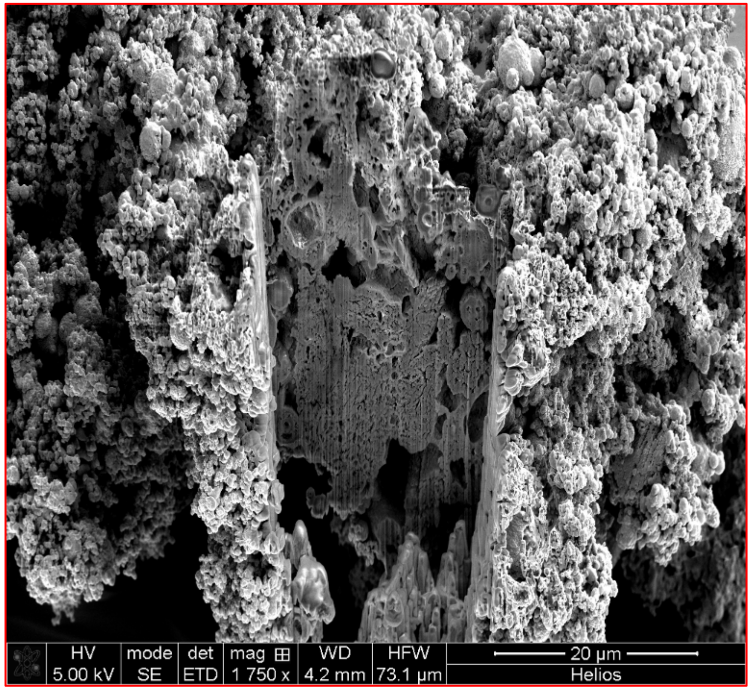


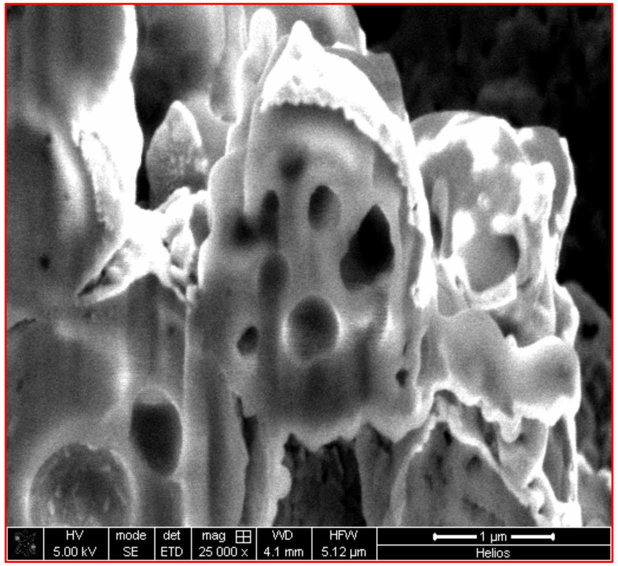
Particle most likely formed from sintering/agglomeration of ash precursors.

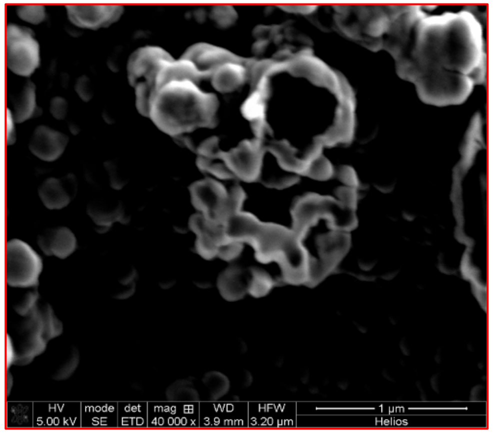
Ash Particles and Agglomerates Porous Shells!

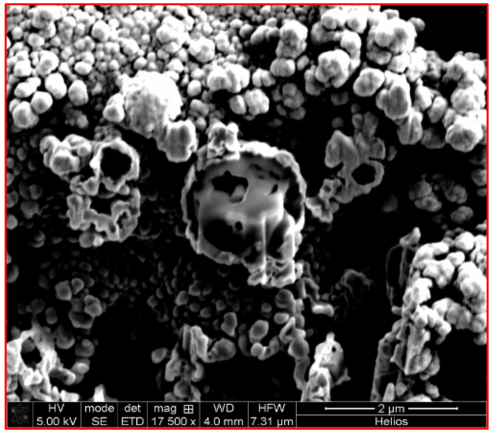
SLOAN AUTOMOTIVE LABORATORY

SAE 2012-01-0836







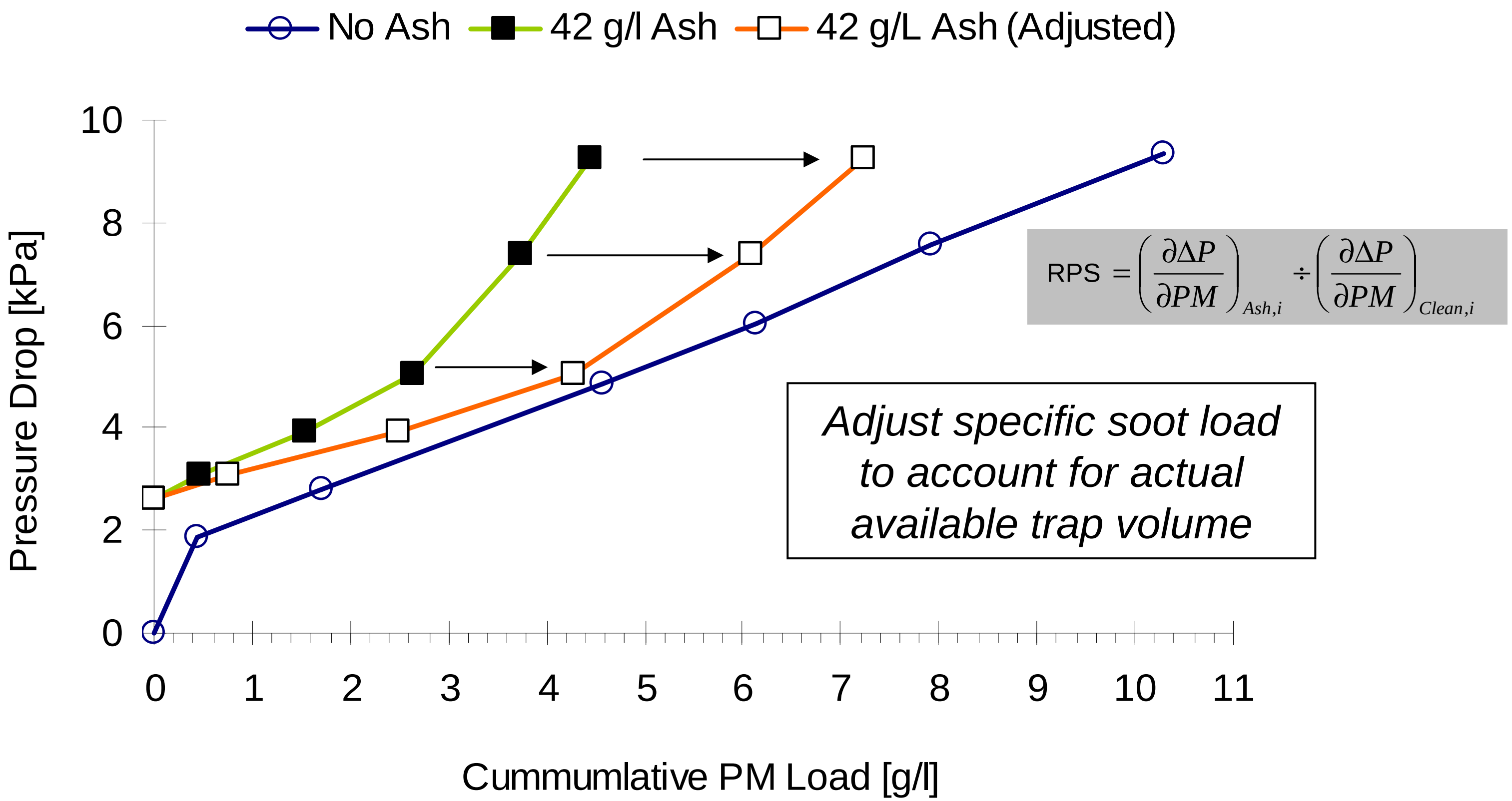


- Ash agglomerates consist of porous particles
- Consistent with low packing density and high porosity measurements

Images: C. Kamp

Ash Accumulation Also Influences Soot Properties

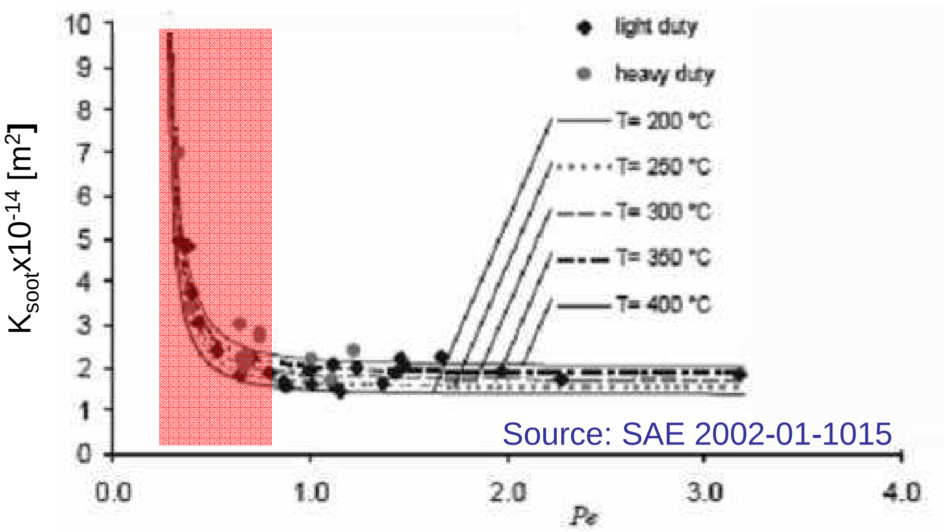
SAE 2010-01-0811

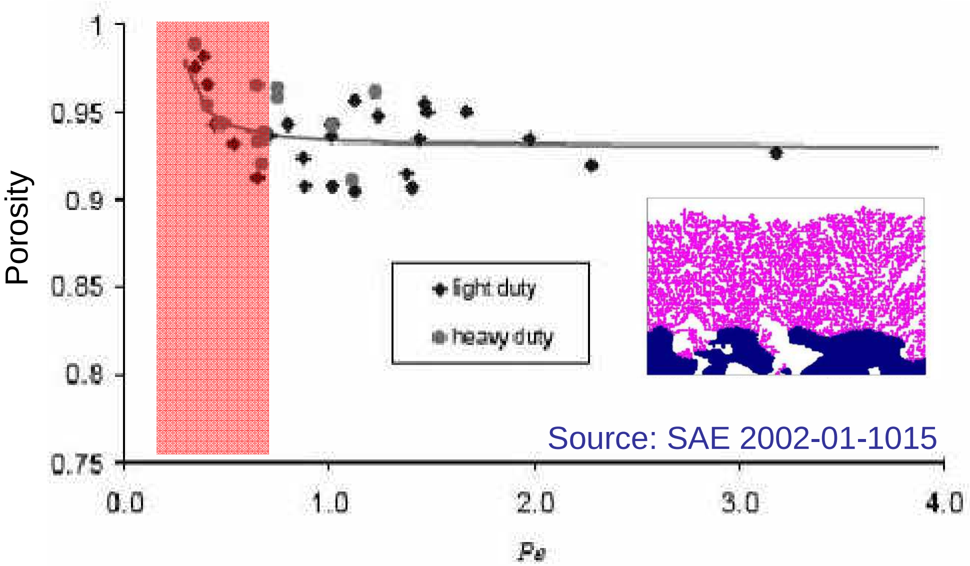


Ash deposits displace soot in DPF – higher local soot loads

Variation in PM Layer Properties with DPF Flow Well-Known

SLOAN AUTOMOTIVE LABORATORY





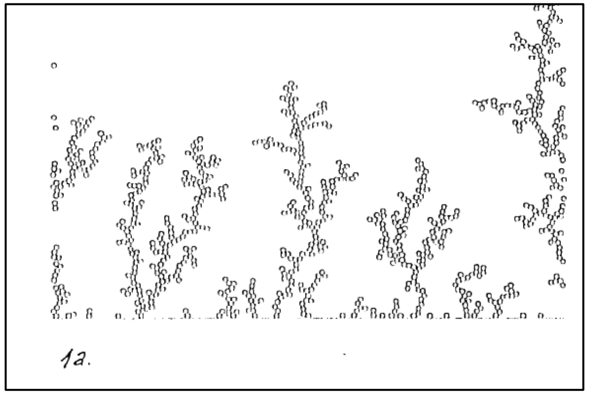


Image: Menelaos, T., Ph.D. Thesis, Yale, 1991.

$$Pe = \frac{U_w \cdot d_{Primary}}{D}$$

$$Pe = \frac{Inertia}{Diffusion}$$

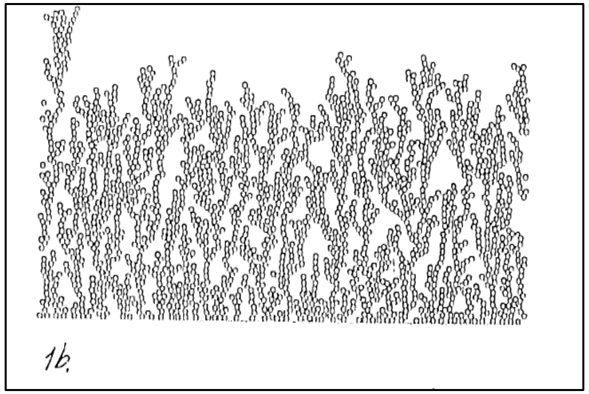
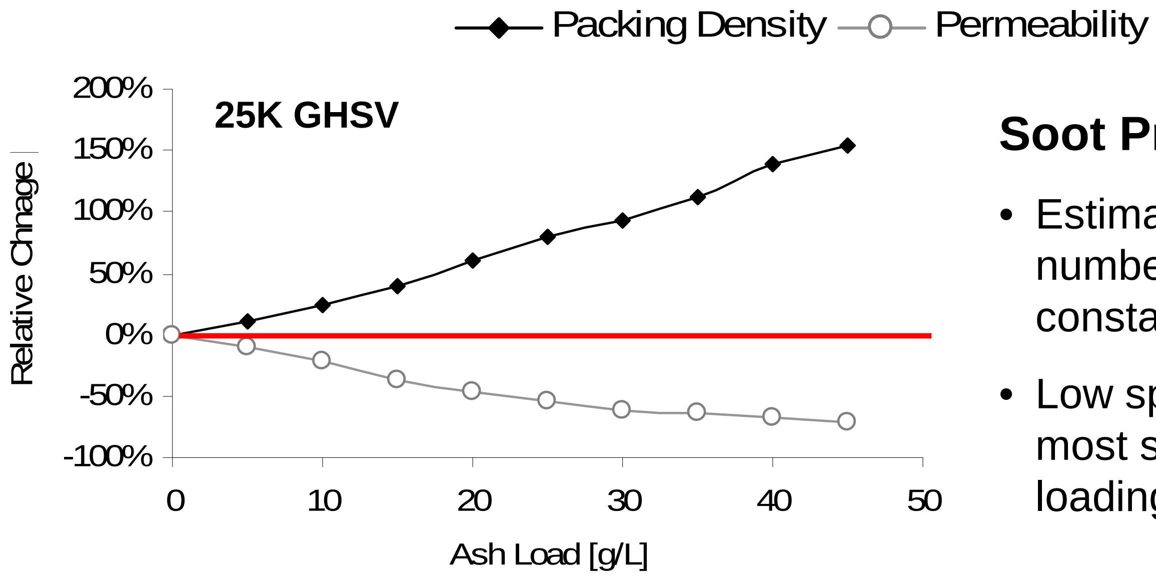


Image: Menelaos, T., Ph.D. Thesis, Yale, 1991.

