Characterization of Field-Aged Exhaust Gas Recirculation Cooler Deposits

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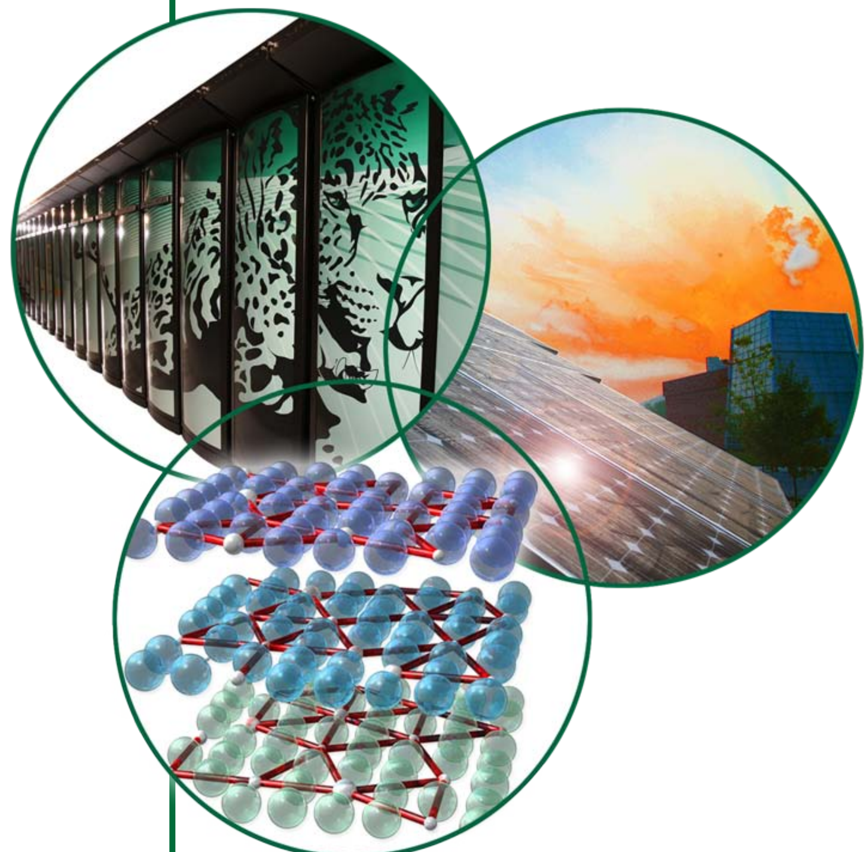

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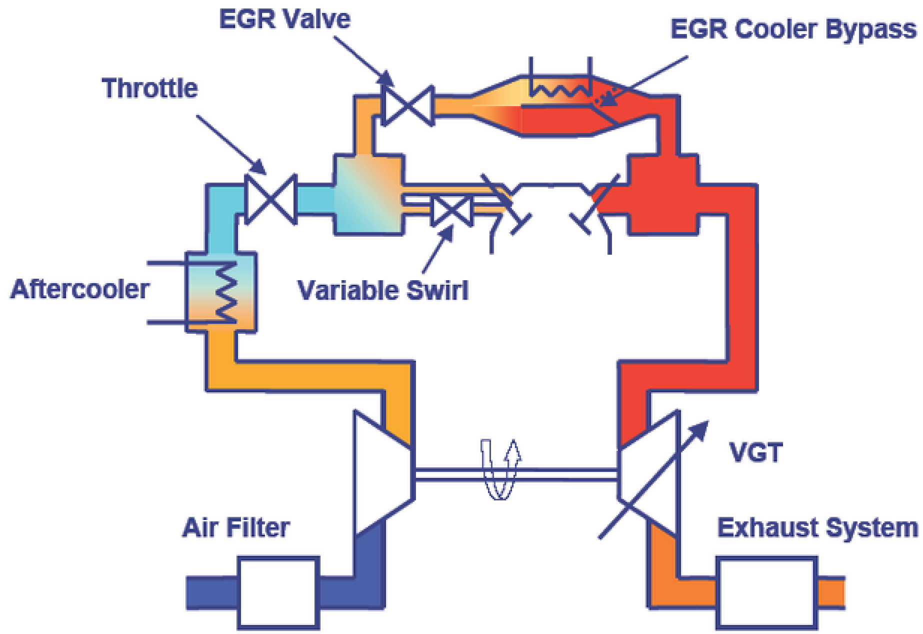
DOE-Funded Project (through Propulsion Materials):
Materials Issues Associated with EGR Systems

- **Feb-09 Milestone: An advisory team consisting of chief engineers responsible for EGR systems from nine Diesel Crosscut Team members was assembled:**
  - **Caterpillar, Cummins, Detroit Diesel, Ford, GM, John Deere, Navistar, PACCAR, Volvo/Mack.**
  - **Newer Members: Modine and DAF Trucks.**
- **Feb-09 Go/No-Go Decision**
  - **Surveyed EGR Team Members as to what the greatest materials issues are relating to EGR systems. The survey results clearly indicated EGR cooler fouling as the primary concern**

