

WE START WITH YES.



ASH-DURABLE CATALYZED FILTERS FOR GASOLINE DIRECT INJECTION (GDI) ENGINES (2016 AOP LAB CALL)

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DOE Annual Merit Review & Peer Evaluation Meeting

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Office of Vehicle Technologies

Project ID: ACE024

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start: Oct. 2015
- End: Sept. 2017
- 30% finished

Budget

- Total project funding
 - \$1.5M (presumed)
- Funding received in FY15: \$500K
- Funding for FY 2016
 - \$500K (presumed)

Barriers

- B. Lack of cost-effective emission control
- C. Lack of modeling for combustion and emission control
- E. Durability

Partners

- Corning and Hyundai Motor Company
- University of Illinois at Urbana-Champaign
- Afton Chemical
- Korea Automotive Technology Institute (KATECH)

Relevance

- GPFs have been recognized to be an enabling technology for PM reduction.
 - Mercedes Benz has already adopted GPFs in S500 for the European market.
 - Other auto makers have been considering GPFs for PM control.
- The combination of three-way catalysts (TWCs) and GPFs is a logical strategy that will meet gaseous and particulate emissions standards.
 - Key technologies to be considered
 - Inner-wall coating of TWC on high porosity filters
 - TWC amounts and TWC constituents (PGMs, OSC)
- Engine oil-derived ash is known to deactivate TWCs.
 - More significant impact with decreased Ca/ZDDP in oil (SAE 940746).
 - Phosphorous (P) has been well recognized to be a major inhibitor (Zn-P that decreases porosity, CePO_4 & AlPO_4)

Relevance

- Surface-coated TWC on monolith shows the most significant ash loading in inlet part of the path.
- Ash loading in DPFs was mostly inclined toward plug position, with continuous regeneration.
- Also, ash distribution in GPFs has been reported to be on plug position (SAE 2014-01-1513, 2016-01-0941).

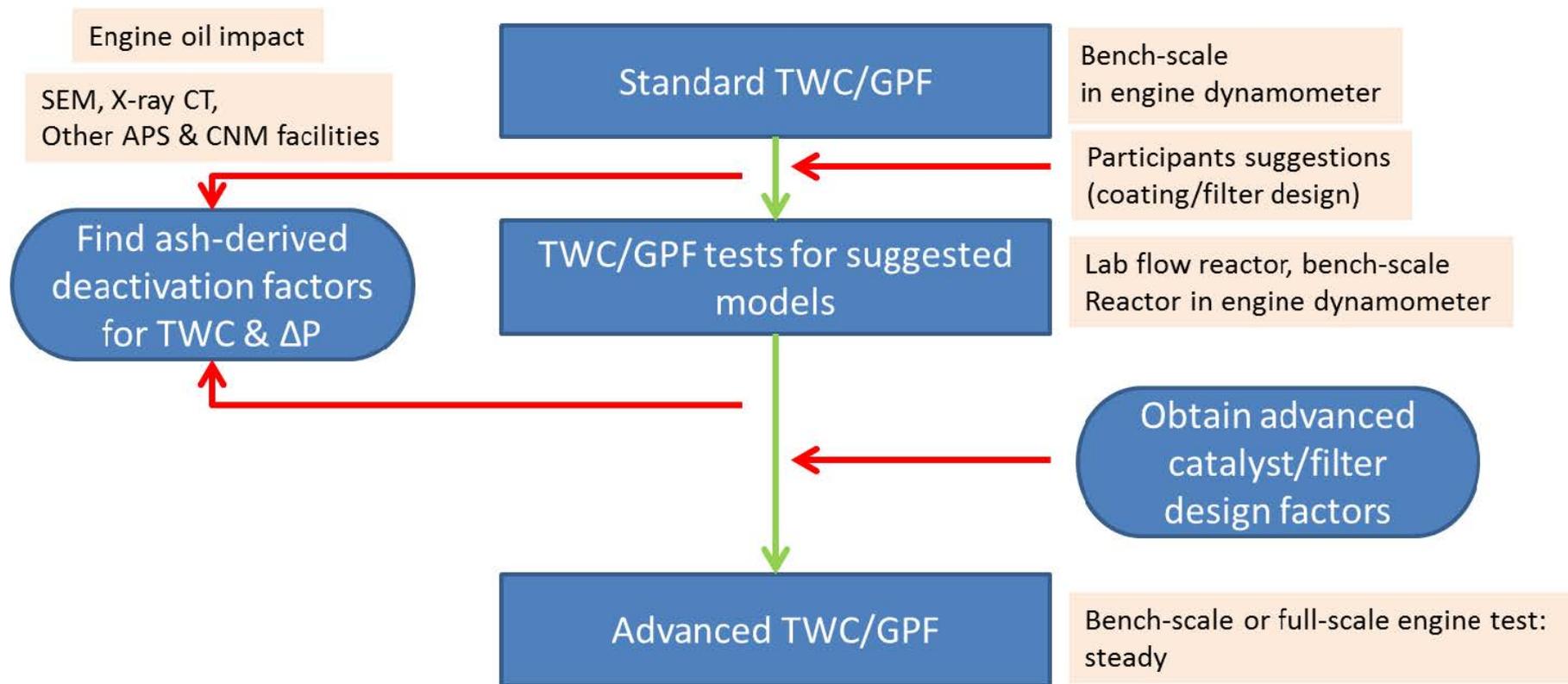
Objectives

- Project Objective
 - Understand performance of TWC/GPFs with variation of filter/coating design parameters.
 - Propose an ideal combination of filter/coating design parameters that benefits TWC performance and back-pressure increase under engine oil-derived aging conditions.
- Objectives in FY2016
 - Evaluate performance of TWC/GPFs with different filter/coating designs for gaseous and particulate emissions.
 - Examine if TWC inner-coated GPFs are deactivated with engine oil-derived ash.
 - Investigate ash distribution in the field-aged GPF and lab-aged GPFs.
 - Initiate research on ash chemistries that affect TWC functionality with chemical attack/physical block.

Milestones

Quarter, Year	Milestone Description	Status
Q1, 2016	Baseline catalyzed GPFs available for evaluation	Complete
Q2, 2016	Performance evaluation of fresh and aged baseline GPFs completed	Complete
Q3, 2016	Advanced catalyzed GPFs available for evaluation	On-going
Q4, 2016	Performance evaluation of fresh and aged advanced GPFs completed	On-going

Overall Approach

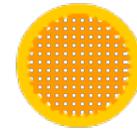
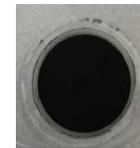


Approach/Strategy

- TWC/GPF evaluation
 - Harsh experimental conditions
 - Bench-scale flow reactor (single block down-sized TWC/GPFs)
 - Accelerated oil injection in a GDI engine
 - Coating/Filter design impact:
 - TWC loading, PGMs/OSC
 - Filter cell density & wall thickness
- Ash distribution
 - X-ray CT & tomography for overall ash loading in filters
 - Elemental mapping of wall cross-section with SEM & XRF tomography
- Potential ash inhibitors
 - Nature of ash compounds, focused on P-related ash or ash precursors
 - Ash interactions with OSC & PGMs, ash layers
 - TEM, FTIR, EXAFS and etc.