Variation of Soot Properties Due to Ash Deposits

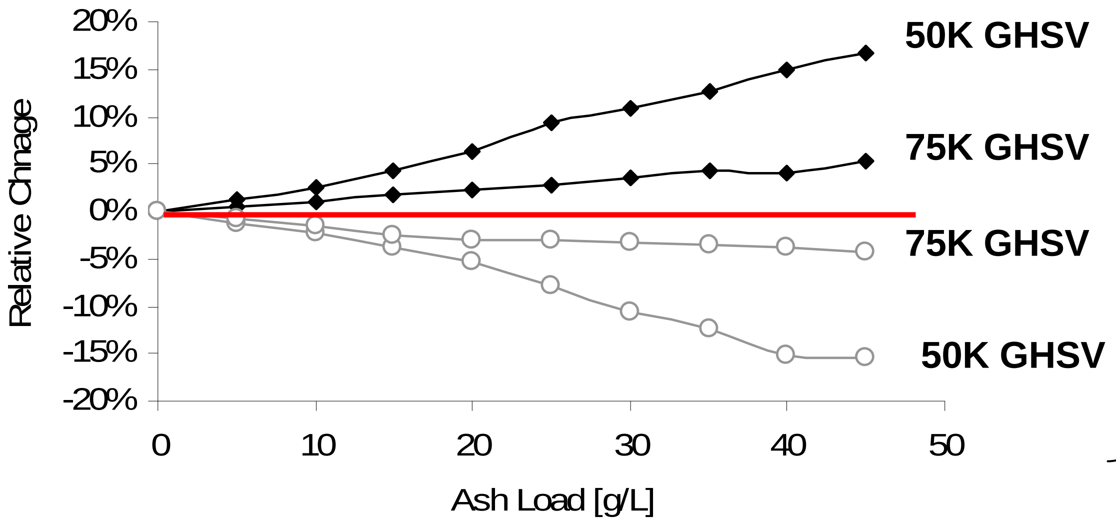
SLOAN AUTOMOTIVE LABORATORY

SAE 2010-01-0811



Soot Properties

- Estimated from empirical Pe number correlations for constant flow rate
- Low space velocity conditions most strongly affected by ash loading



Soot deposited at flows > 75K 1/hr insensitive to ash loading

Key Parameters Controlling Ash Deposits and DPF Impacts

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash

- *Substrate materials, pore size & distribution, porosity*

Role of Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

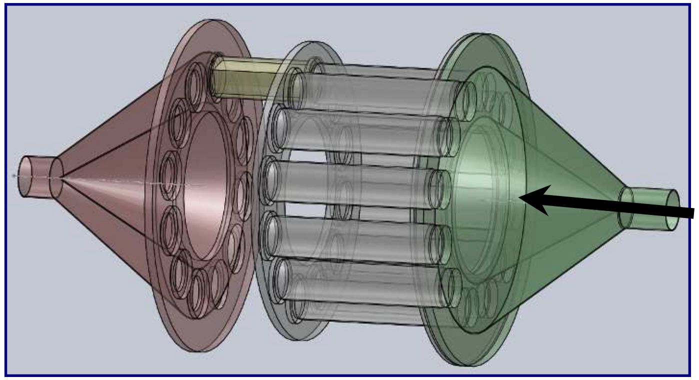
Sensitivity of DPF Design Parameters to Ash

Matrix	Porosity	Mean Pore Size
1st Trial	Low High	Low
2nd Trial	High	Low High
3rd Trial	Moderate	Low

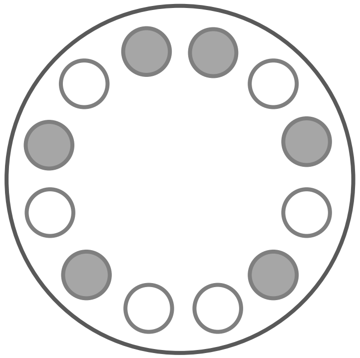
Additional DPF Parameters

- Filter/substrate materials
- DPF coatings and catalysts
- Filter geometry and cell configuration

Multi-Cartridge Filter Holder



12 DPF Segments

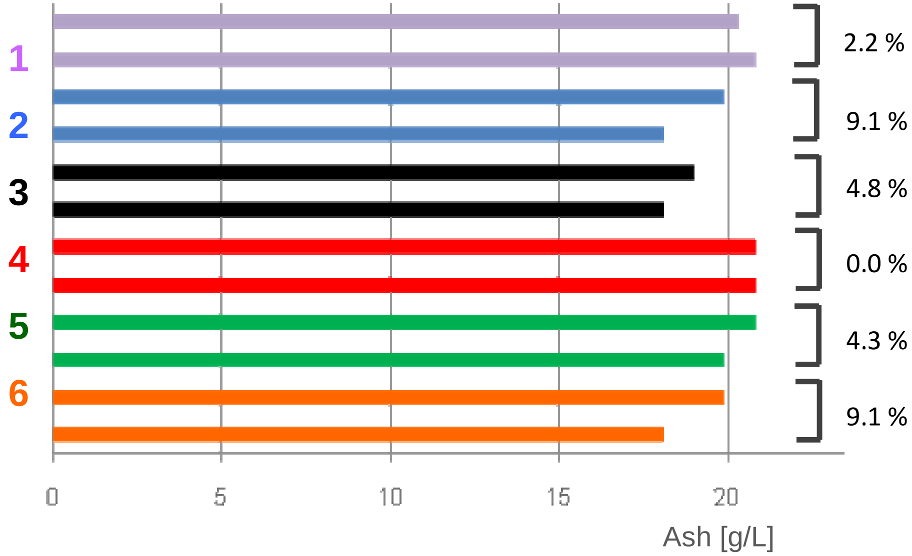


Ash Loading

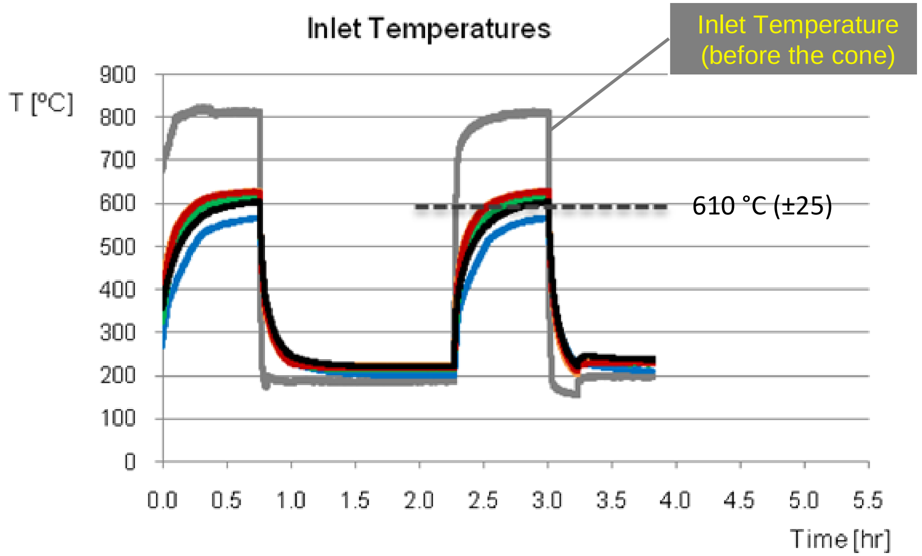
DPFs Experience Even Ash Loading and Temperatures

SLOAN AUTOMOTIVE LABORATORY

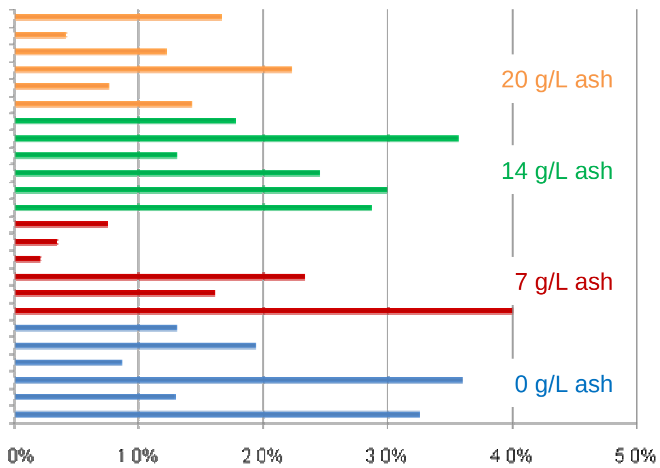
Average Ash Deposition after 60 hrs of operation: 20 g/L



- **Ash evenly distributed in core samples**
- **Little ΔP variation between duplicate samples**



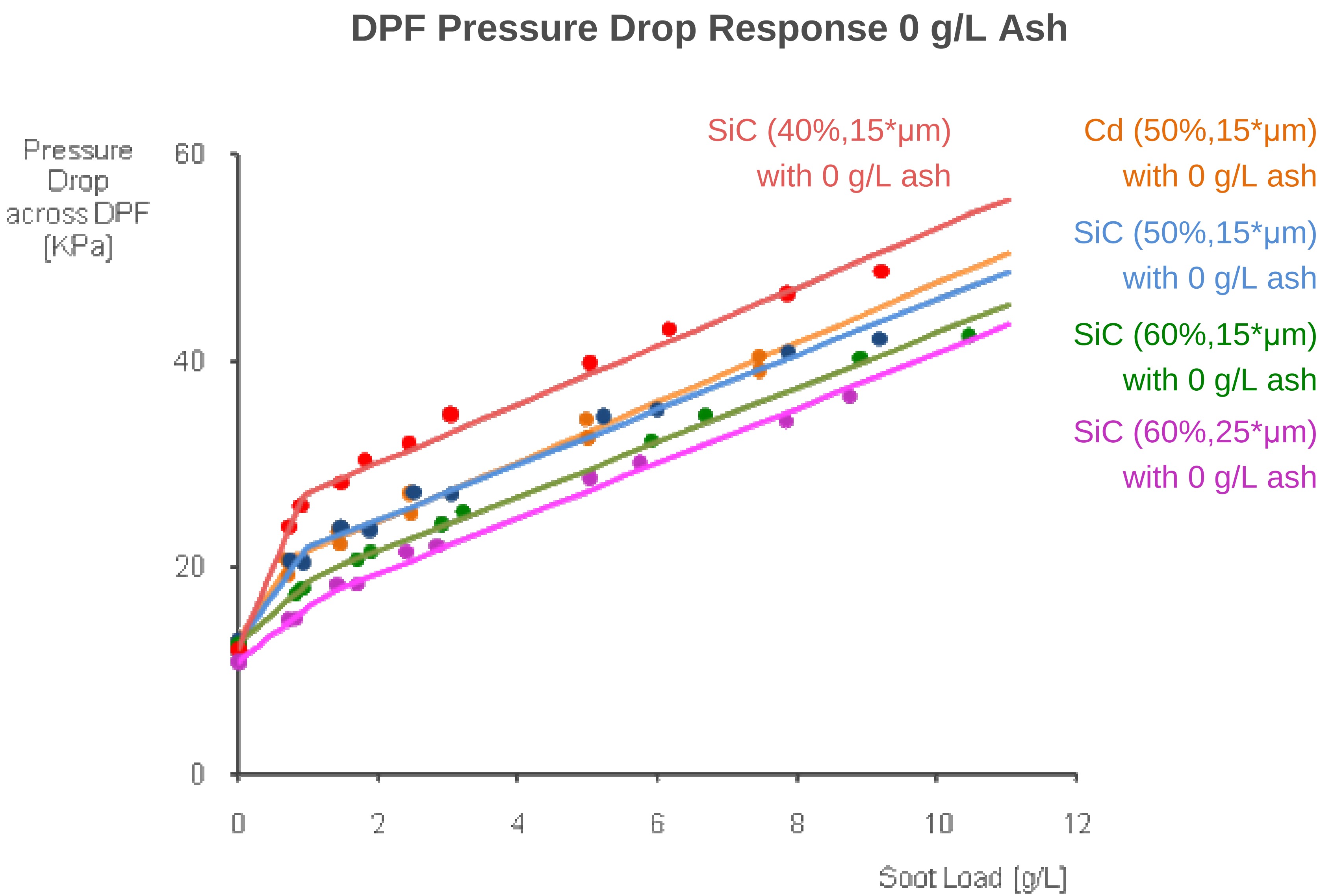
Pressure Drop Variation



(Space Velocity range: 6,500 – 55,000 [1/hr])