	Problem	
Component	***Fouling***	***Corrosion***
(HP) EGR Cooler	#1	
(HP) EGR Valve	#2	
(HP) Flow Meter		
(LP) EGR Cooler		
(LP) EGR Valve		
(LP) Flow Meter		
(LP) Charge-air Cooler		

Background: Exhaust Gas Recirculation Cooler Fouling



- High-pressure EGR is the dominant NO_X-reduction technology.
- Exhaust gas laden with PM flows through the EGR cooler which causes deposits to form through thermophoresis and condensation.
- The deposit thermal conductivity is very low, which reduces the effectiveness of the EGR system.
- Increasing demands placed on the technology by more stringent NO_X emissions, advanced combustion, increasing use of non-petroleum-based fuels, and engine/aftertreatment system optimization requirements are leading to expansions of the technology into operational conditions that are relatively unknown or known to be problematic.

Project Objective: Provide information to industry EGR specialists about fouling deposit properties

- Characterize the thermo-physical properties of the deposit under different operating conditions on model EGR cooler tubes.
- Determine the long-term changes in deposit properties due to thermal cycling and water/HC condensation.
- Enable improved models and potential design improvements to reduce fouling and its impact on performance.
- Possibly develop a protocol for regenerating the EGR cooler during use.

Progress FY2010

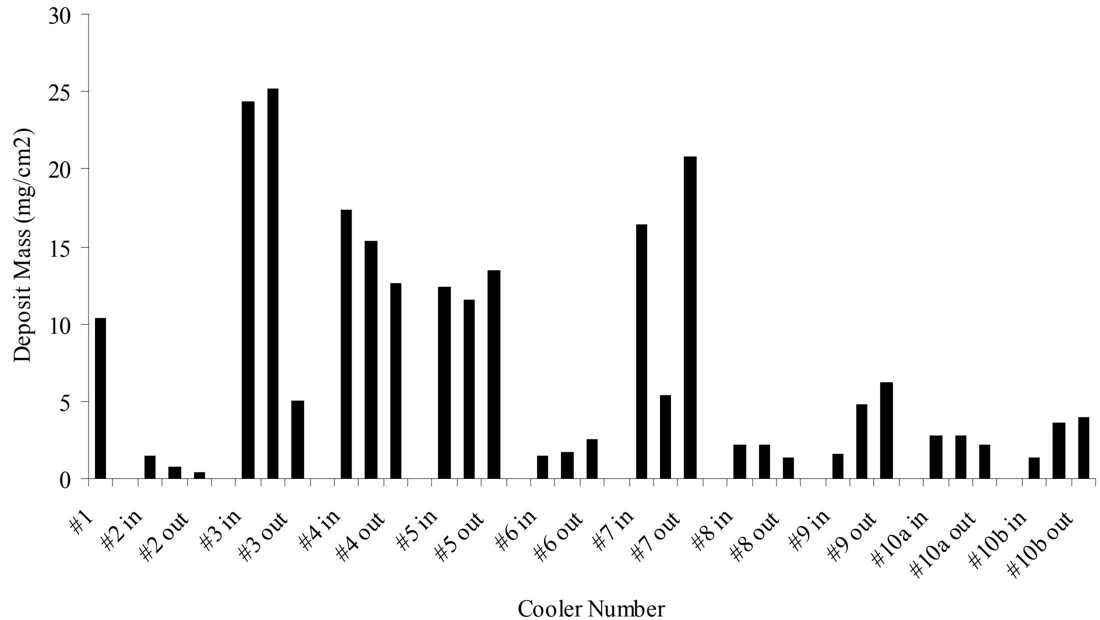
- **Task 1: Experimental Setup**
  - A GM 1.9 L engine on a Drivven controller is operational in standard and PCCI modes.
  - Deposit will be formed on model cooler tubes with the coolant flow and temperature controllable using an external loop.
  - Samples generated by the engine will be aged in a tube reactor.
- **Task 2: Obtain and Evaluate Representative (Half-Useful-Life) EGR Coolers from Industry Members**
  - Seven companies have provided eleven coolers for analysis.
  - This will provide a reference point that will guide our future research.
  - It will also provide an opportunity to refine effective characterization tools:
    - Microstructural Analysis: SEM, Electron Microprobe, Optical Microscopy
    - Chemical Analysis: EDS, FTIR, XPS, Raman, GC-MS, XRD
    - Thermal Analysis: Thermal Conductivity, TGA/DTA
    - Neutron Tomography

Deposit Mass per Area

Industry-Provided Coolers

Cooler #	*Miles*	*Hours*	*Condition*	*Heat Transfer Surface Area (m^2)*
1	280000		Field Aged	1.29
2			Dyno-cell	2.84
3			Dyno-cell	0.51
4			Dyno-cell	0.90
5	89478		Field Aged	1.04
6	113764		Field Aged	1.09
7	249128		Field Aged	4.38
8		315	Dyno-cell	1.50
9		1389	Field Aged	1.10
10a	140000		Dyno-cell	0.46
10b	140000		Dyno-cell	0.46

Mass per Unit Area (mg/cm^2)



- Mass of deposit was measured by heating ¾ inch long sections of tube near the inlet, middle and outlet at 600 C, cleaning them and measuring weight change.
- With the exception of #4 & #7, the trends were confirmed with optical microscopy.
- There was no consistent trend between all of the coolers in the change in deposit mass along the length.