Gravimetric sampling



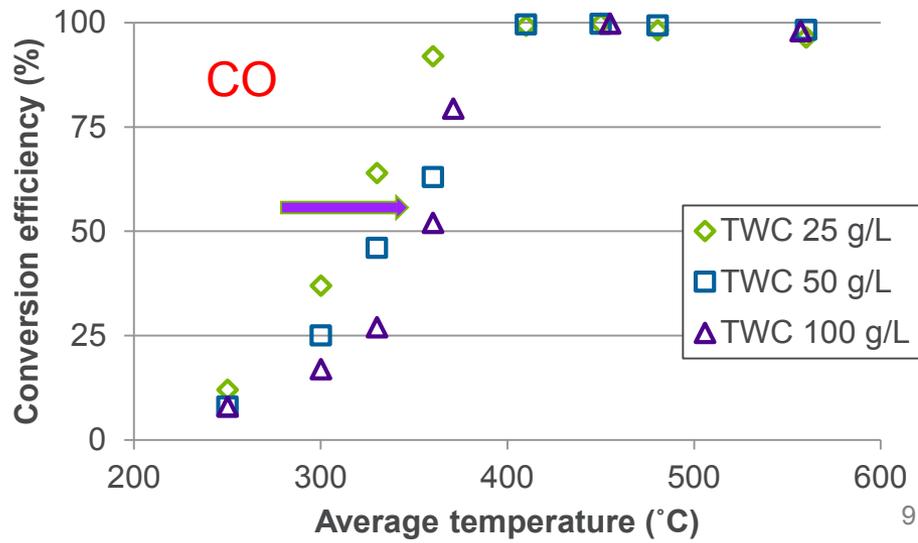
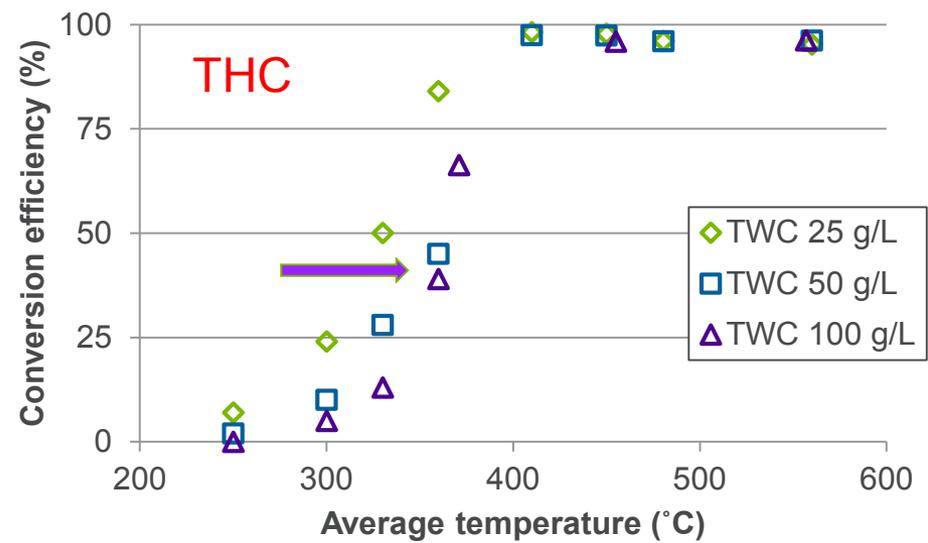
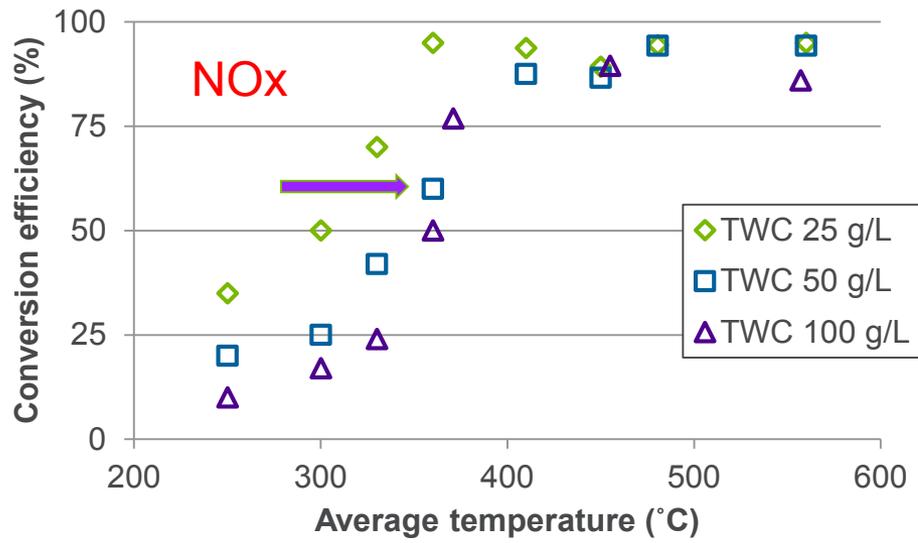
TEM sampling



Characterization of GDI soot and filter substrates
(APS, CNM, UIUC, KATECH)

Technical Achievements in FY16

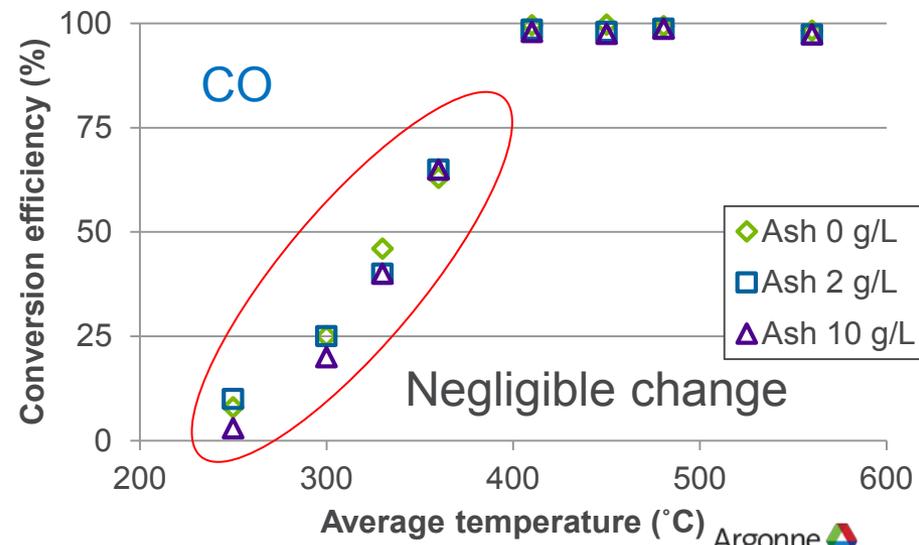
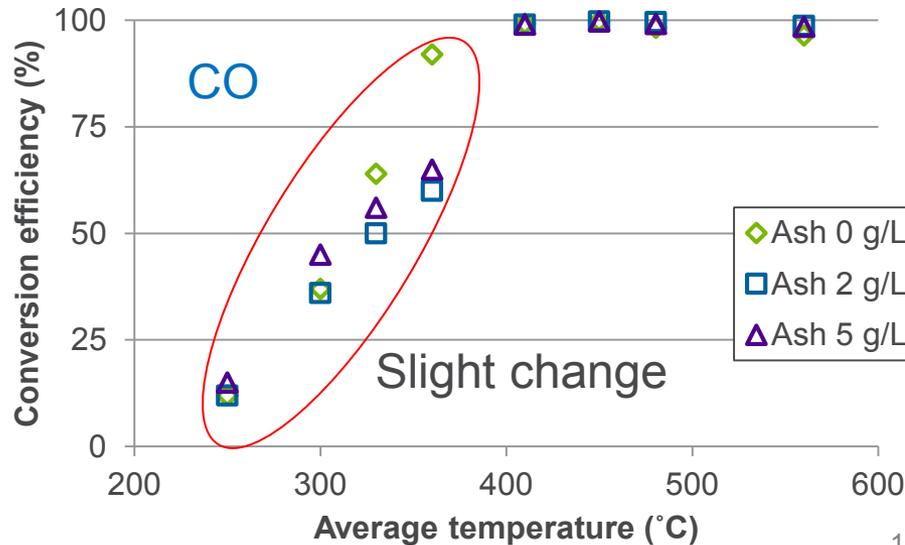
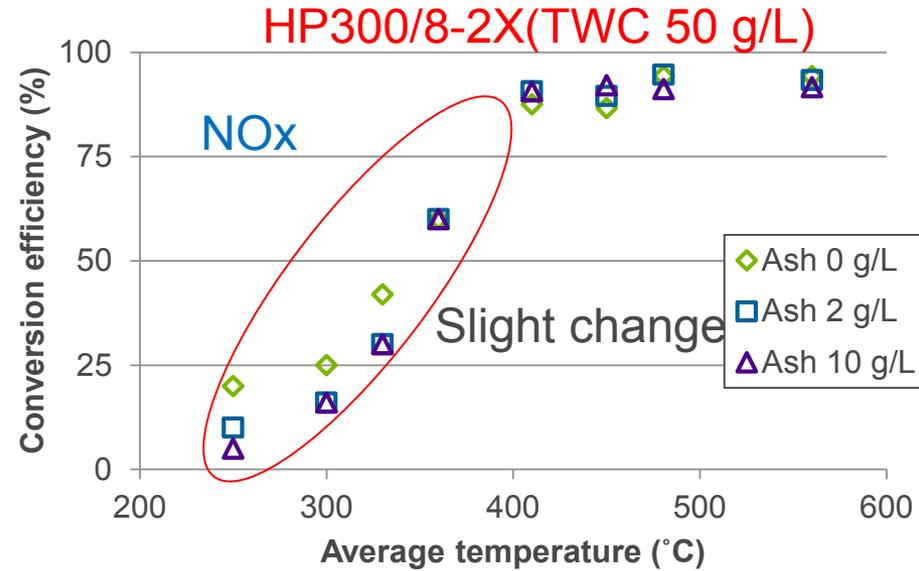
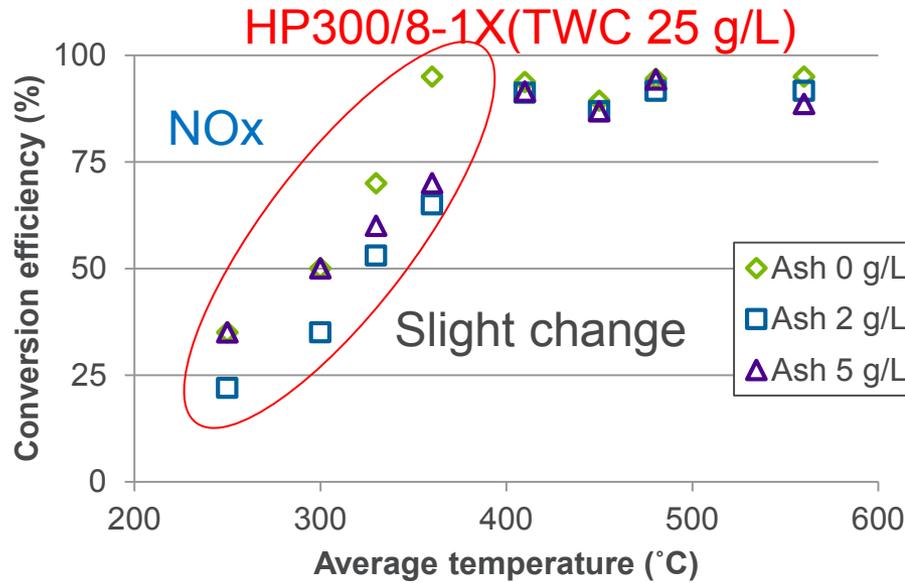
Initial TWC performance was impacted differently by TWC coating levels