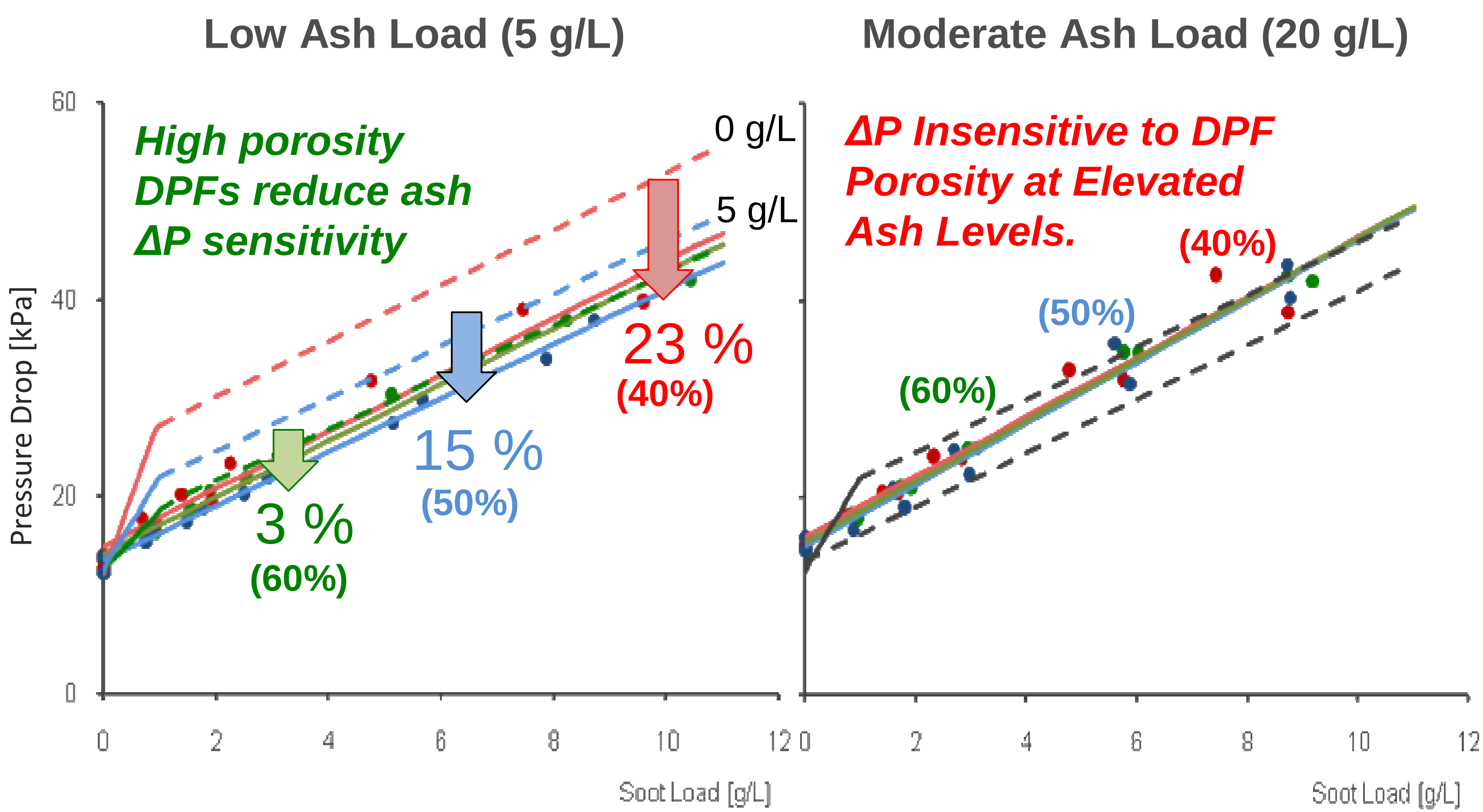
Similar ΔP Response to PM Accumulation for All DPFs

SLOAN AUTOMOTIVE LABORATORY



* Indicates pore and porosity size class

Sensitivity of DPF Porosity to Ash Accumulation Varies



- **Sensitivity of ΔP to ash accumulation increases with decreasing DPF porosity at low filter ash levels**
- **At high ash loads, ash dominates ΔP, which is insensitive to initial DPF porosity of filter, over range tested**

Key Parameters Controlling Ash Deposits and DPF Impacts

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash Accumulation

- *Substrate materials, pore size & distribution, porosity*

Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

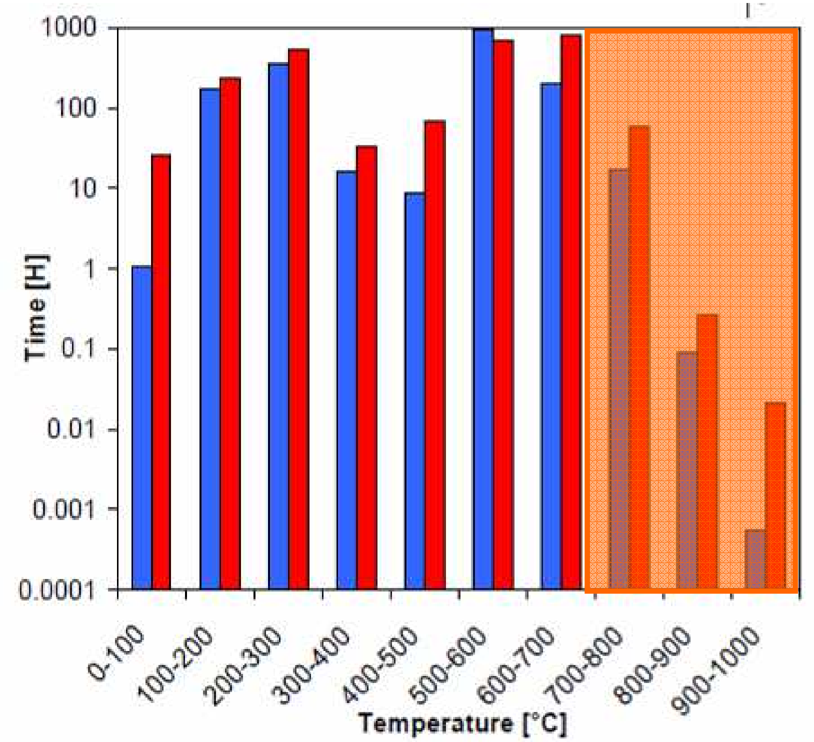
Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

Exhaustive Conditions Are Continually Changing

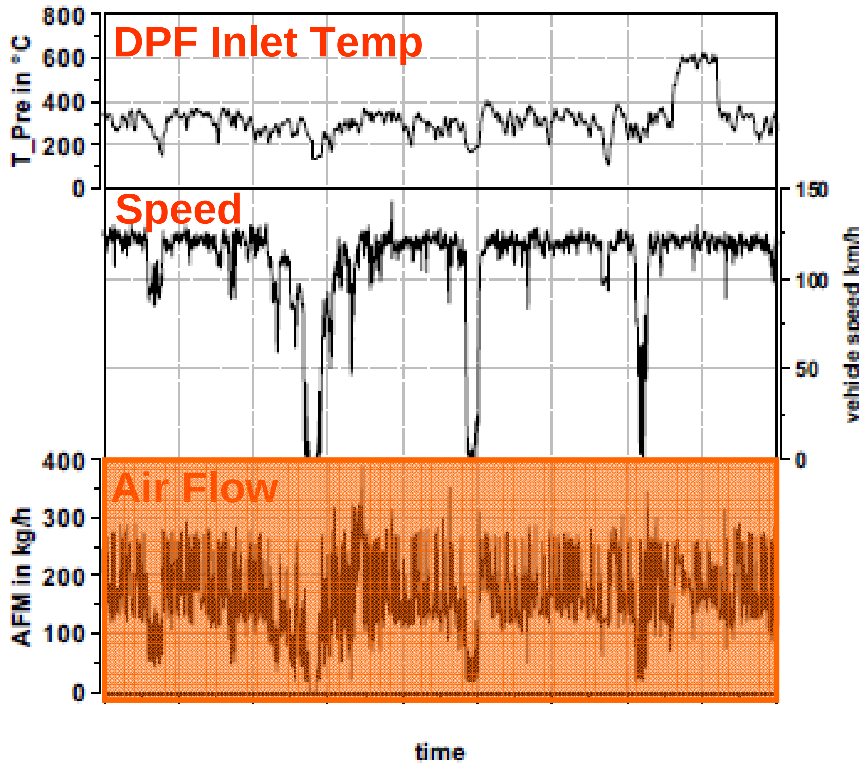
DPF Temperature Distribution

(300-420K Miles, HD Diesel)



Corning Deer 2006

Typical Highway Drive Cycle



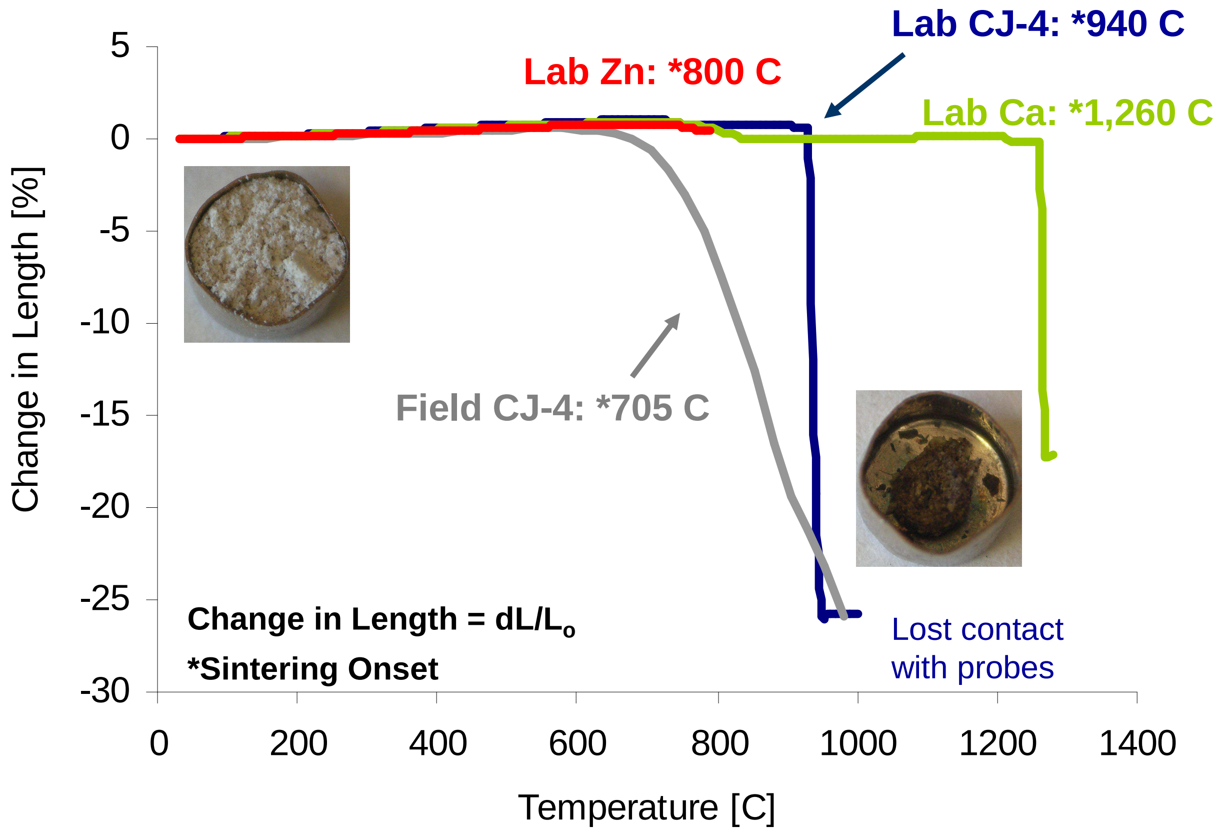
SAE 2009-01-1262

- Potential for short excursions above 700 °C over DPF operating history
- Exhaust flow rates also vary considerably, even over highway drive cycle

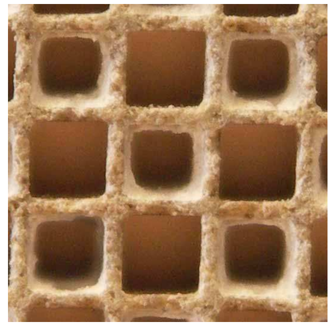
Exhaust Temperature Significantly Affects Ash Volume

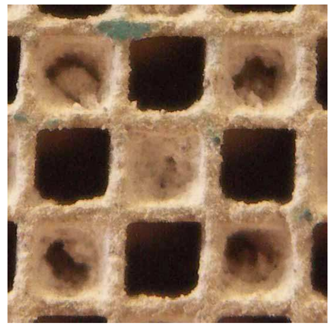
SLOAN AUTOMOTIVE LABORATORY

SAE 2012-01-1093



Competing Effects on ΔP Based on Ash Distribution





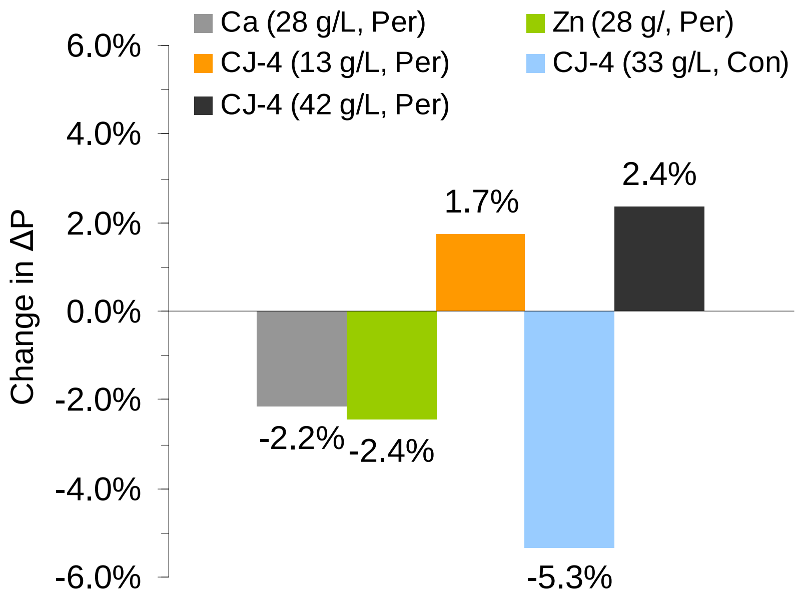
- **Large decrease in ash volume for temperatures over 700 °C**
  - Reduction in ash weight over temperature ranges less than 10%
  - Typical ash porosities 85% - 95% means large potential to reduce volume