Hydrocarbon Analysis

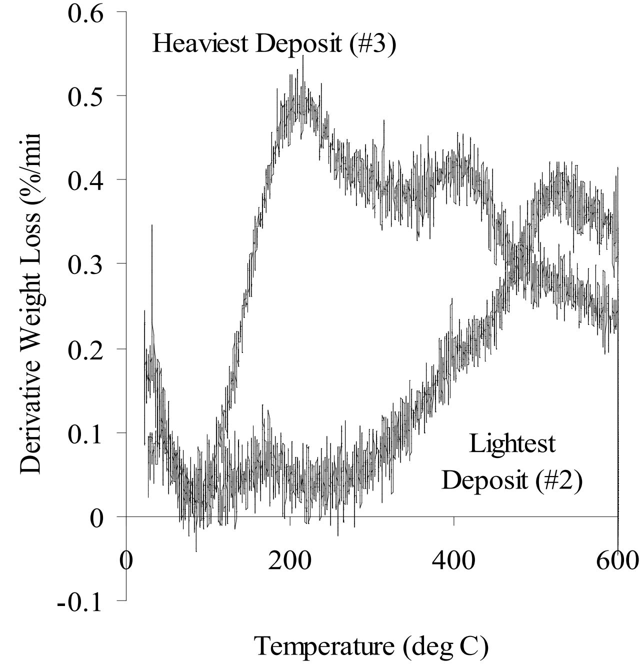
Gas Chromatography-Mass Spectrometry (GC-MS)

Mass (in ng/µg) of 4 common HC Species

Cooler #	*naphthalene*	*nonadecane*	*pentacosane*	*naphthalenic anhydride*
1	0.0	0.3	0.0	0.2
2	0.6	0.2	0.5	0.0
3	18.0	8.4	0.0	5.4
4	0.4	1.5	0.6	0.6
5	11.0	87.8	49.6	0.0
6	0.5	1.6	1.1	0.4
7	0.0	3.9	0.0	0.2
8	0.1	0.3	2.7	0.1
9	0.9	0.1	0.0	0.3
10a	0.0	1.7	0.0	1.0
10b	0.0	0.0	0.0	0.0

Thermal Gravimetric Analysis (TGA)

Mass Loss Rate vs. Temp in Argon



- Naphthalene and nonadecane correspond to aromatic and alkane species in diesel fuel; pentacosane = oil; naphthalenic anhydride = partially oxidized fuel.
- Mass loss was first measured in argon up to 600°C (volatiles), then in air up to 700°C (non-volatiles).
- Coolers #3 and #5 had significant hydrocarbon devolatilization between 120 and 350°C which suggest the presence of fuel and/or oil components in these deposits.

Energy Dispersive Spectroscopy (EDS) for Element Concentration

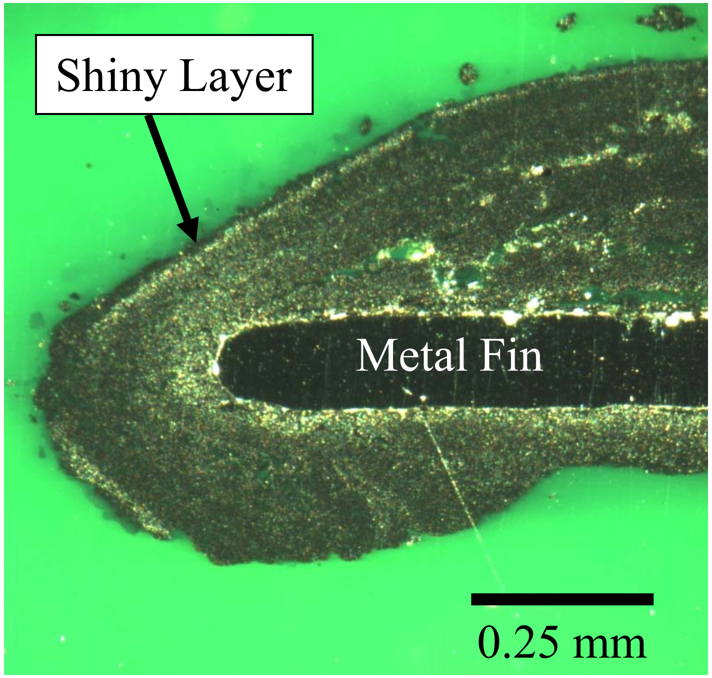
Cooler #	*C*	*O*	*S*	*Fe*	*Si*	*Cr*	*Na*	*K*	*P*	*Ca*
1	50.1	32.4	10.7	4.9						
2	87.0	12.1								
3	82.3	17.3								
4	85.7	12.8								
5	76.1	11.0	0.2	9.0	0.1	2.8				
6	83.5	15.3			0.3					
7	14.0	44.0	0.2		29.5		6.7	2.0	0.6	1.3
8	83.7	13.9	0.4		0.1					0.7
9	32.8	39.0	14.3	10.8	0.4	1.2				
10a	85.8	13.3	0.3							
10b	83.5	16.0								

Standardless Values in Wt%

- Powder collected from the coolers was put into an SEM and the X-ray spectra measured using EDS.
- Coolers #1 & #9 had large amounts of sulfur and iron. These two were the only coolers that exhibited evidence of corrosion.
- Cooler #7 had elements common in dirt (Si, Na, Ca, K, P).
- Corrosion results were independently confirmed by X-ray Diffraction.