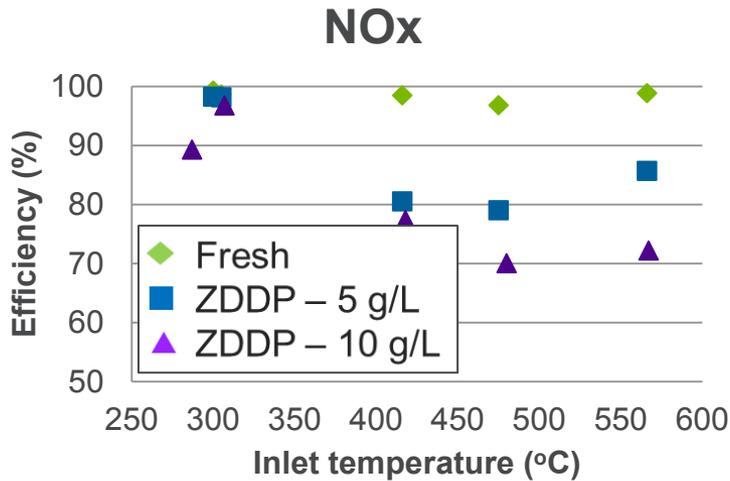
- Experiments
 - Filter: HP300/8
 - PGM: all 0.5 g/L
- With the increased TWC coating, the performance became degraded at low T.
→ PGM particle size & TWC distribution influenced the performance.

300/8-1X tends to present more decreased performance at low T with ash loading, although the decreasing level is minor

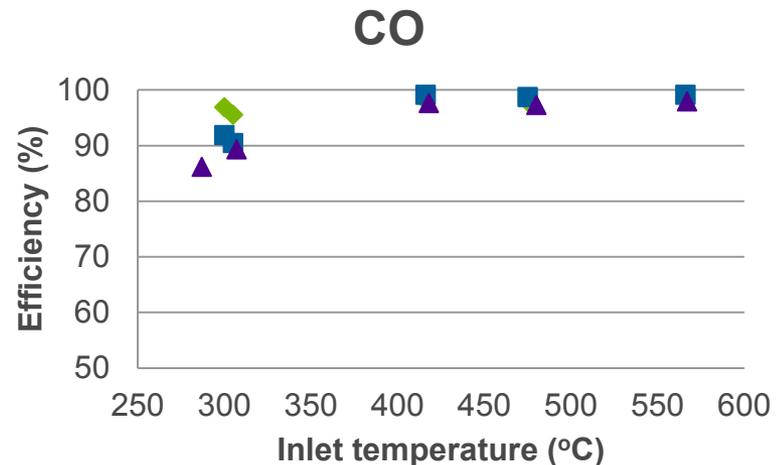
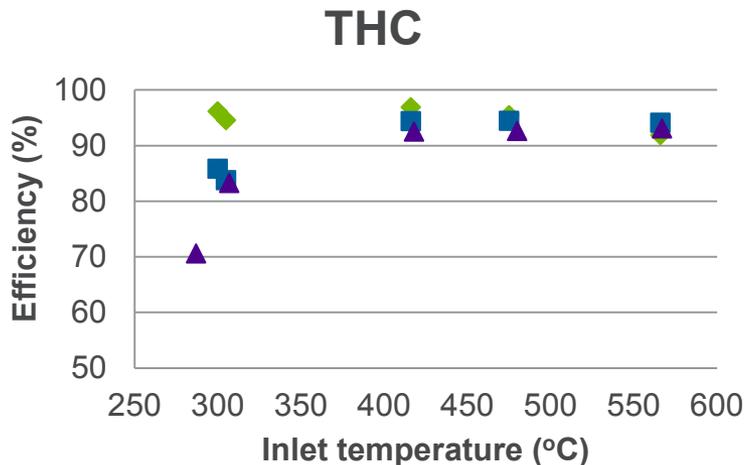
- 2% conventional oil in fuel ((Zn+P)/Ca=0.78wt.%)



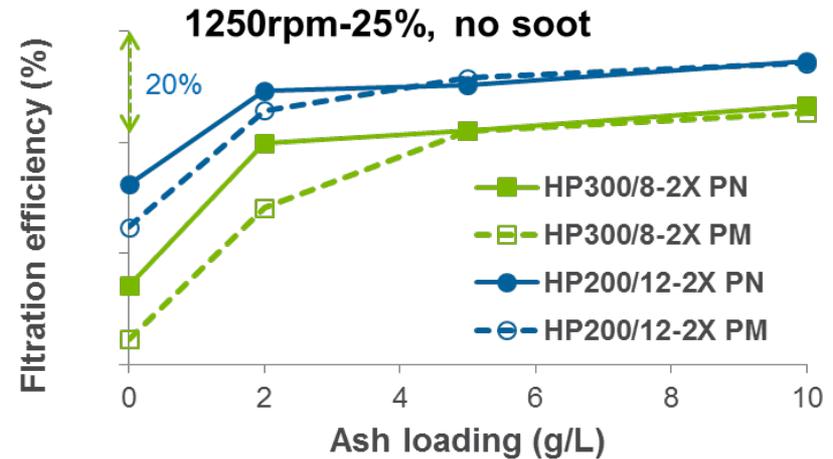
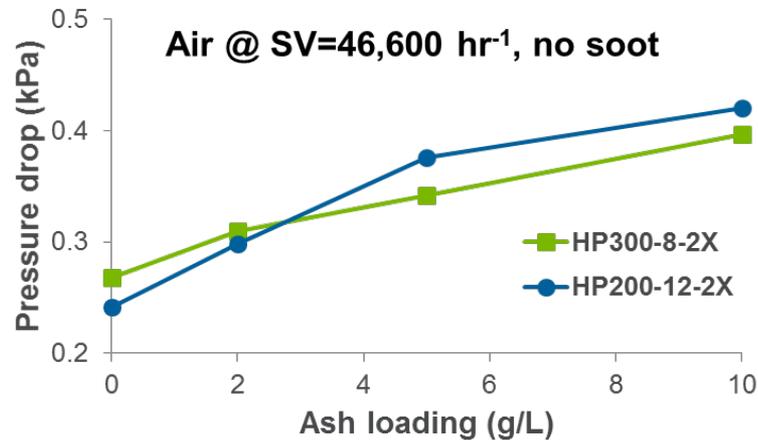
However, with ZDDP-strengthened engine oil, inner-wall coated TWC was observed to be appreciably deactivated



- Experiments
 - Accelerated oil injection: 2% in fuel
 - Filter: AC200/8
 - Formulated oil: (Zn+P)/Ca=3.1wt.%
 - With increased ash loading, decreased TWC performance was obvious, especially NOx removal efficiency.
- Confirms that ash from ZDDP affects inner coated TWC.