Elevated Temperatures Exert Large Effect on Ash Packing

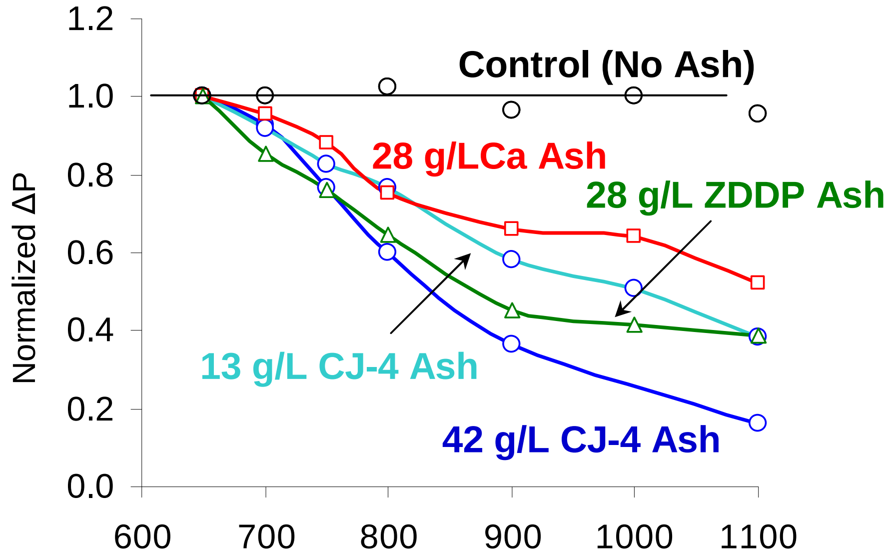
SLOAN AUTOMOTIVE LABORATORY

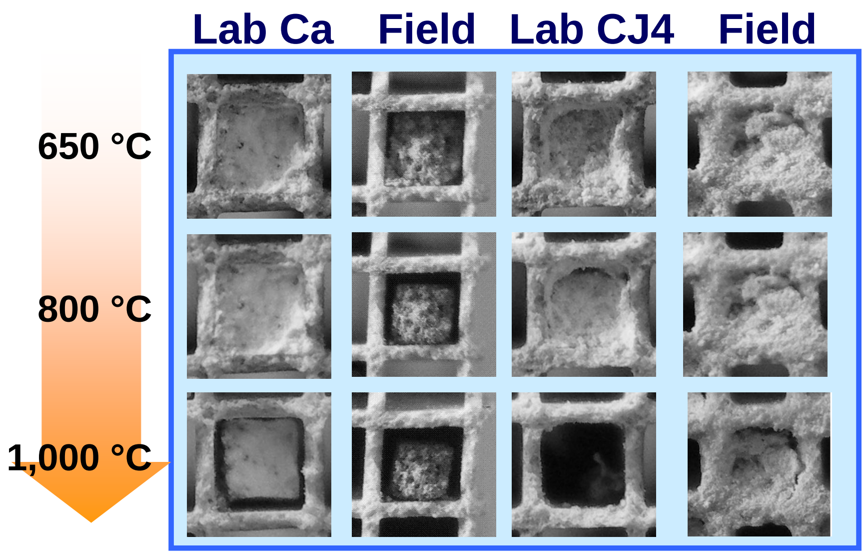
SAE 2012-01-1093

High Flow Exposure to 200,000 hr^{-1}



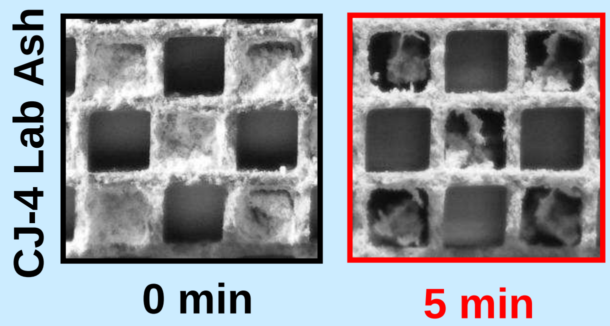
High Temperature Exposure





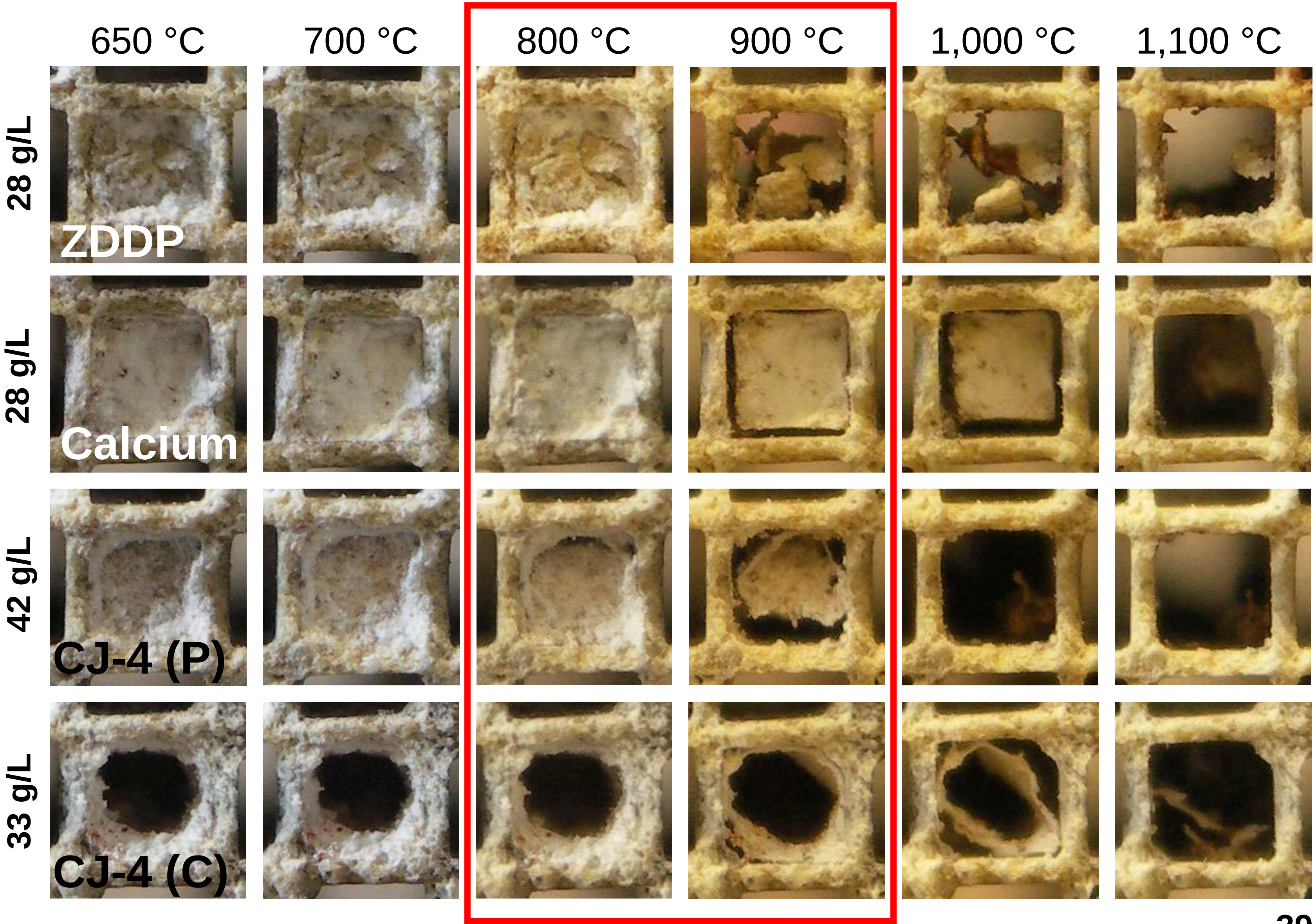
Ash Volume Reduction Fast

DPF core heated to 880 °C in 5 min, then quenched.



Large Reduction in Ash Volume at Elevated Temperatures

SAE 2012-01-1093



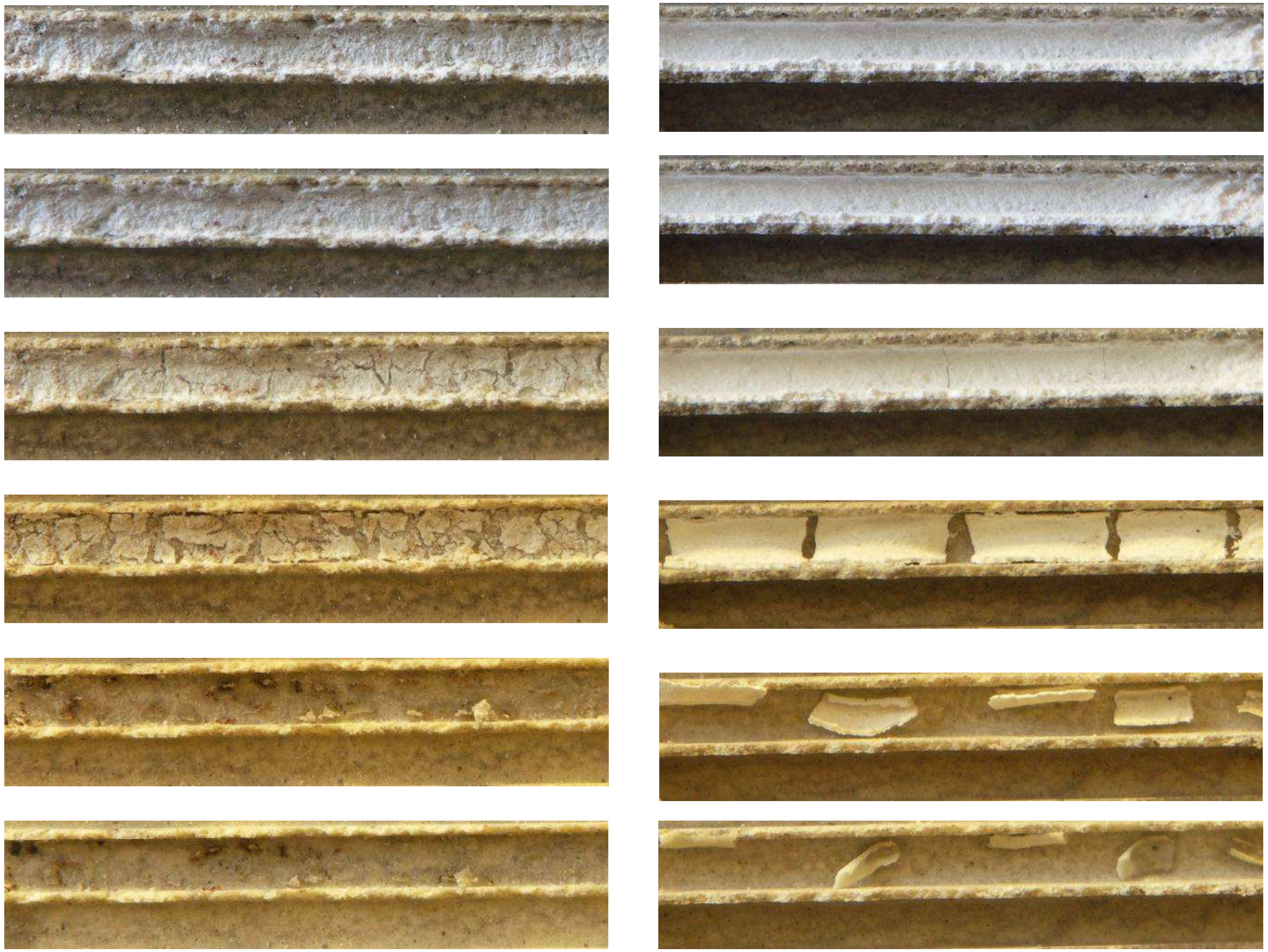
High Temperatures Cause Ash Layer Cracking/Shrinking

SLOAN AUTOMOTIVE LABORATORY

SAE 2012-01-1093

42 g/L CJ-4 Ash (Periodic) | 33 g/L CJ-4 Ash (Continuous)