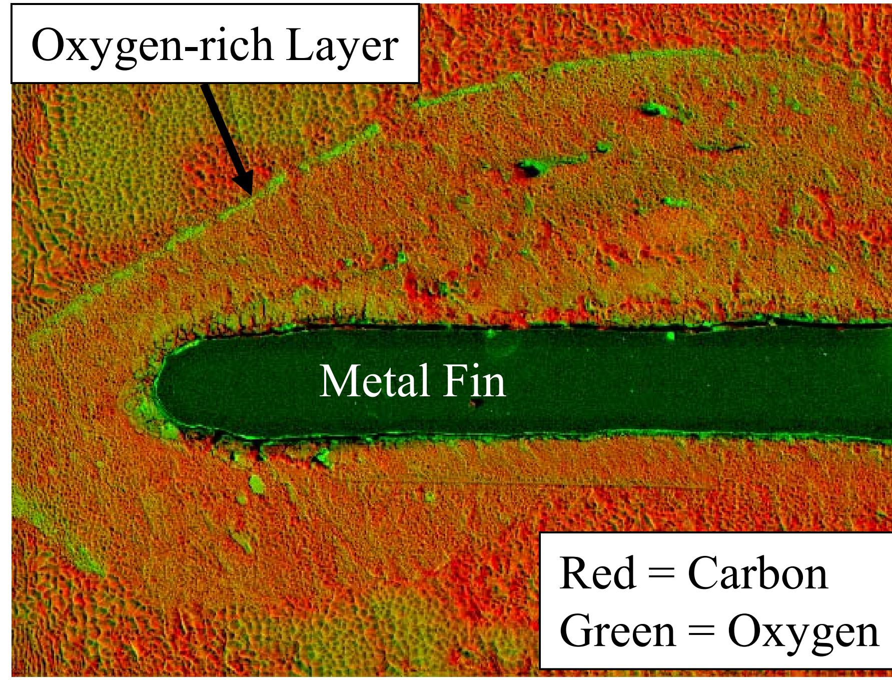
Location of Hydrocarbon in the Deposit (Cooler #3)

Optical Microscopy



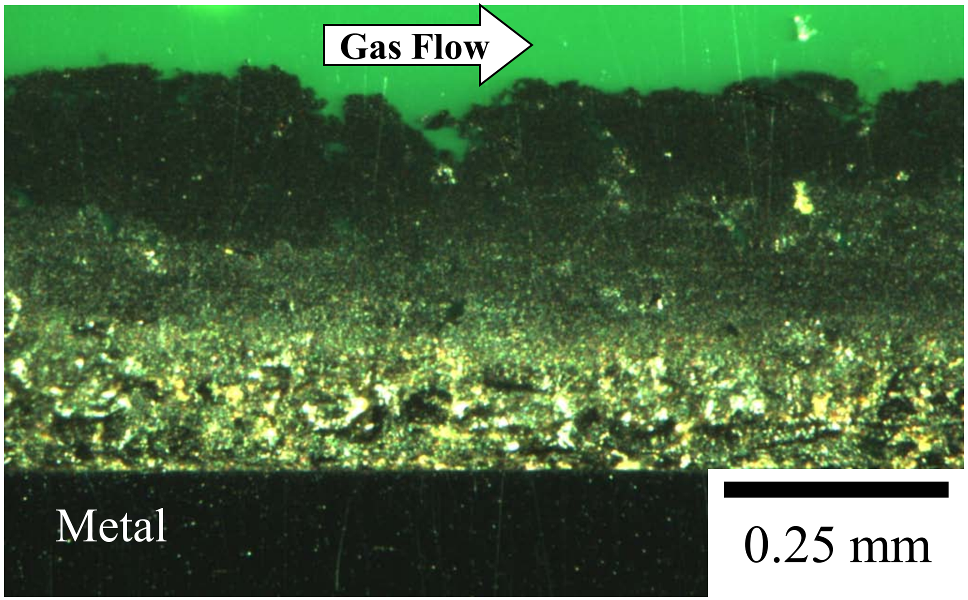
= (Same Area)

Electron Probe Microanalysis (EPMA)



- This epoxy mounting technique is useful for seeing the interaction between the tube geometry and the deposit and seeing where the HC is distributed throughout the deposit cross-section.
- As the black soot is covered in HC, its reflectivity increases, providing contrast when using optical microscopy.
- This technique is NOT useful for determining deposit thickness since the epoxy tends to collapse the soot microstructure.
- The shiny layer on the outer edge of the deposit contains more oxygen than the rest of the deposit (as measured by EPMA). This suggests it has a high HC content.