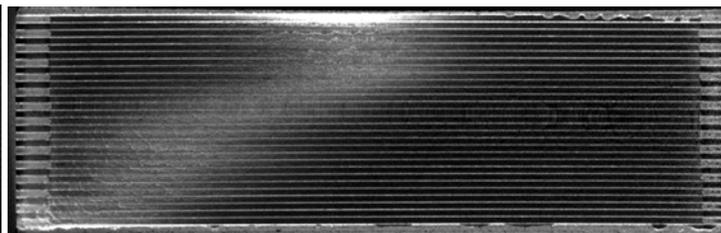
Low cell density with thicker wall appears to be advantageous in η of filtration, while showing increased ΔP



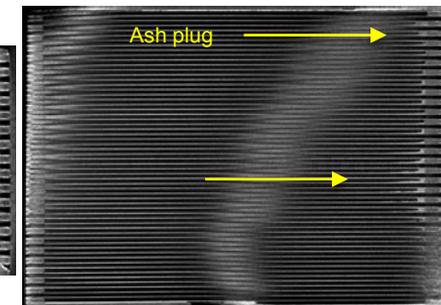
Gas flow →



200/12 (10g/L case)



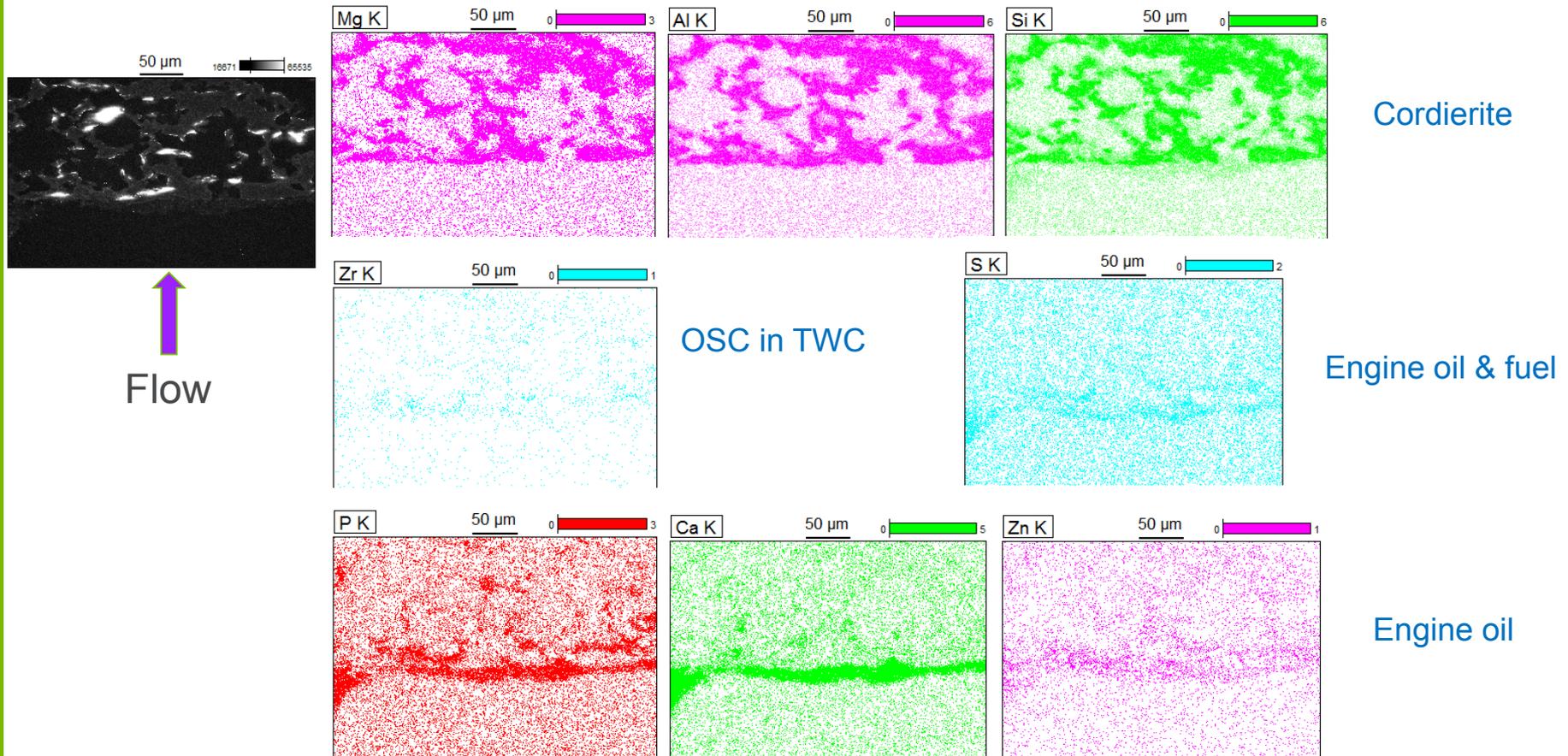
300/8 (10g/L case)



Field-aged
(100k-mi)

- Filters: prototype high porosity filters (200/12 vs 300/8)
- Catalysts: TWC inner-wall coating (50 g/L coating, 0.5 g/L PGM)
- Accelerated oil injection: conventional oil in fuel (2%)
- Ash deposits were not observed for lab-aged filters

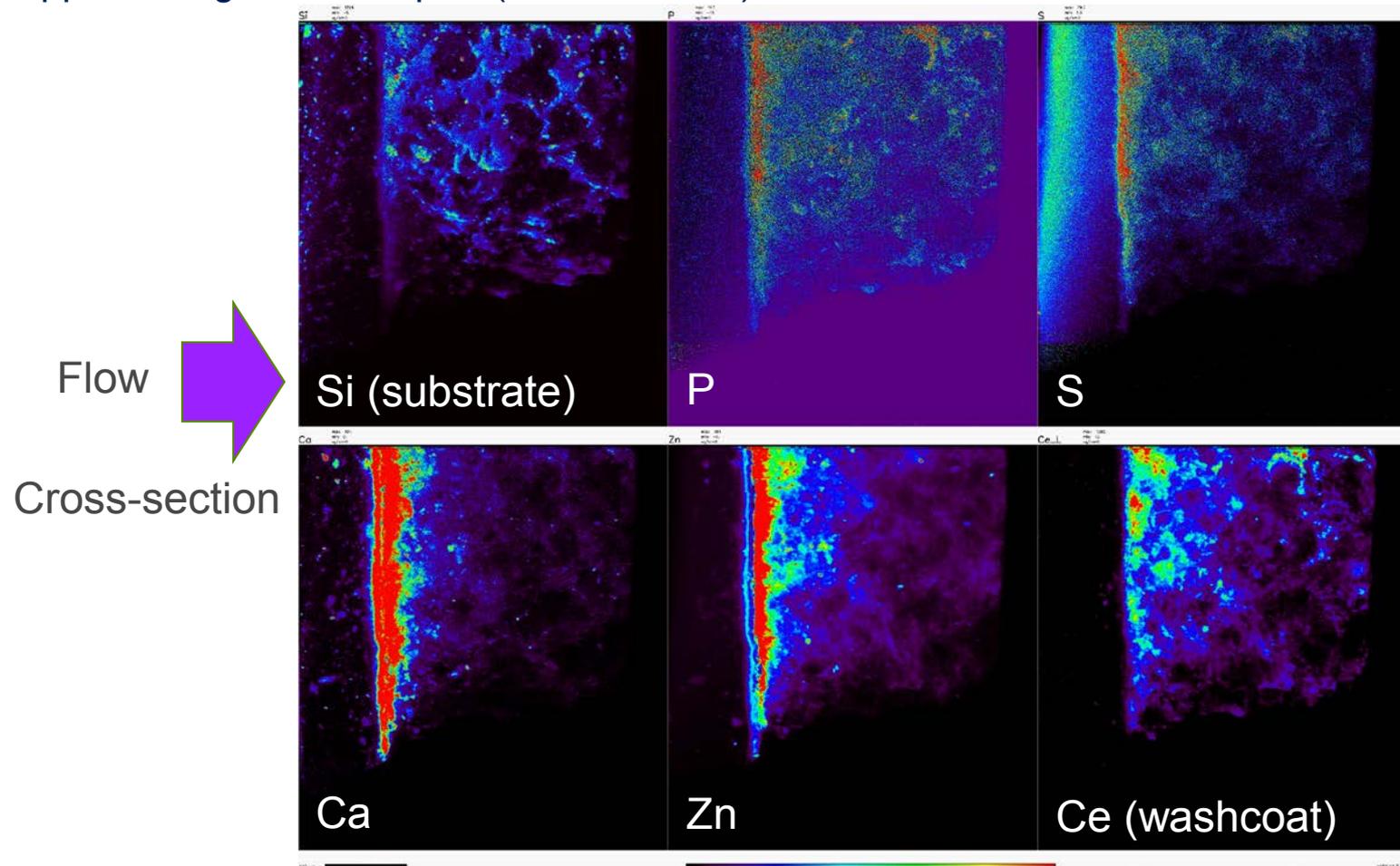
Initial mapping analysis of field-aged filter indicates low penetration of ash through wall