650 °C
700 °C
800 °C
900 °C
1,000 °C
1,100 °C

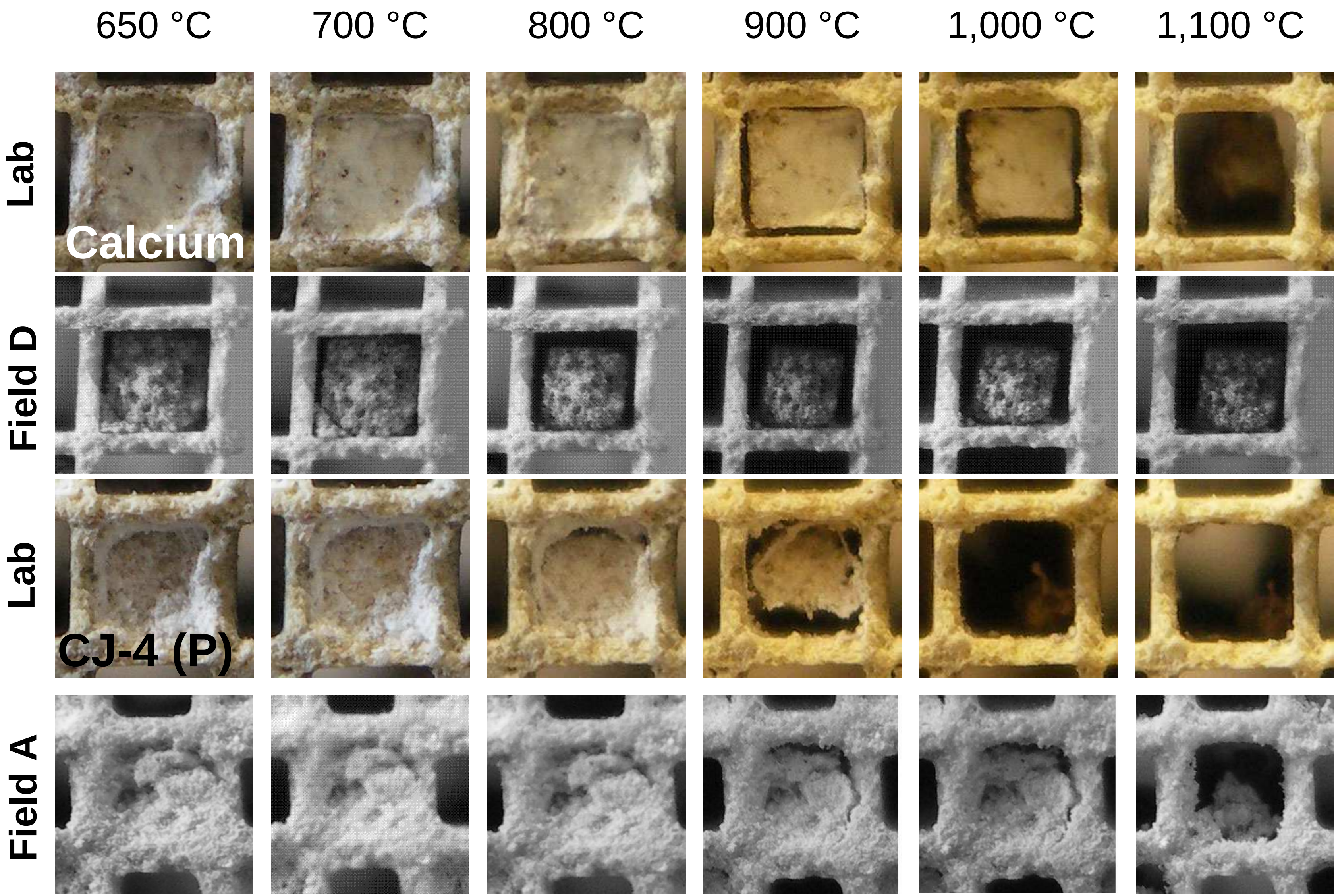


Despite large volume reduction, ash weigh change < 7%

Similar Behavior in Lab/Field Ash May Be Due to Chemistry

SLOAN AUTOMOTIVE LABORATORY

SAE 2012-01-1093

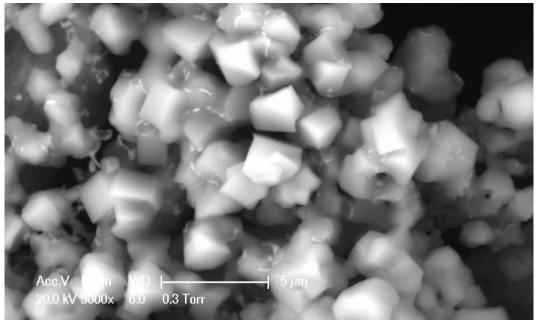


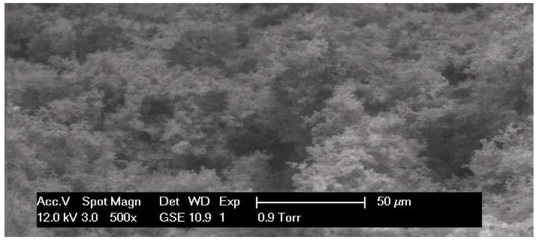
Chemical and Physical Changes in Ash at High Temps.

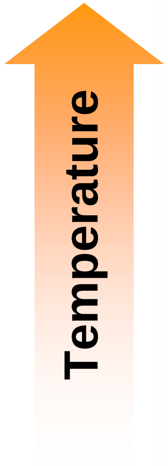
SLOAN AUTOMOTIVE LABORATORY

SAE 2012-01-1093

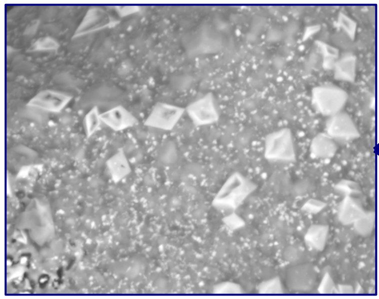
Equilibrium Crystal Structures formed at High Temperatures

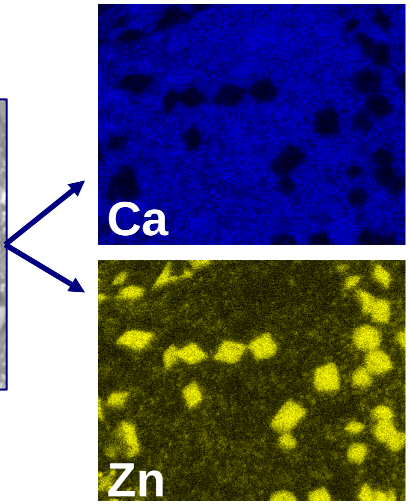




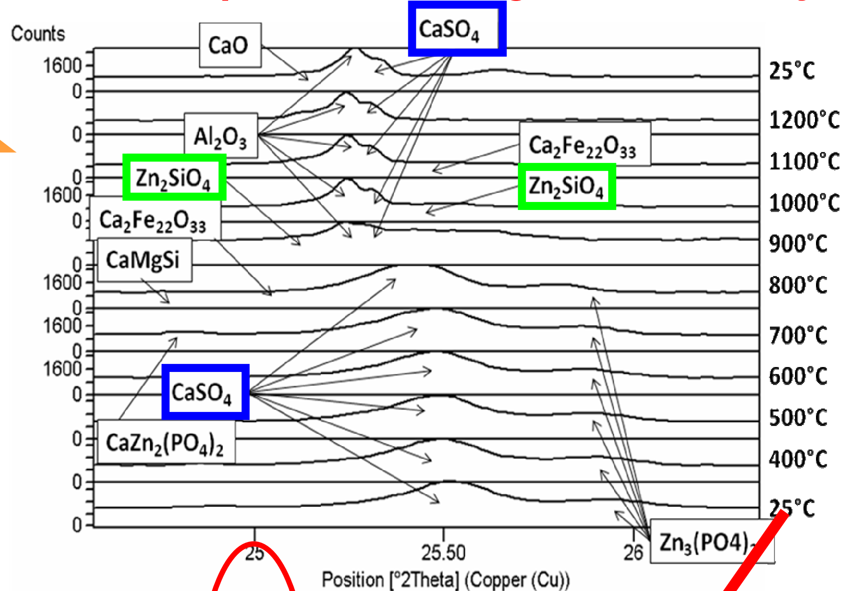


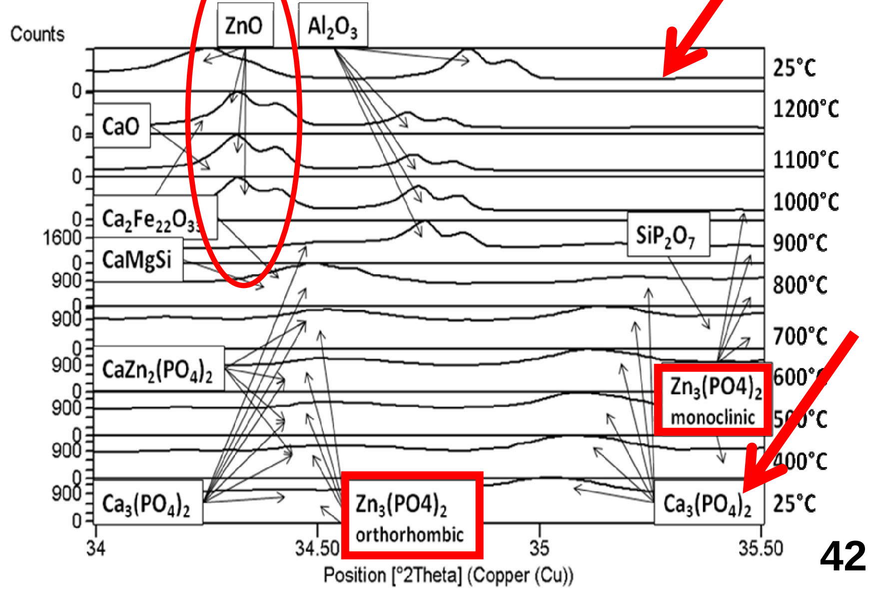
$$\min(\int \gamma_S dA_S)$$





Ash Composition Changes Irreversibly

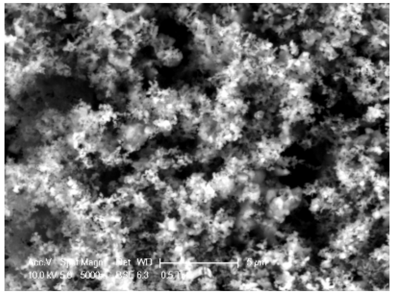




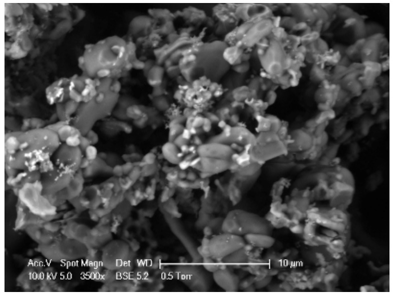
Applications to Understand Field DPF History