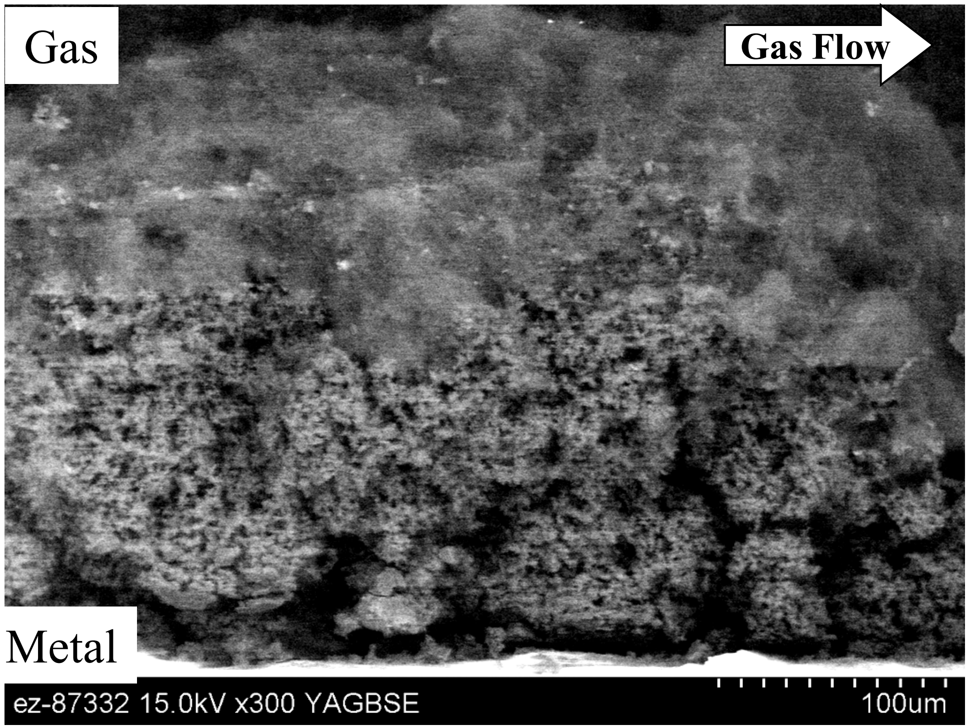
Hydrocarbon Condensation (Cooler #4)



- A common feature of most of the coolers is the higher HC concentration at the metal. This is seen here by the increasing reflectivity near the metal.
- This is caused by a thermal gradient across the deposit with lower temperatures near the metal which allows heavy HC species to condense.
- More HC condensation was observed near the outlet than the inlet on most coolers.
- HC may be beneficial in low amounts by causing the deposit to be denser.

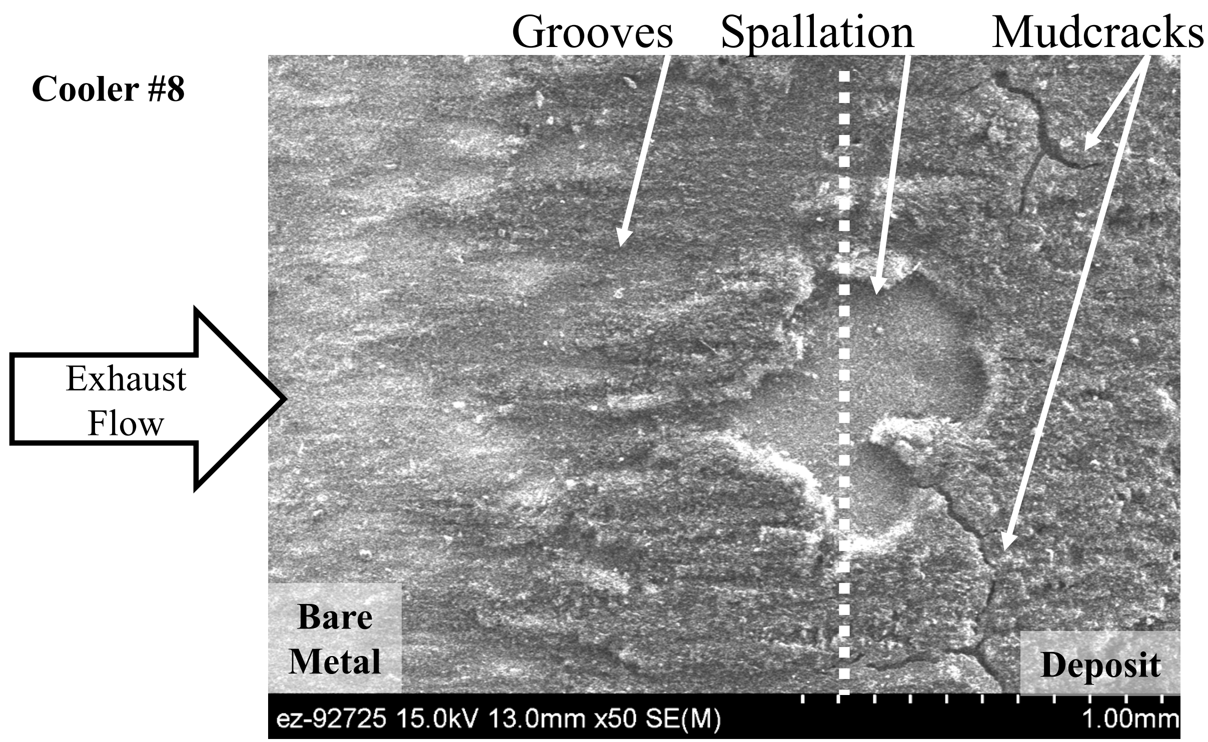
Effect of HC on Microstructure (Cooler #6)

