

Characterization of Field-Aged EGR Cooler Deposits

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ABSTRACT

Exhaust gas recirculation (EGR) cooler fouling has become a significant issue for compliance with nitrogen oxides (NO_x) emissions standards. In order to better understand fouling mechanisms, eleven field-aged EGR coolers provided by seven different engine manufacturers were characterized using a suite of techniques. Microstructures were characterized using scanning electron microscopy (SEM) and optical microscopy following mounting the samples in epoxy and polishing. Optical microscopy was able to discern the location of hydrocarbons in the polished cross-sections. Chemical compositions were measured using thermal gravimetric analysis (TGA), differential thermal analysis (DTA), gas chromatography-mass spectrometry (GC-MS), x-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD). Mass per unit area along the length of the coolers was also measured. Despite coming from different sources and applications, many common features were observed in the cooler deposits including mud-cracking, hydrocarbon condensation near the metal surface, and erosion of the deposit. Differences and commonalities between the coolers will be discussed in the context of better understanding cooler fouling and ways to prevent it.

INTRODUCTION

High-pressure exhaust gas recirculation (HP-EGR) is the dominant engine-out NO_x-reduction technology used by the diesel engine community today. [1, 2, 3, 4, 5] High-pressure EGR systems extract a portion of the exhaust gas upstream of the turbine, pass the gas through a compact heat exchanger (EGR cooler) and then introduce it to the intake downstream of the compressor and charge-air cooler (intercooler). As the exhaust gas flows through the EGR cooler, particulate matter (PM) will migrate from the hot exhaust gas to the cooled heat

exchanger surface by thermophoresis forming a porous deposit that has a thermal conductivity comparable to Styrofoam [6] making it a nearly ideal thermal insulator. In addition, hydrocarbons and water vapor in the exhaust gas may condense on the cooled metal wall. As the thickness of the deposit increases, the effectiveness of the EGR system decreases due to the inability to cool the exhaust gas. [7, 8, 9, 10, 11] This is known as cooler fouling. Maintaining the EGR cooler without a significant loss of effectiveness has become a significant issue in terms of achieving compliance with increasingly stringent NO_x regulations. [12, 13, 14, 15, 16, 17, 18, 19] Despite the importance of cooler fouling as a primary failure mode of HP-EGR systems, there do not appear to be many investigations of the material properties and microstructure of field-aged cooler deposits and their effect on the performance of EGR cooling devices. [20]

In February of 2009, a consortium consisting of engineers responsible for EGR systems was assembled from nine diesel engine manufacturers and surveyed to identify the biggest problems facing EGR systems. EGR cooler fouling was identified as a very critical concern. Each member of the EGR consortium agreed to provide a cooler that had seen enough operation to categorize it as 'half-useful-life'. Of the nine members, the seven companies that currently use HP-EGR all sent at least one fouled cooler for analysis with the results to be shared with the entire consortium. The results of this survey will be discussed below.

RESULTS

A total of eleven coolers were obtained and all underwent the same forensic analysis. Table 1 lists the information that was provided by the engine companies about these coolers. Coolers #1, #5 - #7 and #9 came from field engines whereas coolers #2 - #4, #8 and #10a&b came from a dyno-cell. Coolers #10a and #10b were the 1st and 2nd pass from the same HP-EGR loop. All had seen exposure times and fouling