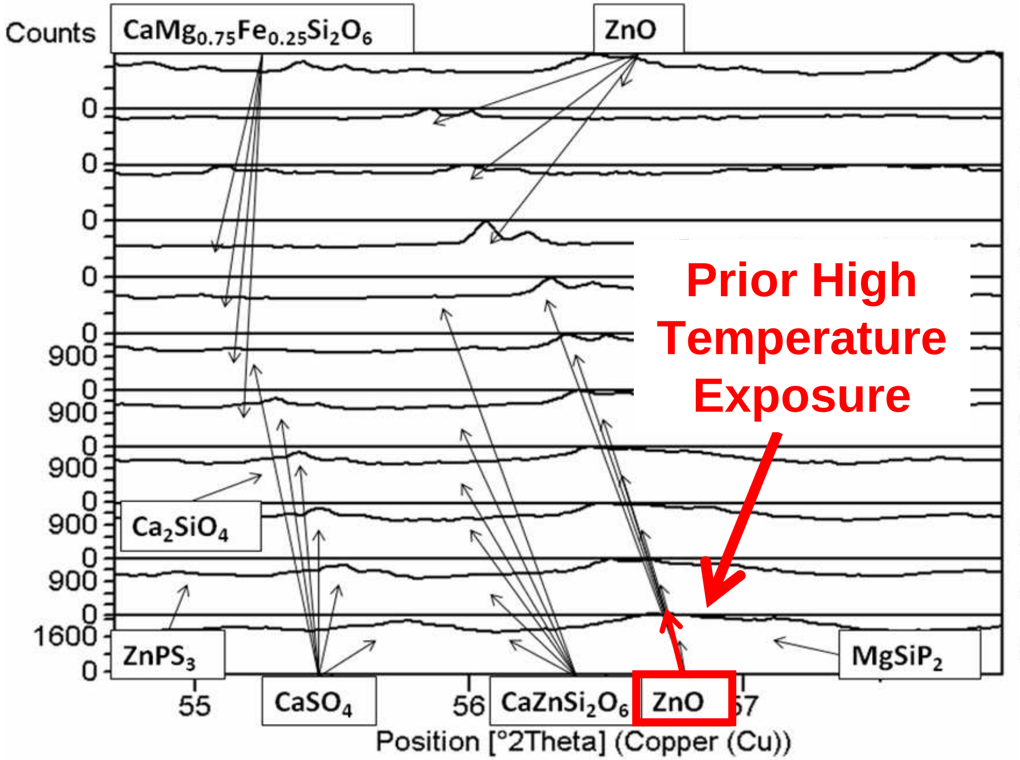
SAE 2012-01-1093

“Normal” Field Ash

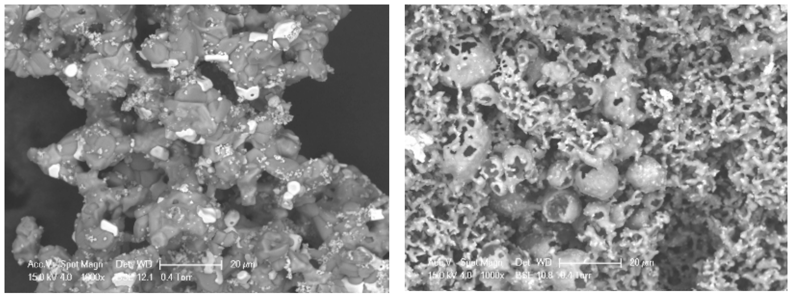


Field Ash Exposed to Thermal Event

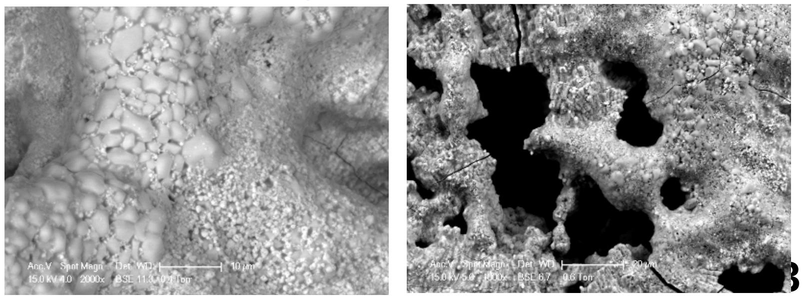




Ash Necking & Agglomeration

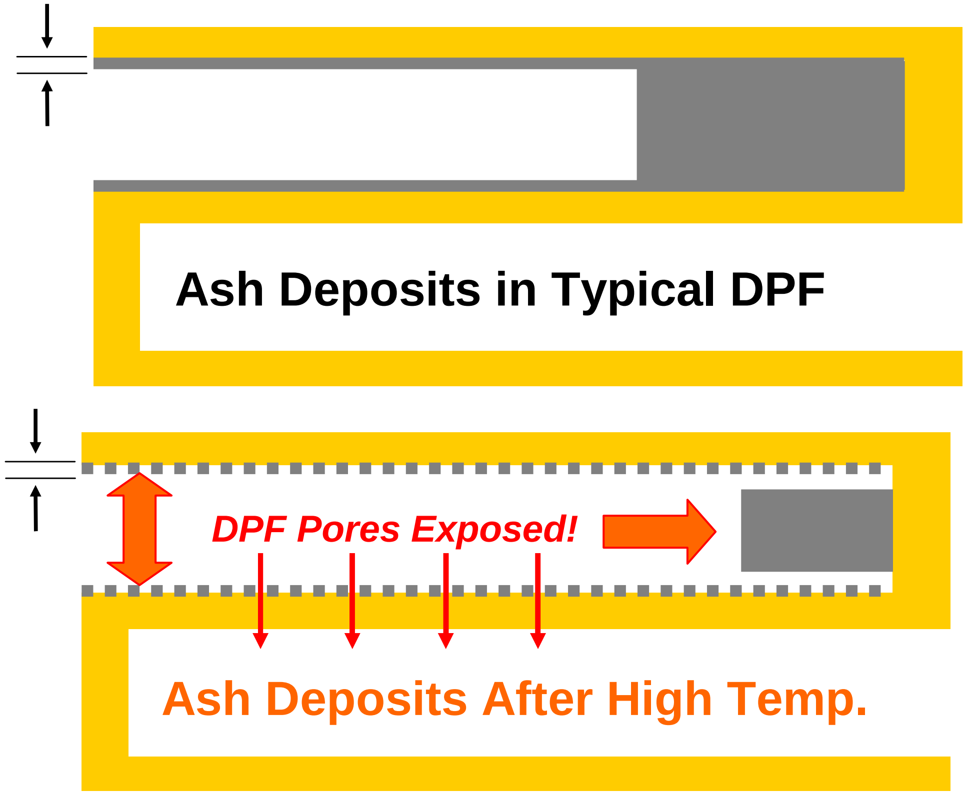


Wetting on Substrate



Conceptual Description of Temperature Effects on Ash

Possible Effect of Temperature on Ash Deposits



Competing Processes Require Detailed Understanding

- Elevated temperatures result in significant ash volume reduction
- Location of ash deposits (channel vs. wall) plays a large role in impact on ΔP
- Deterioration of ash cake layer could result in increased Δ P with soot

Key Parameters Controlling Ash Deposits and DPF Impacts

SLOAN AUTOMOTIVE LABORATORY

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash Accumulation

- *Substrate materials, pore size & distribution, porosity*

Role of Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

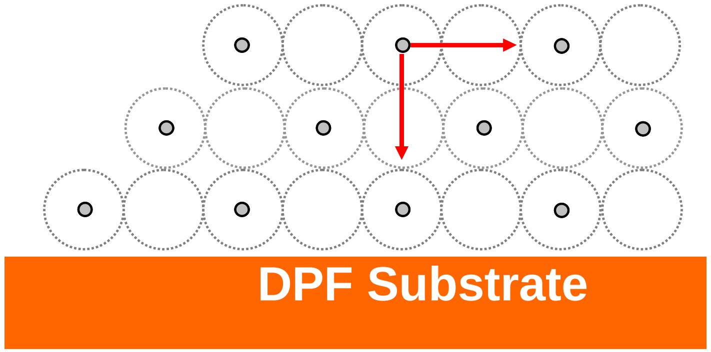
Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

Optical Access System for DPF Regeneration Studies

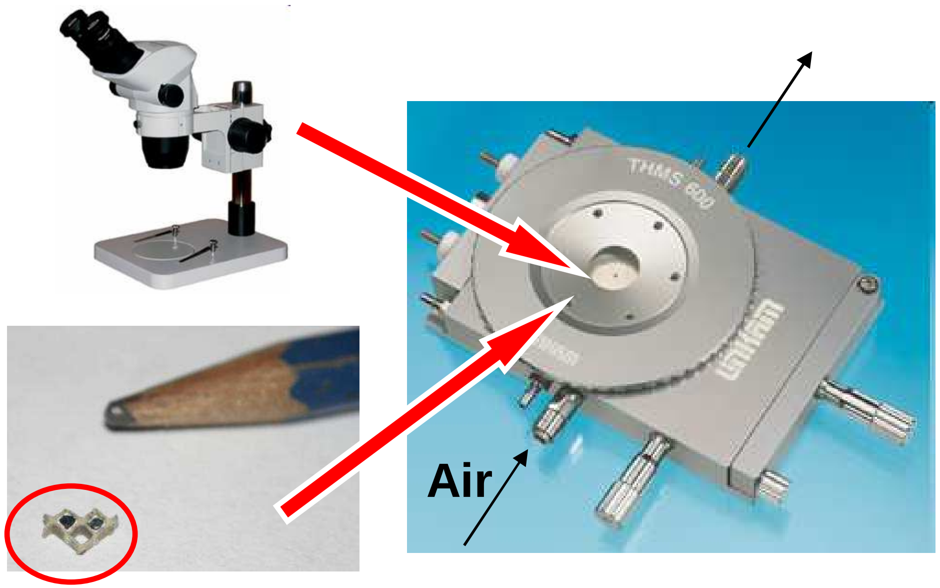
SLOAN AUTOMOTIVE LABORATORY

- **Understand Influence of Regeneration on Ash Properties**
  - **Active/Passive strategies may impact ash agglomeration and mobility**
  - **Role of soot interactions with ash during regeneration important**

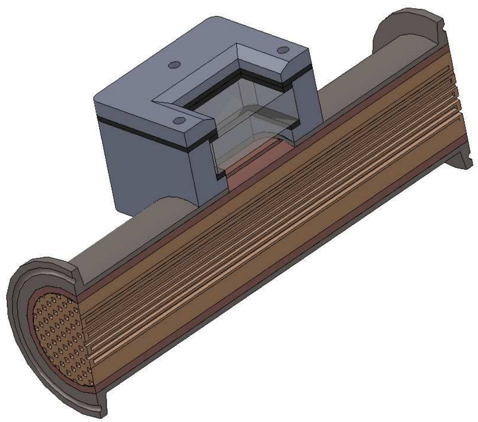


Regeneration Parameters

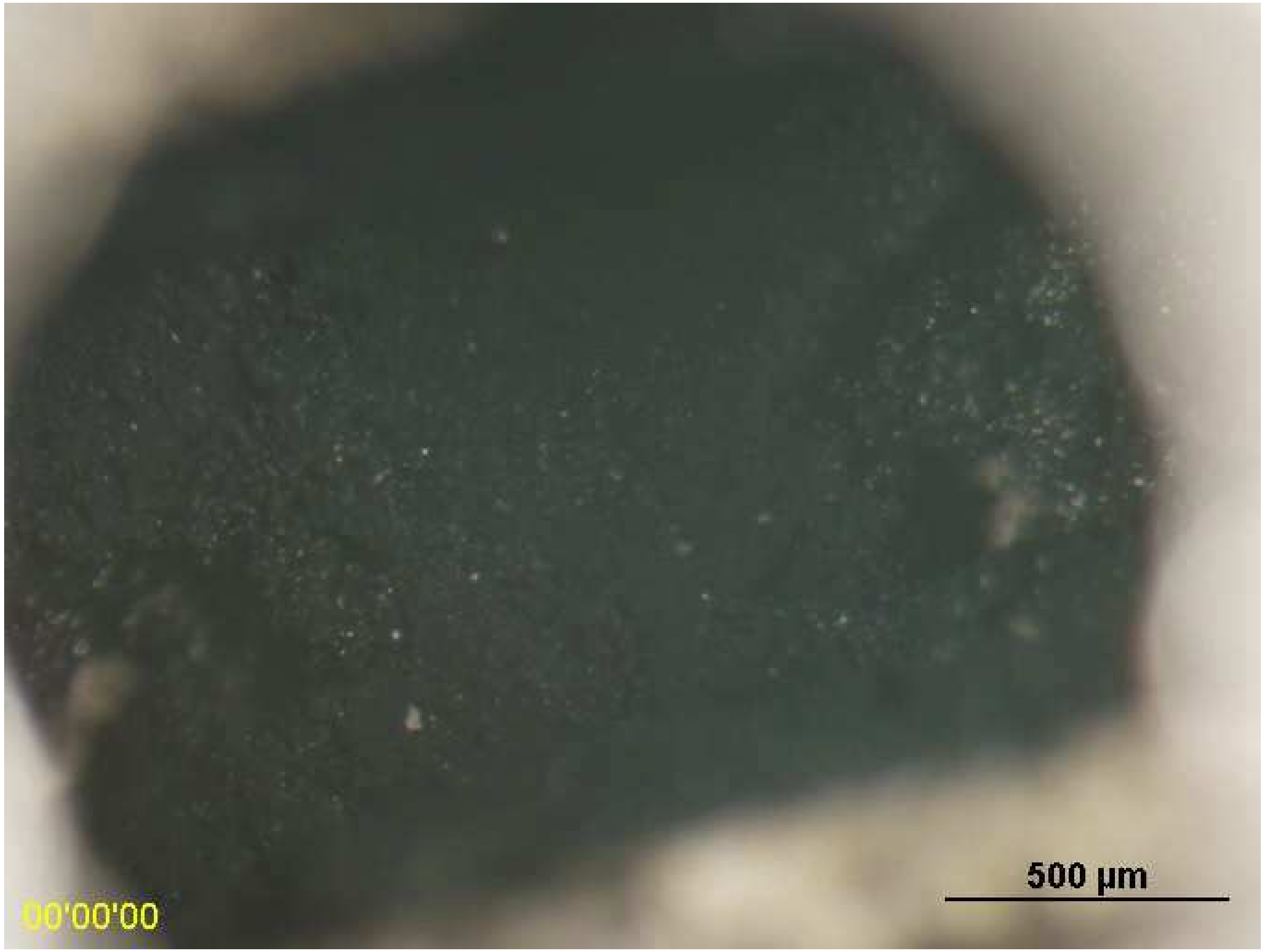
- Thickness of PM Layer
- Role of NO_2 from DOC vs. CDPF
- Temperature and flow conditions
- Catalysts interactions



2nd Generation

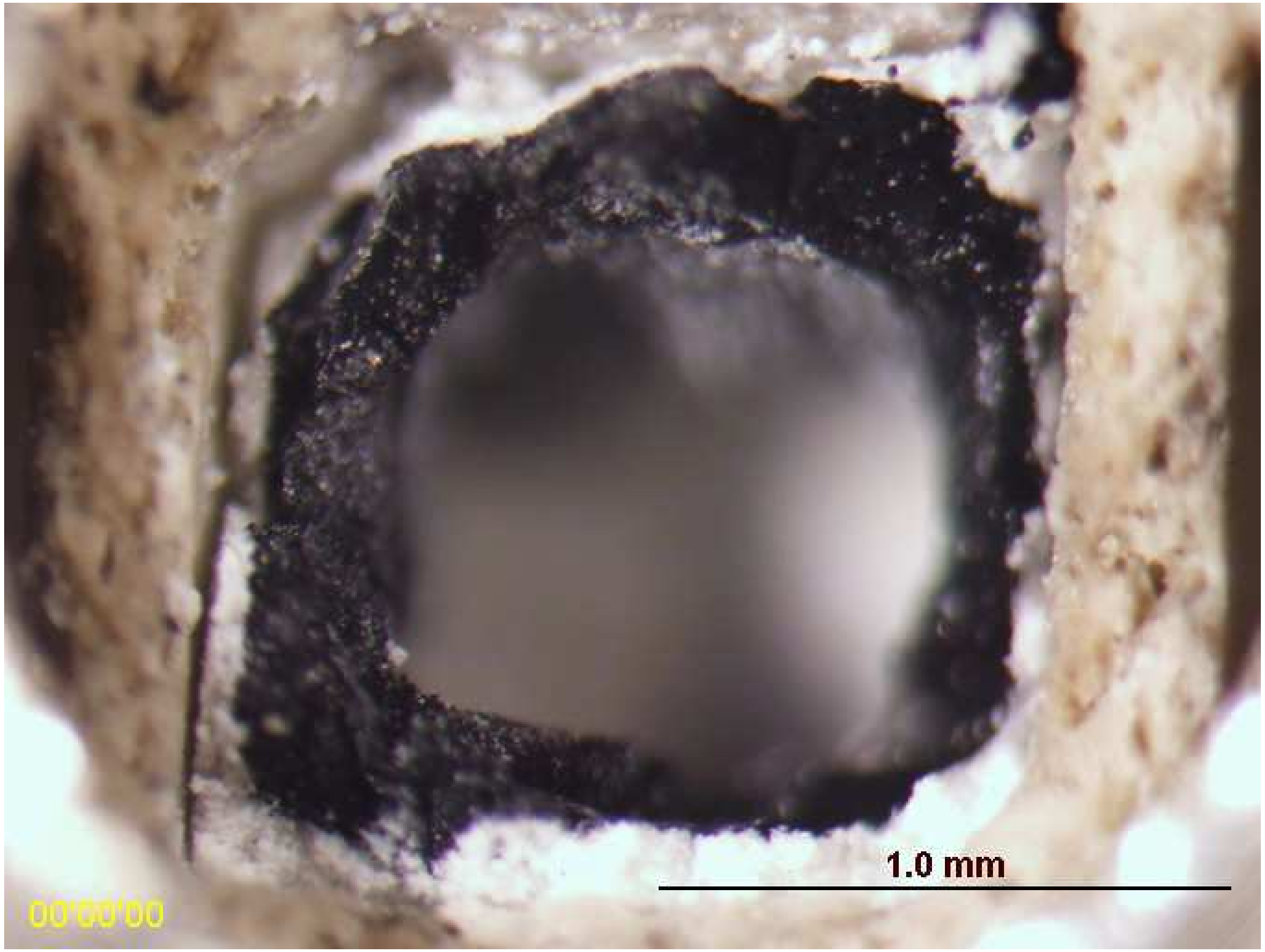


Video: PM Oxidation on Clean DPF Surface (Heavy PM)