Back-scattered Electron Image



- The back-scattered electron images are good for identifying local regions of higher density.
- There appear to be two distinct regions in the deposit cross-section: a coarse HC-rich region near the metal and a fluffy dry region near the exhaust gas.
- The condensing of HC on the PM appears to collapse the porous structure of the deposit causing it to be denser and therefore more thermally-conductive.

Three Common Removal Mechanisms



Dashed line indicates the peak of the sinusoidal fin.

1. Longitudinal **Grooves** form on the leading edge of the turbulation structure (here a sinusoidal wave down the length of the cooler). These grooves could be formed by debris hitting and eroding the deposit propelled by the exhaust gas. This debris may then roll along the deposit, collecting more deposit forming a groove.

2. **Mudcracking** which will form as the deposit shrinks in the plane of the metal substrate presumably due to hydrocarbon and water condensation. Conversely, mudcracks may also form during drying of the deposit after the engine is turned off.

3. **Spallation** which seems to be linked to mudcracking. Once mudcracks have encircled a region of the deposit, and if shrinkage of the deposit continues, it will begin to buckle and eventually spall.

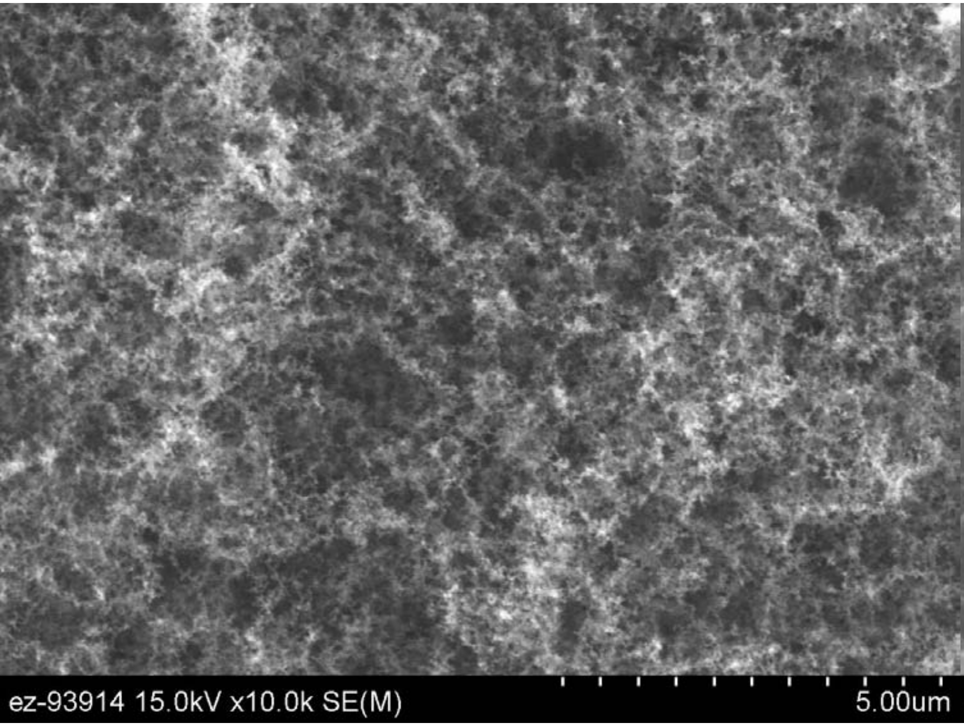
Summary of Observations on all Industry-Provided Coolers

Observation	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10a*	*10b*
Plugging			X	X							
Corrosion	X								X		
Density Gradient	X	X	X	X		X	X	X	X	X	X
Mudcracking	X	X	X			X	X	X			
Spallation	X	X						X			
Grooving		X					X	X	X		
Silicates							X				