- Majority of ash was accumulated on wall surface
- Weak, but ash components were observed inside wall
- Will present more results of ash distribution along the path

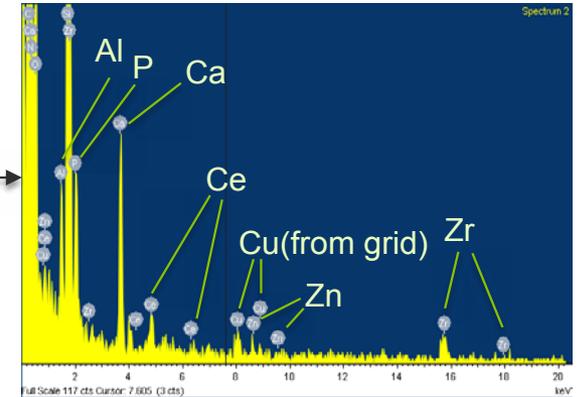
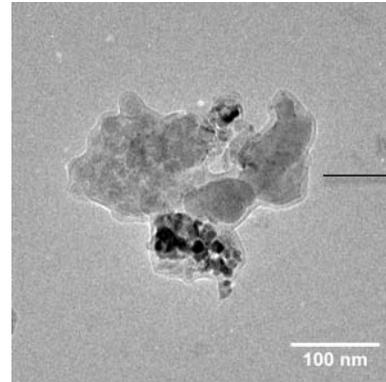
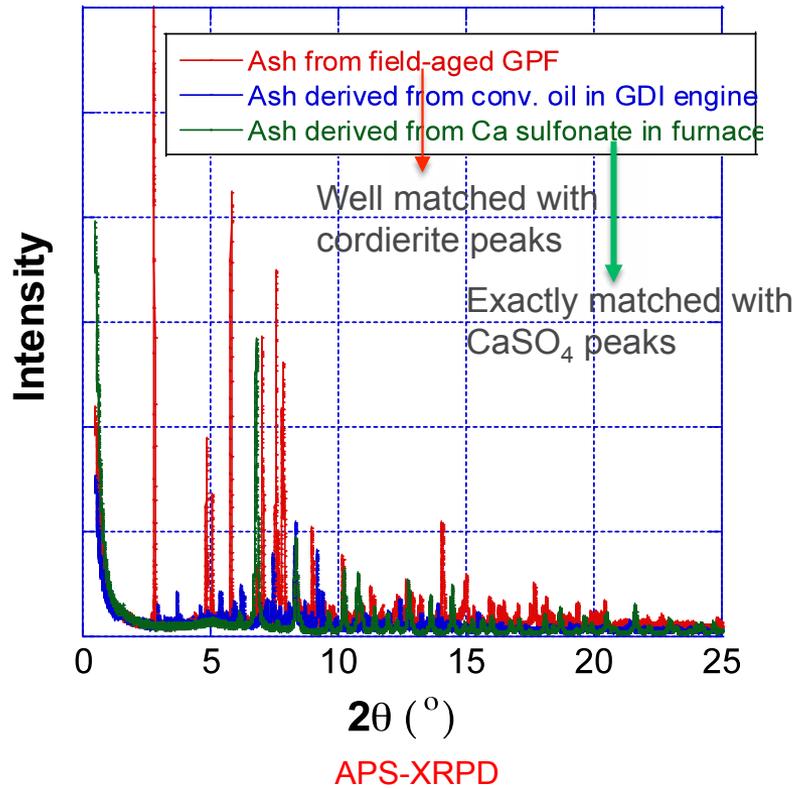
X-ray fluorescence (XRF) tomography clearly presented elemental distribution – ash penetration!

- Approx. 10 g/L, middle part (HP200/12-2X)

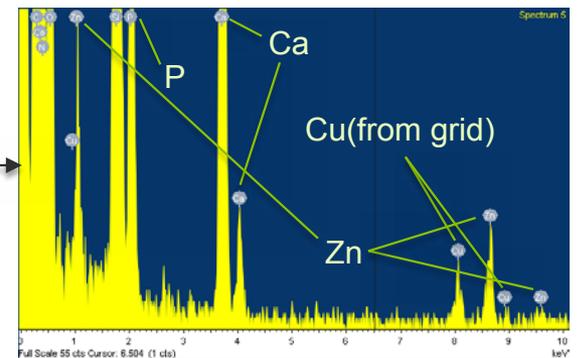
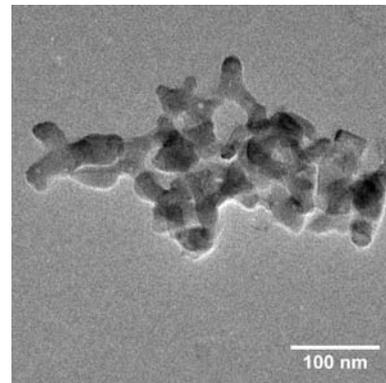


- XRF tomography showed excellent elemental distribution than SEM-EDS.
- Penetration of P & S into wall was apparent.
- Ca and Zn accumulation was limited to surface wall.

Interestingly, complex ash from GDI engines does not show the presence of CaSO_4 , which is a main component from diesel engines