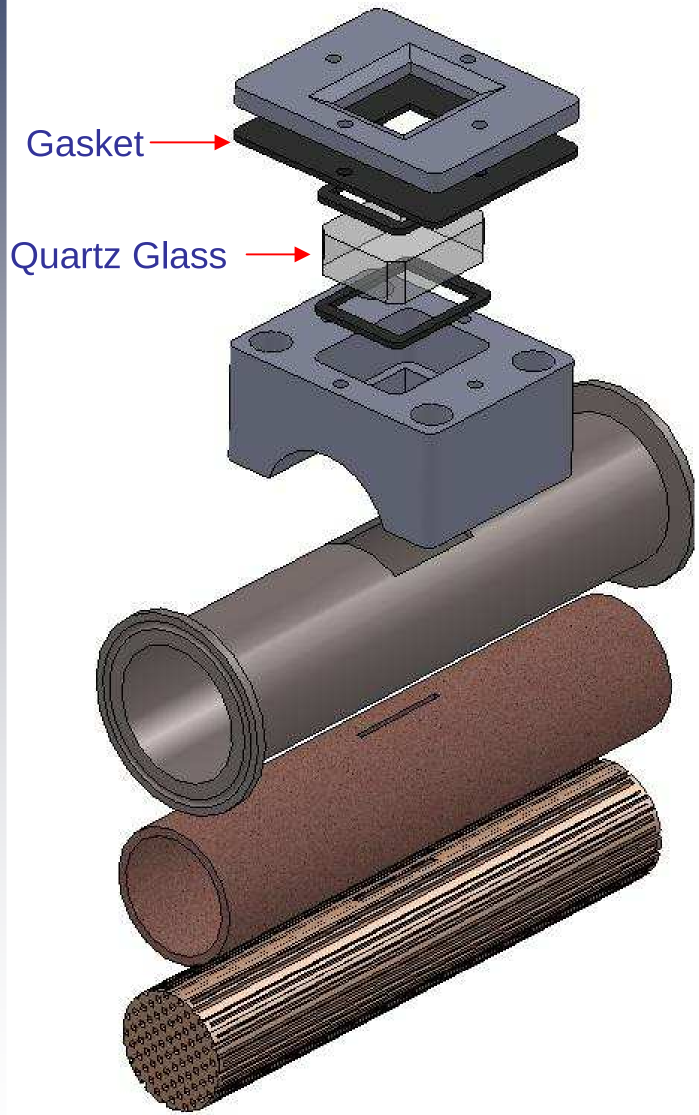
Video: PM Oxidation with Ash (DPF Cross Section)

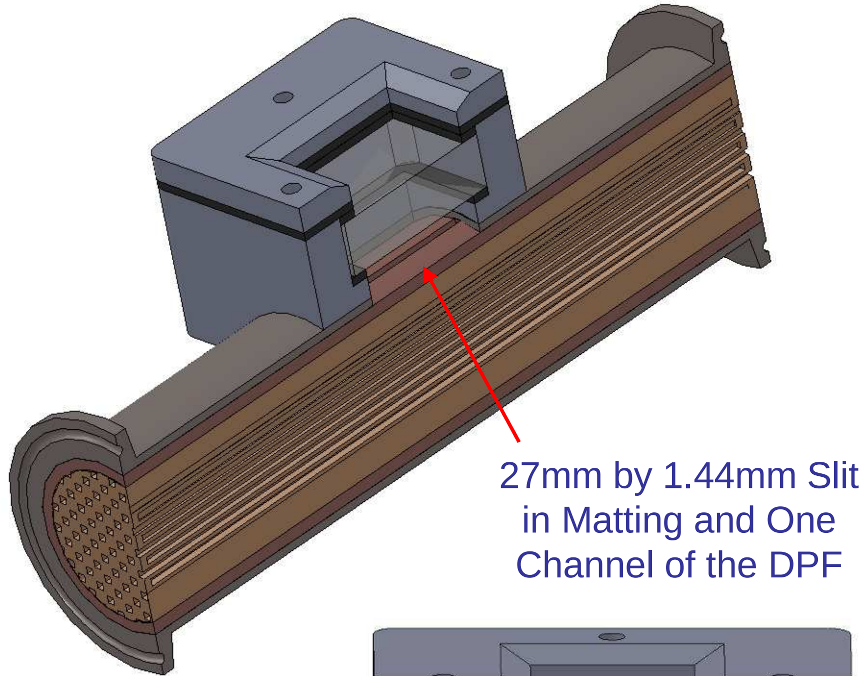
SLOAN AUTOMOTIVE LABORATORY

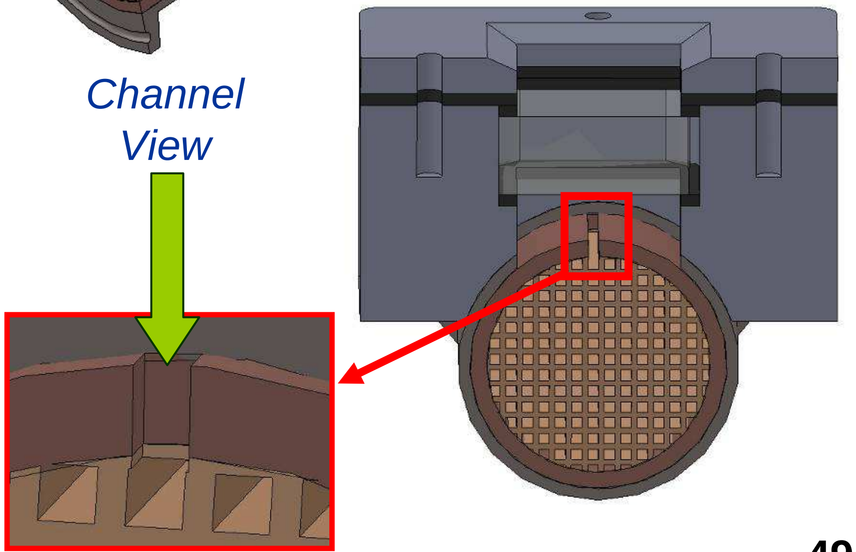


Current Optical Setup for Flow Reactor Testing

SLOAN AUTOMOTIVE LABORATORY

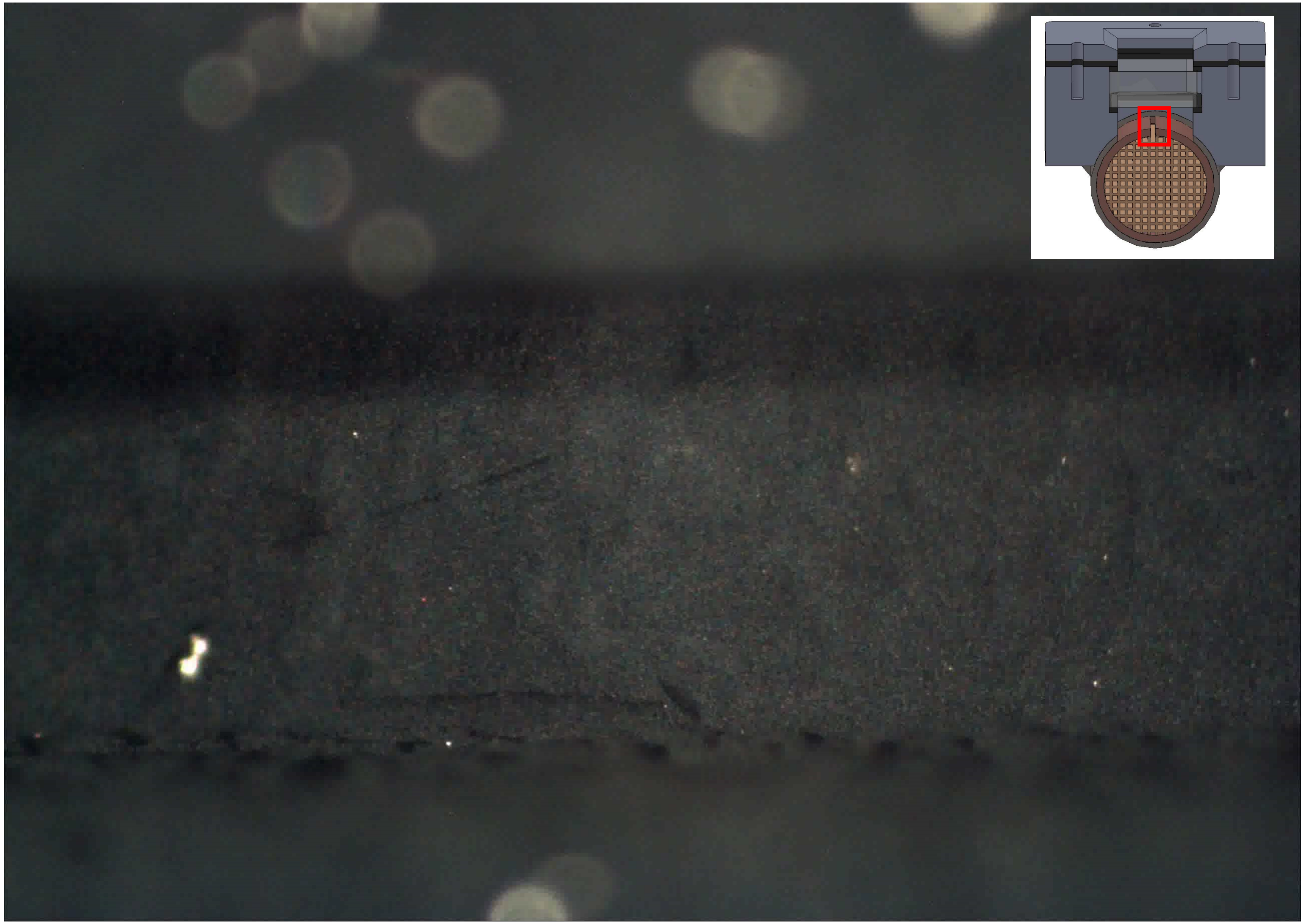






Video: PM Oxidation on Clean DPF Surface (Heavy PM)

SLOAN AUTOMOTIVE LABORATORY

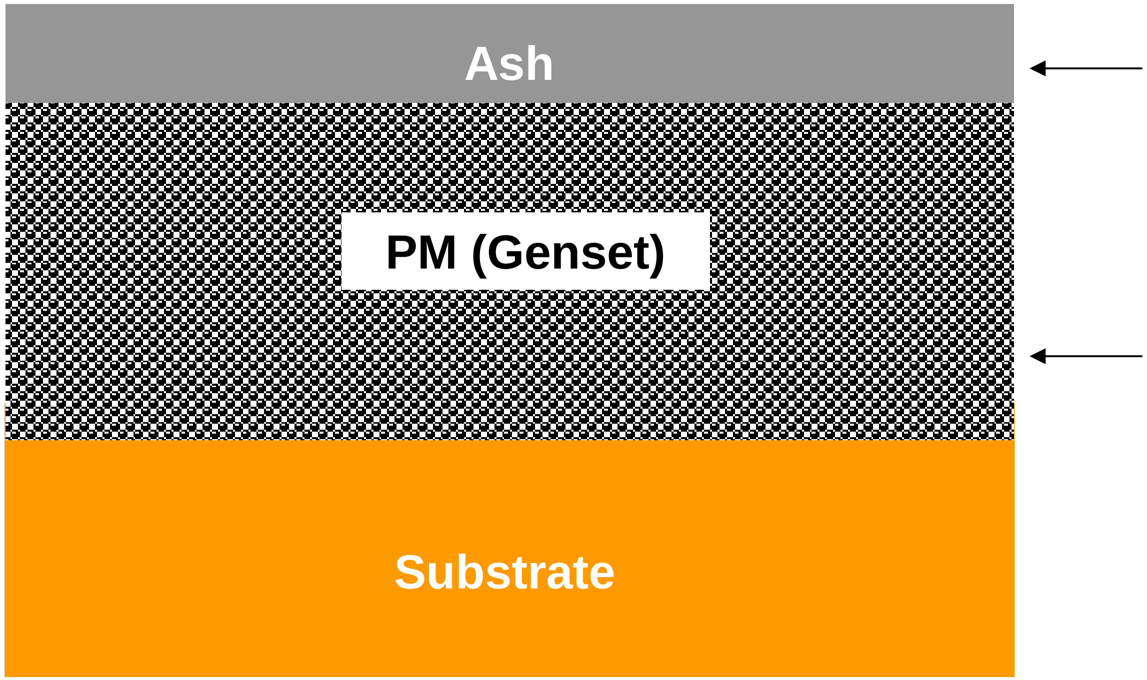


Ash Deposition on Top of PM Layer: Regeneration

SLOAN AUTOMOTIVE LABORATORY

Coat surface of soot cake with thin layer of ash

- Allows for visualization of ash/PM mobility during regeneration
- Enables visualization of ash agglomerate formation