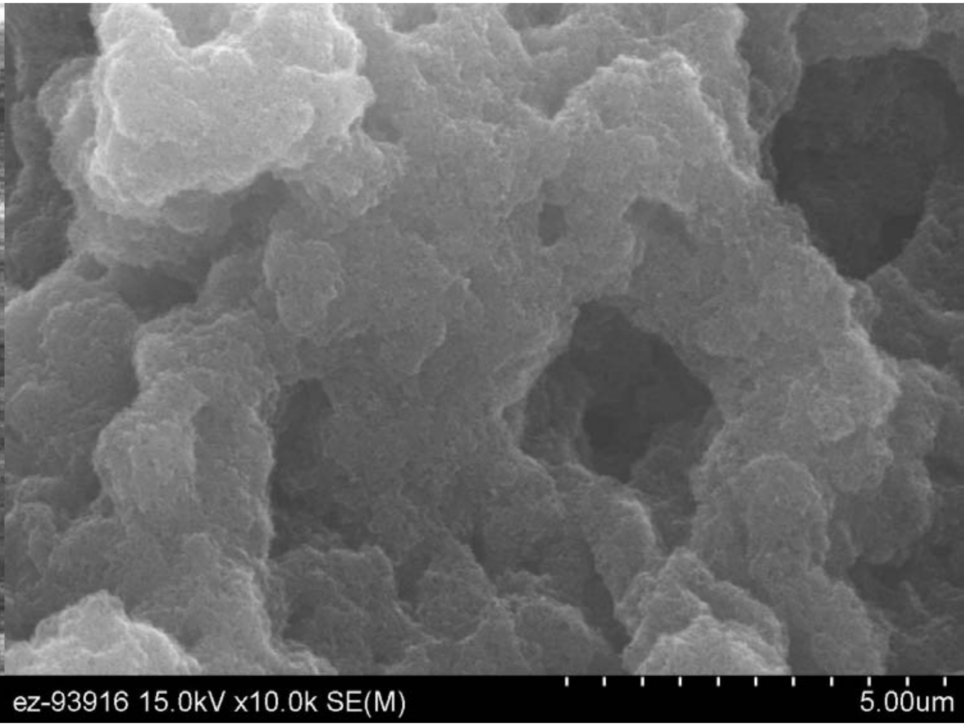
- Every cooler showed a gradient in the deposit microstructure from coarse to fine moving away from the metal.
- This effect may be caused by the collapsing of the PM nanostructure due to hydrocarbon and/or water condensation during operation.
- This work will be presented and published at the October SAE meeting (SAE 2010-01-2091).

Future Work (Task 3):
Effect of Water/HC Condensation and Drying on Microstructure: A Route to EGR Cooler Regeneration

Lab-Generated Deposit (ULSD, 90 C Coolant)



After Water Immersion and Drying

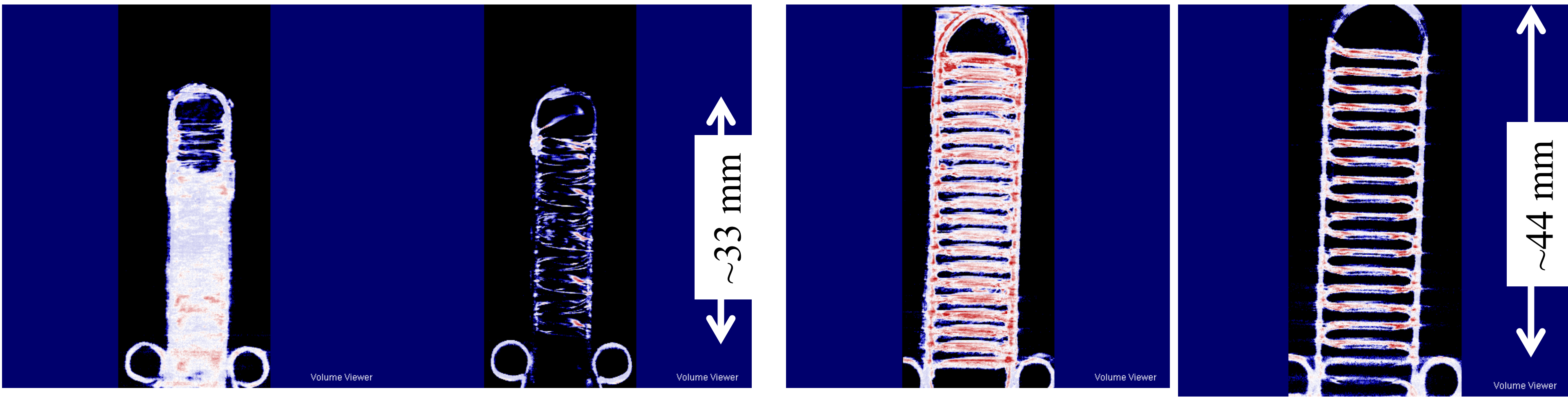


1. Produce deposits using engine and tube sampling system.
2. Condense water or HC on deposit-coated tubes using bench flow reactor.
3. Measure change in microstructure, density, and thermal conductivity.