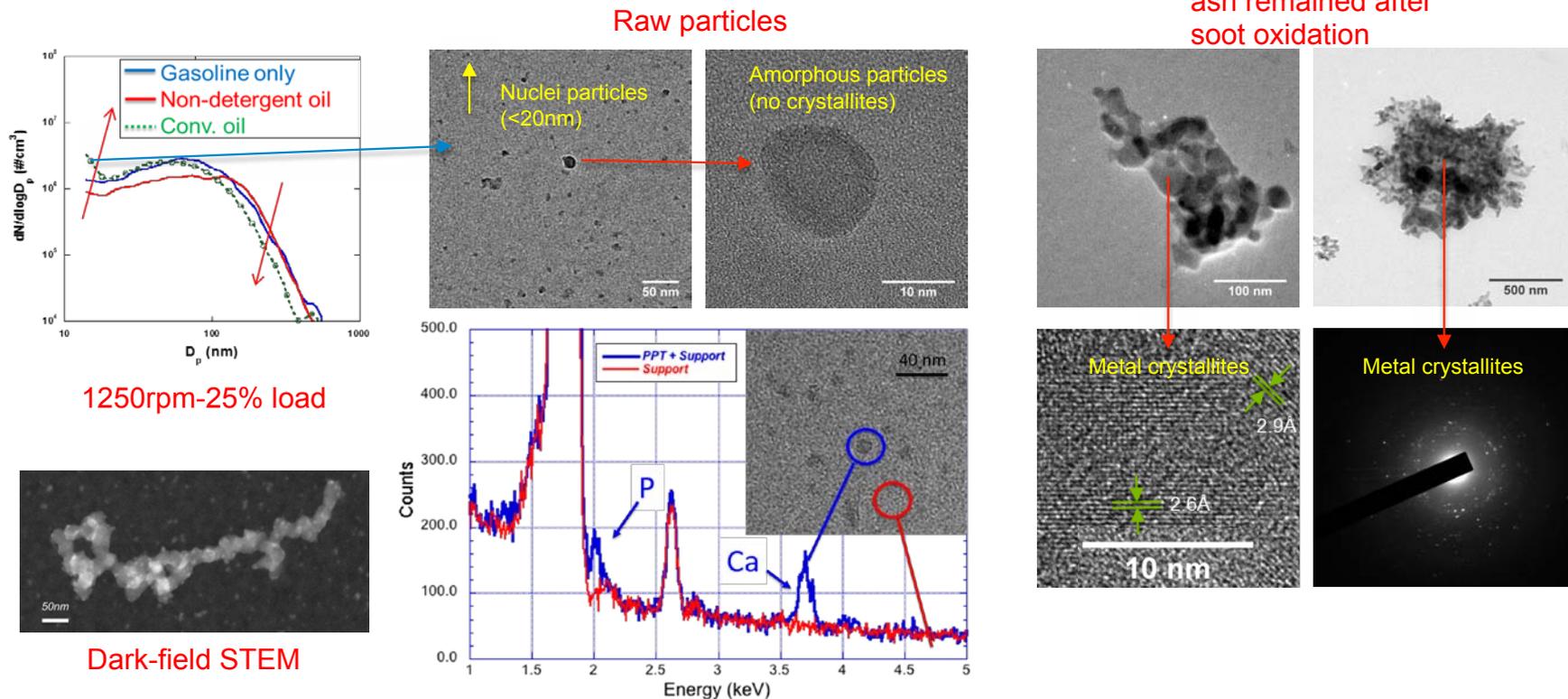
TEM-EDS result of ash taken from a field-aged GPF



TEM-EDS result of ash derived from engine oil in GDI engine

- Typical ash chemicals from diesel engines, CaSO_4 , $\text{Ca}_3(\text{PO}_4)_2$ and etc., are not detected.
- This result is not consistent with Ford (SAE 2016-01-0941)
→ Will continue to show convincing data.

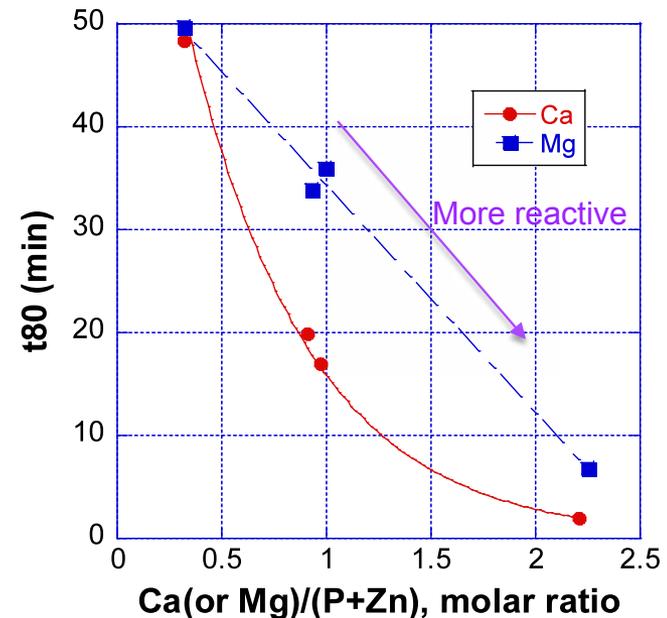
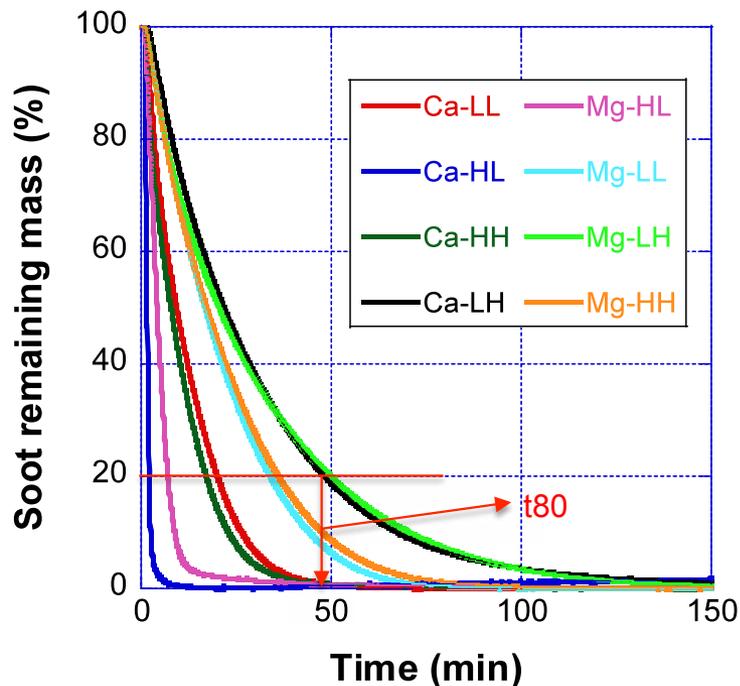
Amorphous nuclei particles from engine oil might have phase transition into crystalline agglomerates with oxidation



- The nature of nuclei particles derived from engine oil has been rarely examined.
- While most nuclei particles in the sub-20-nm were observed to be amorphous metal particles, ash agglomerates in the sub-micron were metal crystallites.
 - Suggest phase conversion from amorphous into crystalline state during oxidation
 - Major elements of sub-20-nm particles were observed to be P and Ca
 - Need more investigation when the engine is run at high speed & load
 - Will inform ash chemistries affecting TWC functionality

Collaboration with Afton Chemical proposes that ash chemistries have a strong impact on soot oxidation, which may provide insights into TWC deactivation

Experimental Oil samples (Afton provided)	Ca-LL	Mg-LL	Ca-LH	Mg-LH	Ca-HL	Mg-HL	Ca-HH	Mg-HH
Boron, ppm	180	180	180	180	180	180	190	180
Calcium level	Low	-	Low	-	High	-	High	-
Magnesium level	-	Low	-	Low	-	High	-	High
Phosphorus level	Low	Low	High	High	Low	Low	High	High
Zinc level	Low	Low	High	High	Low	Low	High	High
Sulfated Ash, %	0.56	0.51	0.65	0.63	1.02	0.93	1.1	0.96
Ca/(P+Zn) or Mg/(P+Zn), molar	0.91	0.93	0.32	0.32	2.21	2.25	0.97	0.97



Responses to FY15 Reviewer Comments

- This is a new project starting from October, 2015.
- However, the project was created based on the previous CRADA project performed between 2013 - 2015. The related comments are addressed.

Comments	Answer
Chemical/physical mechanism about why Ca presence would enhance soot oxidation	Originally CaSO_4 , which is a major ash compound from diesel engines, was thought to enhance soot oxidation due to the redox capability of S from S K-edge XANES. However, it was not found in GDI ash based on many characterization tools. CaO would be a candidate and the study of its presence is on-going concerning impacts of ash chemistries.
More regular technical interactions among the partners	More frequent conference calls & e-mail contacts have been made to discuss results & future directions
Knowledge on catalyst wash-coat, soot and ash distribution profiles, especially for the field aged filters	X-ray CT & XRF tomography have been used. We will be address comprehensive results in the following years.