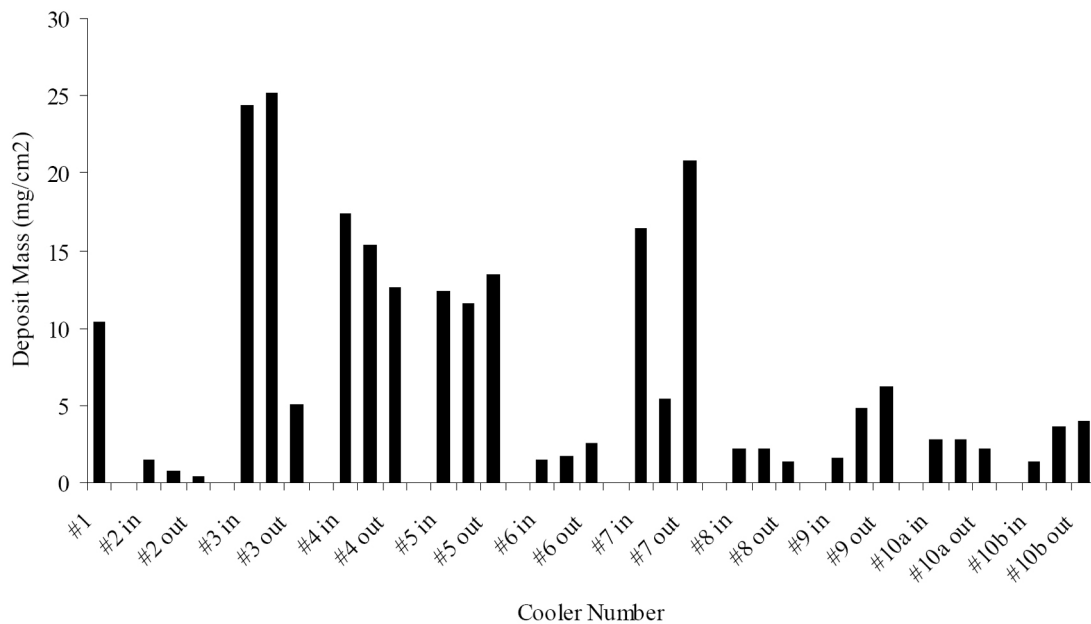


Figure 1. Deposit mass per unit area for each cooler measured near the inlet, middle and outlet. Due to lack of space, only the inlet and outlet are labeled here, the center bar for each set of three data points corresponds to the deposit collected from the middle of the cooler tube. Only one data point is shown for cooler #1 due to its unique geometry.

levels that would be considered at least half-useful-life for their application. Each cooler was cut open with a band saw and two of the tubes from near the center of the shell were selected to be further cut into $\frac{3}{4}$ -inch segments so they could fit into 2-inch mounts for machining and polishing. The sawing was done without water and slowly so as to minimize vibration and local heating of the deposit. Most of the cooler deposits were tacky enough such that the deposit easily survived the cutting. Qualitatively, the samples did not exhibit significant material release during handling of the tubes.

Table 1 also shows the approximate total surface area of the coolers. Larger coolers like #7, which weighed 37 lbs., came from an off-road truck whereas coolers #3 and #10a&b came from light-duty engines. Other coolers fell in between these two extremes. This shows that the samples analyzed represent a broad cross-section of all EGR cooler platforms.

Figure 1 shows the deposit mass per unit area for the inlet, middle and outlet of each cooler. The mass of the deposit was measured by weighing the tube section before and after heating to 600°C and cleaning them to remove all of the residue. There was significant variation in deposit mass/area among the coolers. Coolers #3 and #4 both exhibited significant clogging whereby entire channels were blocked with deposit which accounts for the high mass/area of these coolers. Cooler #5 was very tacky and smelled of hydrocarbon which likely increased the deposit mass significantly. Coolers #1 and #7 also showed heavy deposits

with the remaining coolers having average deposit masses less than 5 mg/cm².

Table 1. Industry-provided cooler specifications. No information was provided for the duration of testing on coolers #2 - #4. Heat transfer surface area was estimated by measuring the internal dimensions of the cooler tubes.

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

The trends in deposit mass per area along the length of the cooler were independently confirmed using optical microscopy, with the exception of coolers #4 and #7. There was no consistent trend between all of the coolers in the change in deposit mass along the length with some increasing in mass and others decreasing. In the case of sample #10, the

first pass decreased in mass (#10a) and the 2nd pass increased in mass (#10b).

The elemental compositions of the deposits were measured using energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM) (Table 2). X-ray Fluorescence (XRF) was not used because it is insensitive to oxygen and carbon. Also, the analysis of micron-scale surface areas using SEM helps one to avoid metal debris produced during cutting when collecting spectra. Coolers #1 and #9 had large amounts of sulfur and iron suggesting the presence of corrosion in these two coolers. Cooler #5 had significant amounts of Fe and Cr due to metal debris from cutting in the deposit since this deposit was very tacky which allowed metal chips to stick to it. Cooler #7 had elements common in soil (Si, Na, Ca, K and P).

Table 2. Elemental composition of cooler deposits measured by energy dispersive spectrometry (EDS). All values are in standardless weight percent.