Neutron Tomography of Industry-Provided Cooler Tube Sections

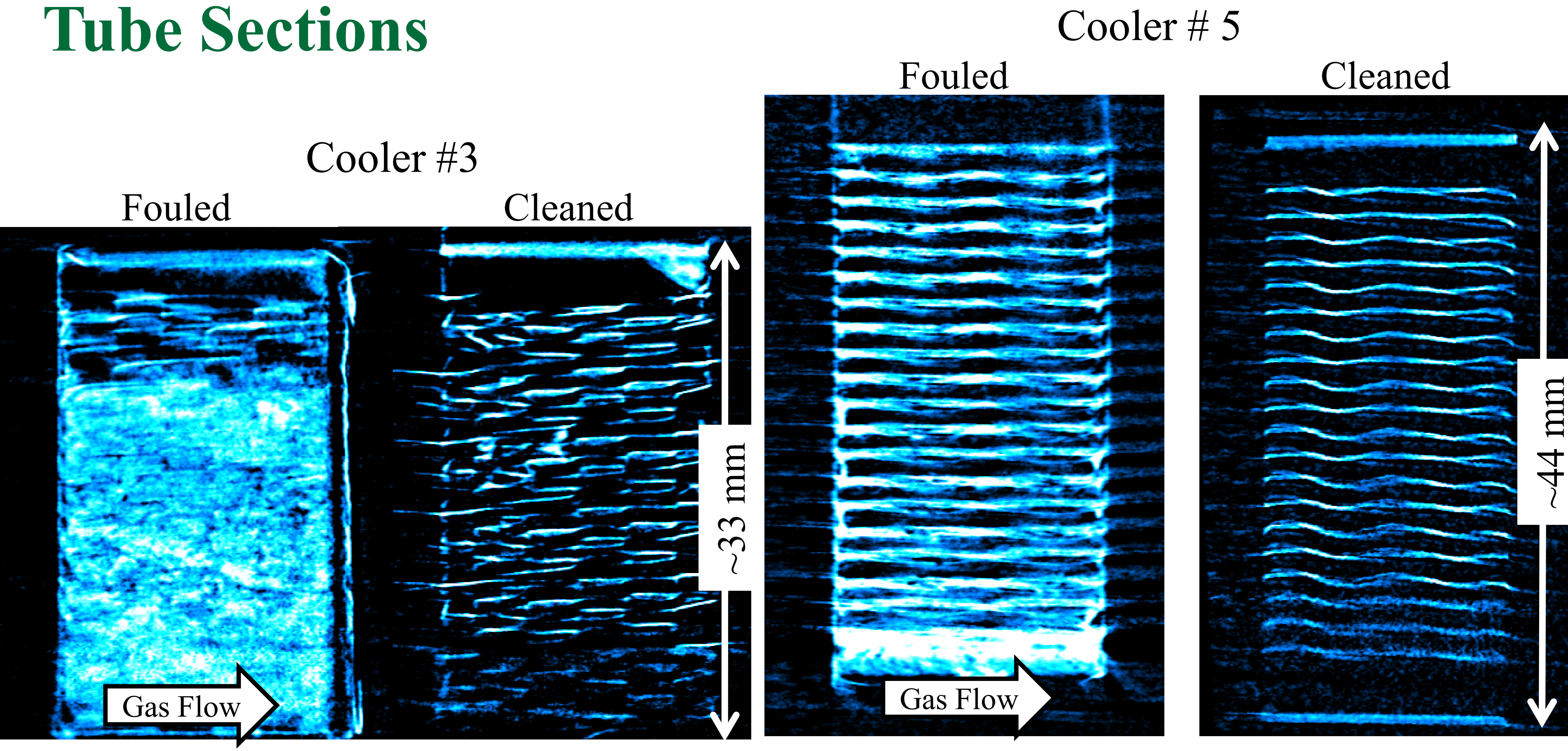
Cooler #3 — Fouled | Cleaned

Cooler # 5 — Fouled | Cleaned



- **Neutrons are strongly attenuated by hydrogen which allows for non-destructive imaging of the deposit through the metal.**
- **The two coolers with the most HC were selected for neutron tomography.**
- **720 2-D projections of the cooler sections were acquired by rotating the sample around its axis of symmetry.**
- **The spatial resolution was ~70 µm which may soon improve to 35 µm.**

Neutron Tomography of Industry-Provided Cooler Tube Sections



- **The resolution was not high enough to measure thickness directly but we can still gather useful information about the deposit location relative to the heat exchanger geometry.**
- **A new project funded by the US Army (partnering with Modine) has just started which will focus on the effects of internal heat exchanger geometry on fouling.**
- **We are seeking letters of support from industry for VENUS (Versatile Neutron Imaging Instrument at SNS [Spallation Neutron Source]).**

Summary

- Hydrocarbon/Water condensation plays a pivotal role in EGR fouling and will affect plugging, densification, thermal conductivity, mud-cracking and adhesion.
- Corrosion was observed on two coolers but didn't appear to present a large problem.
- Microstructures indicating deposit erosion were observed on many coolers.
- Forensic analysis of cooler deposits may allow one to infer deposit formation and removal mechanisms.
- Neutron tomography was shown to be a valuable tool for imaging EGR cooler fouling and will have broad application to many other emission control technologies.