Collaborations

Collaborating Partners

- *Corning Incorporated*
 - Filter supply & consulting
- *Hyundai Motor Company*
 - GDI engine and open ECU for full control
 - Technical advice on test results & catalyst-coated samples from the previous CRADA

Other Internal and Outside Partners

- *Korea Automotive Technology Institute (KATECH)*
 - X-ray CT analysis of filters
- *Afton Chemical*
 - Collaboration for ash study using experimental oils
- *University of Illinois at Urbana-Champaign*
 - User agreement for XPS and SEM-WDS
- *User Facilities at Argonne (Advanced Photon Source & Center for Nanoscale Materials)*
 - XRF tomography, X-ray microtomography, TEM, Raman, FTIR and SEM-EDS

Remaining Challenges and Barriers

- TWC/GPFs were shown to be vulnerable toward ZDDP components in this work, but their noticeable deactivation has not been reported by others
 - More samples will be carefully examined.
- Potential P-derived ash inhibition needs extensive investigations
 - Two potential deactivation mechanisms
 - P-derived ash or precursors that reach coating materials inside wall
 - Ash layers on surface wall that block/delay gaseous adsorption on catalysts
- Understandings of ash distribution, chemistries and their nature are insufficient in GPFs
 - Pore-level ash distribution has been rarely studied in terms of 3-D tomography.
 - Detergent/ZDDP ratio, engine operating conditions may impact differently.

Future Work

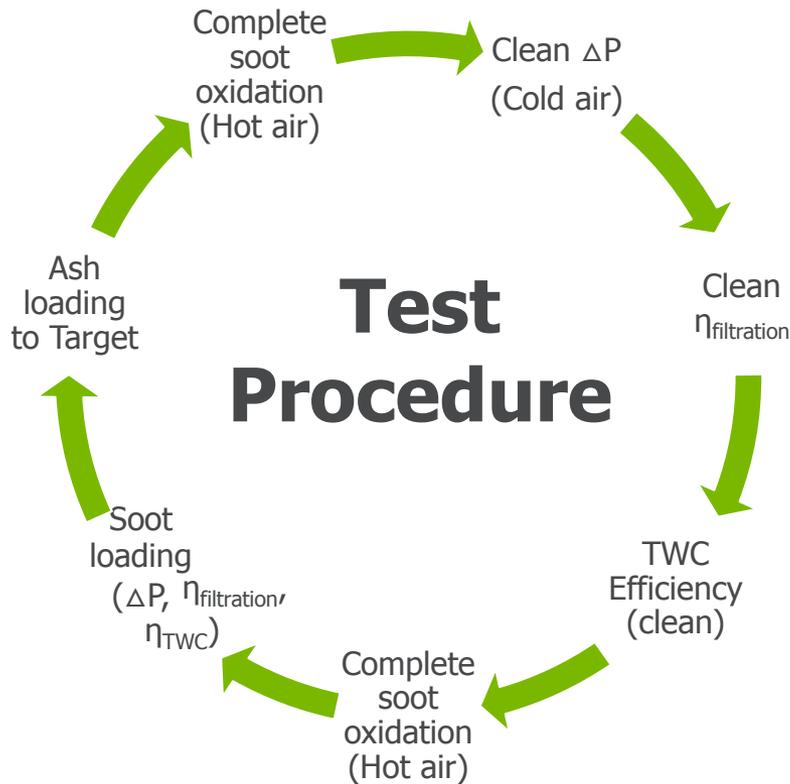
- Examine TWC/GPF performance over engine-oil derived ash loading
 - Different TWC/GPF types & PGM/OSC levels
- Investigate potential TWC deactivation mechanism
 - Kinetic study with aged core-filters using a lab-scale flow reactor
 - Elemental mapping analysis of ash-loaded filters with XRF tomography at APS & SEM-WDS at UIUC to examine ash distribution
 - High-resolution X-ray tomography at APS to examine pore-level ash distribution in filters
 - Ash chemistries relating to deactivation mechanism

Conclusions

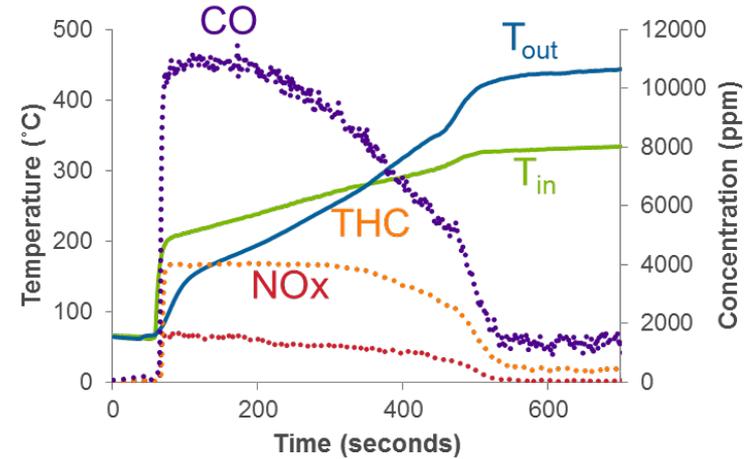
- Inner-wall coated TWC on GPF experienced deactivation with ZDDP-derived ash
 - TWC performance decreased appreciably by ash derived from ZDDP-intensified oil
 - However, TWC deactivation was minor with conventional engine oil-derived ash
- TWC/GPF performance with ash loading was design-dependent
 - Under the same amount of TWC loading, filter design of high cell density with thinner wall was found to be low filtration efficiency, despite lower ΔP increase
 - Will show TWC performance with ash loading
- X-ray CT indicates that ash loading was inclined toward end plugs as others reported, probably because continuous regeneration occurred
- P penetration into wall was observed, but more investigation is required along the path to better understand potential deactivation mechanisms.
- GDI ash chemistries, which seem to be different from those from diesel engines, need more studies concerning ash inhibition impacts on TWC performance and ash formation process in GPFs.

Technical Back-up

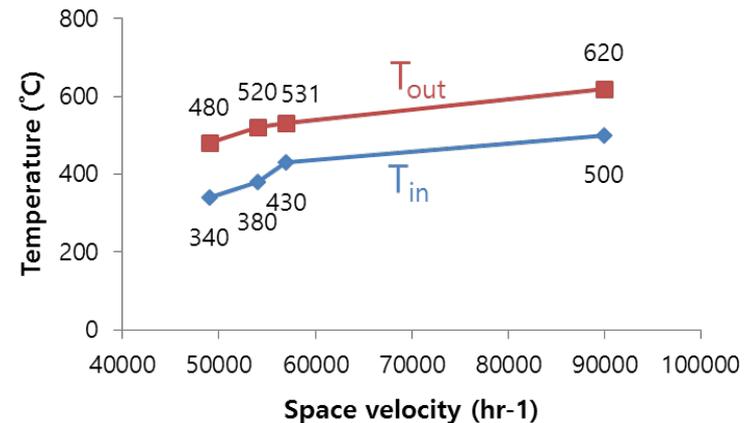
Engine tests were performed systematically for fair comparisons based on prepared engine test procedure



LOT test 1,500rpm-25%
17 kg/hr (SV 46,000 hr⁻¹)