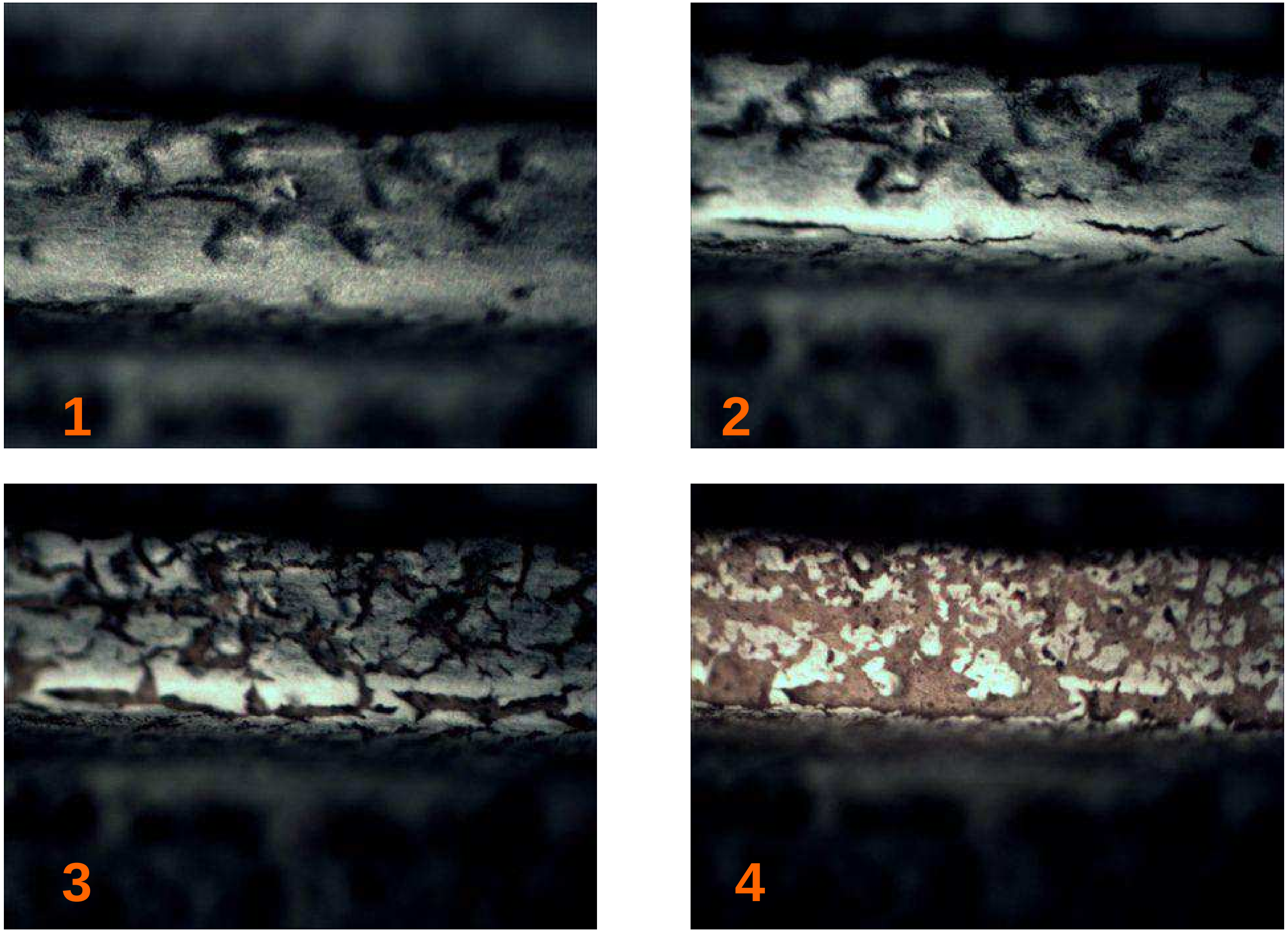


- Thin ash layer not fully-established
- Ash applied via accelerated loading system

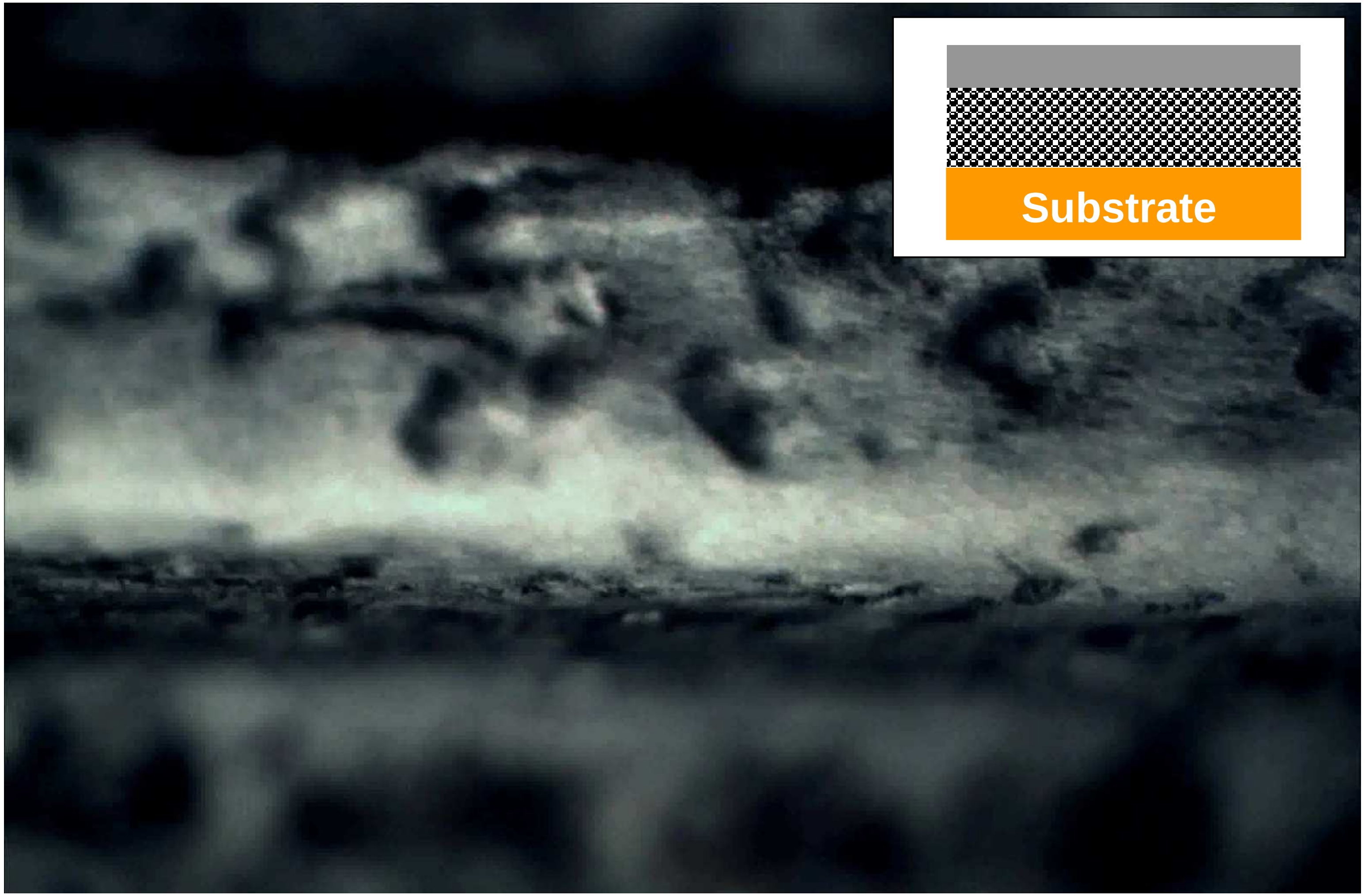
- Thick, fully-established PM layer
- PM loading accomplished using genset

Ash Deposition on Top of PM Layer: Regeneration

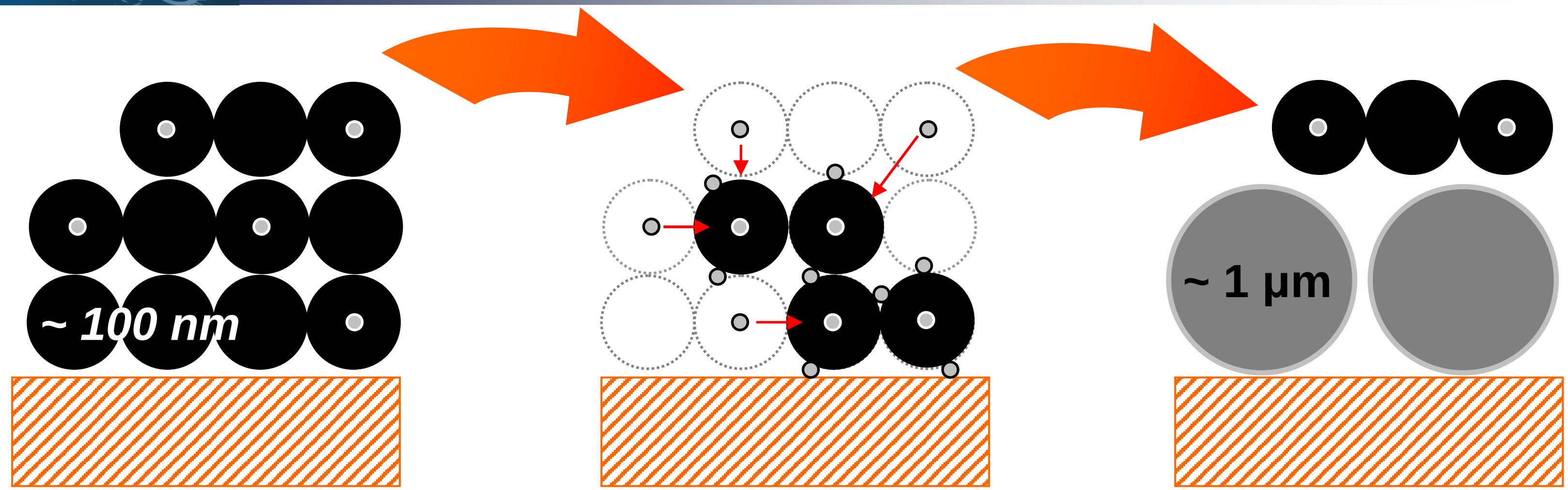
Regeneration with thin ash layer covering PM surface



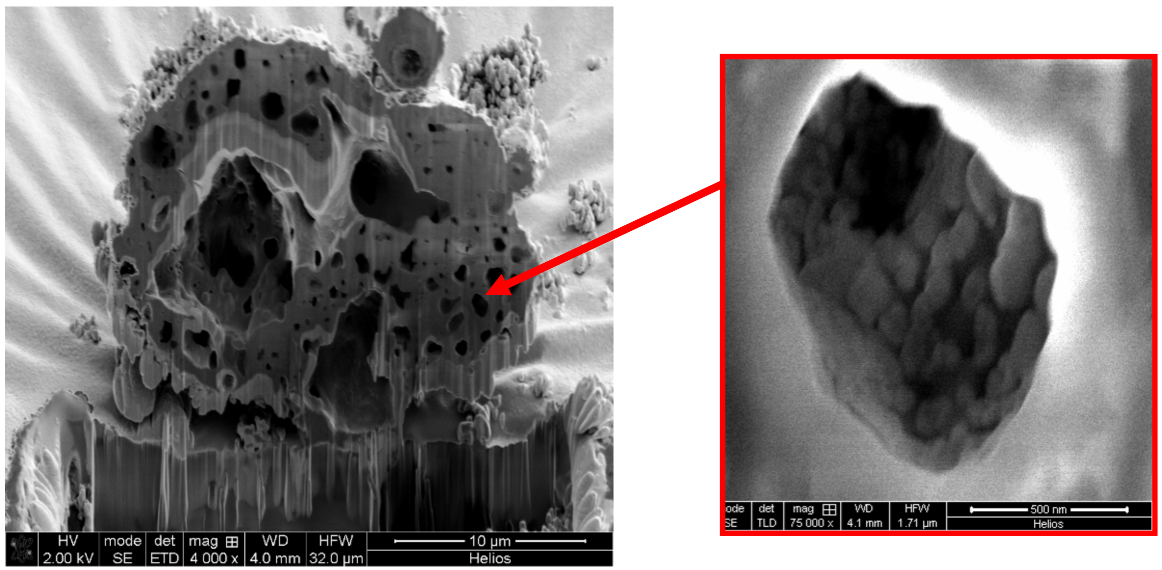
Video: Ash Deposited on Top of PM Layer



Ash Agglomeration Process During Soot Oxidation



Ash residence time in DPF is long ~ 100,000 + Miles



Internal void shows walls composed of ~nm scale particles

Key Parameters Controlling Ash Deposits and DPF Impacts

SLOAN AUTOMOTIVE LABORATORY

Engine-Out Ash Emissions and Transport

- *Form of ash in exhaust/feed gas entering DPF; ash trapping efficiency*

Ash Deposit Accumulation and Build-Up in the DPF

- *Agglomerate formation and ash mobility/distribution in DPF*

Ash Impact on DPF Pressure Drop Response

- *Ash composition and properties relevant to DPF performance*

Sensitivity of DPF Design Parameters to Ash Accumulation

- *Substrate materials, pore size & distribution, porosity*

Role of Engine Control Strategies and Exhaust Conditions

- *Temperature, flow, and feed gas conditions affecting ash deposits*

Regeneration Processes

- *Real-time optical studies of ash formation and mobility*

Ash – Catalyst Interactions

- *Chemical and physical interactions of ash and catalyst/washcoat*

Summary and Conclusions

Detailed understanding of all system parameters important to reduce impact of ash on DPF degradation and fuel efficiency.

I. Ash Build-Up: Ash loading of ~ 10 g/L or around 50,000 miles required to form fully-established ash layer.

II. Ash Morphology: Two porosity scales identified in ash layer and ash primary particles, which are themselves hollow.

III. Lube Chemistry: Ash properties and DPF pressure drop strong function of additive composition.

IV. Exhaust Conditions: Transient changes in temperature induce much larger variations in ash packing than high flow rates.

V. DPF Parameters: DPF pressure drop relatively insensitive to original substrate porosity following ash layer build-up.

VI. Regeneration Effects: Preliminary optical studies highlight importance of regeneration parameters but requires further study.

Acknowledgements

SLOAN AUTOMOTIVE LABORATORY

- Research supported by: MIT Consortium to Optimize Lubricant and Diesel Engines for Robust Emission Aftertreatment Systems
- We thank the following organizations for their support:

- Caterpillar	- Chevron/Oronite	- Cummins
- Detroit Diesel	- Infineum	- Komatsu
- NGK	- Oak Ridge National Lab	- Süd-Chemie
- Valvoline	- US Department of Energy	
- Ciba	*- Ford*	*- Lutek*

- MIT Center for Materials Science and Engineering