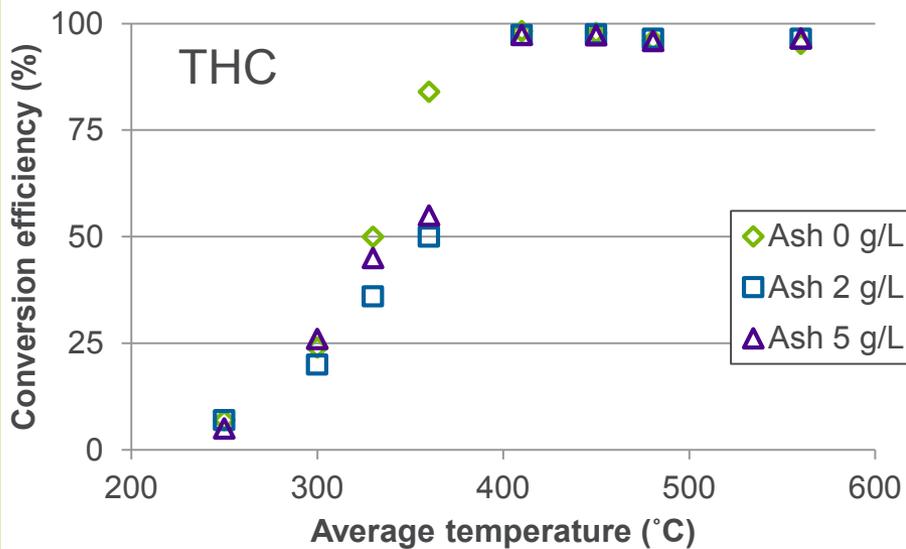


Steady state TWC test

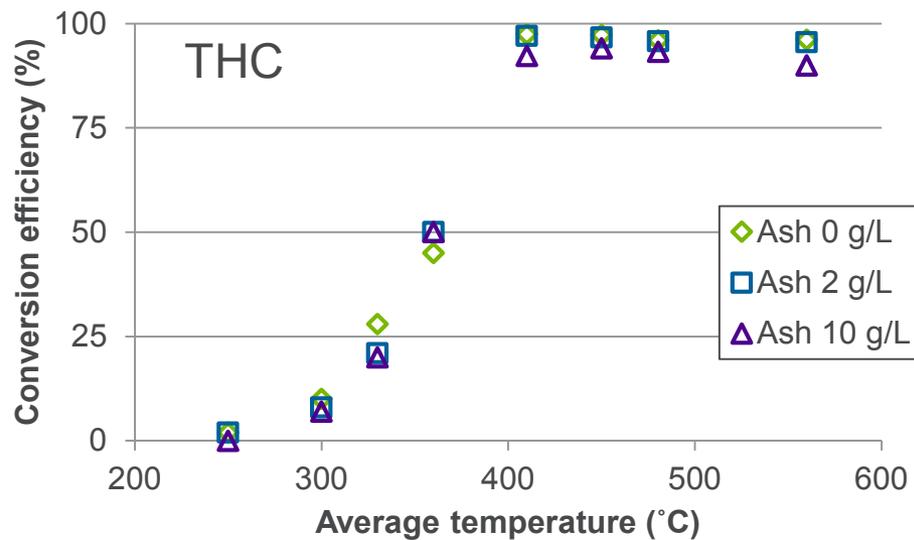


Additional data for page 10

HP300/8-1X(TWC 25 g/L)

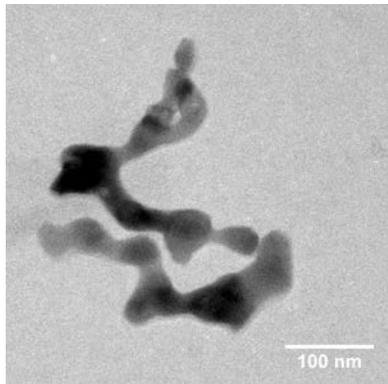
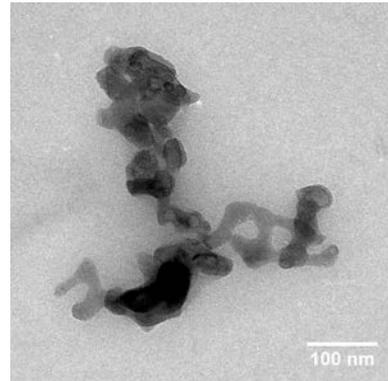
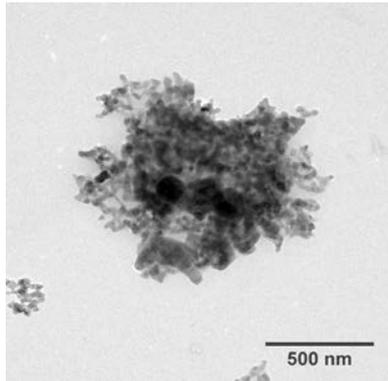


HP300/8-2X(TWC 50 g/L)

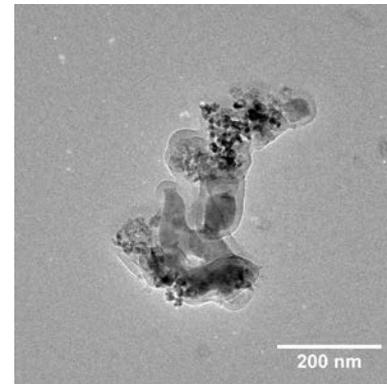
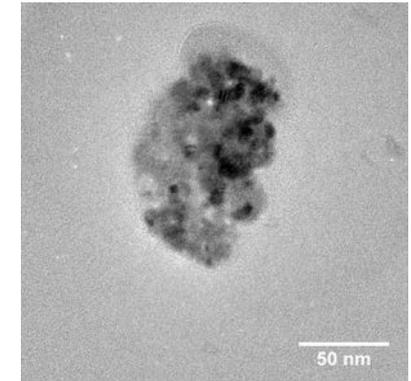
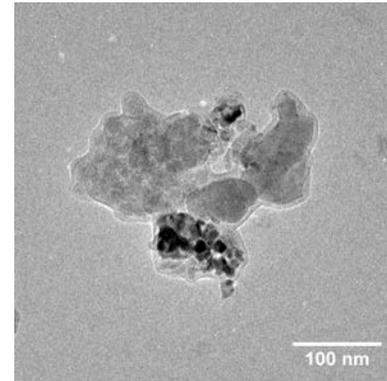


Ash aggregates consist of the form of fused and segregated particles

Ash derived from PM collected from the engine exhaust

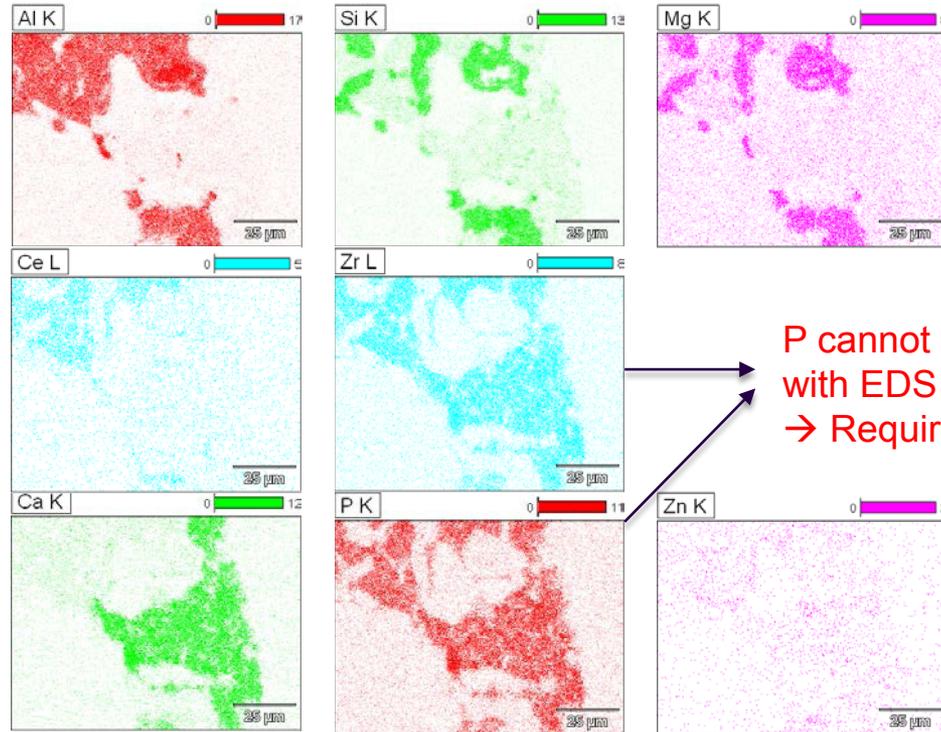
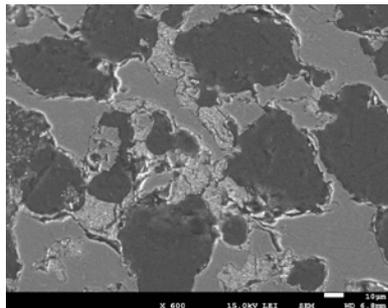
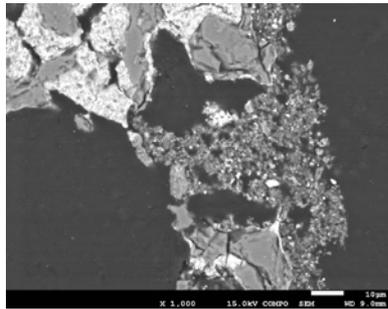


Field-aged ash collected from a GPF



- Somehow ash primary size is below 20 nm, when ash particles are distinct.

WDS is required to differentiate P from Zr because both elements are overlapped in energy levels



P cannot be distinct from Zr with EDS
→ Require WDS