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								

The phases present in each cooler were measured using x-ray diffraction (XRD) (Table 3). Coolers #1 and #9 showed the presence of metal sulfate and cooler #7 showed silicates which confirms the EDS results. Some of the coolers showed trace amounts of steel presumably from the cutting process and nearly all showed amorphous carbon peaks.

Table 3. Phases present in each cooler deposit measured by X-ray Diffraction (XRD). a-C = amorphous carbon.

Cooler #	a-C	Steel	Metal Sulfate	FeS	Na ₂ SO ₄	Silicates	Graphite
1	X		X	X			
2	X						X
3	X						
4	X						
5		X					
6	X						
7	X				X	X	
8	X	X					
9	X	X	X				
10a	X	X					
10b	X						

X-ray Photoelectron Spectroscopy (XPS) was carried out on all deposit samples and the carbon 1s spectra are presented in Figure 2. All samples exhibited the C-C bonding peak at 285 eV, and with the exception of cooler deposit #5, all showed the C-O bonding peak at 289 eV.

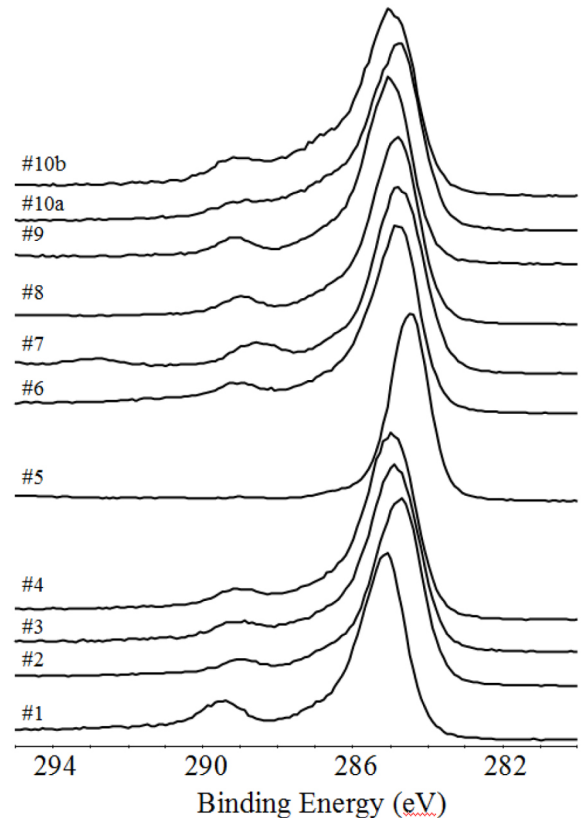


Figure 2. Carbon 1s spectra measured by X-ray Photoelectron Spectroscopy (XPS). The peak positions are uncorrected for sample charging. The large peak around 285 eV is from C-C bonding and the smaller peak around 289 eV is from C-O bonding.

Hydrocarbon profiles were measured with gas chromatography-mass spectrometry (GC-MS). Four species that indicate different hydrocarbon origins (fuel, oil and oxidized fuel) are listed in Table 4. Most samples had concentrations of individual hydrocarbon species below 1 ng per µg of deposit. Cooler #3 had high amounts of fuel hydrocarbons and partially-oxidized fuel but no heavy hydrocarbons from oil. Cooler #5 had large amounts of both fuel and oil hydrocarbon but no oxidized fuel which compares well to the XPS results which also showed no C-O bonding in this deposit.

Table 4. Estimated mass (in ng/μg) of four common hydrocarbon species in the cooler deposits measured by GC-MS. Naphthalene and nonadecane correspond to aromatic and alkane species in diesel fuel, respectively. Pentacosane is a heavier hydrocarbon species more common in oil. Naphthalenic anhydride indicates partially oxidized fuel.

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

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted in argon to determine the volatile mass fraction of all the deposits. Samples were first heated to 600°C in argon at a rate of 5°C/min and held for 1 hour. The remaining nonvolatile deposit was then heated to 700°C in air to determine the mass fraction of the elemental carbon and the non-combustible residue. Table 5 shows the mass percent of three regions of the volatile component; water (25 - 120°C), light hydrocarbon (120 - 350°C) and heavy hydrocarbon (350 - 600°C), and the nonvolatile components; elemental carbon and residue.

Table 5. Mass percentage of volatile and nonvolatile components of the deposit measured by TGA. EC = elemental carbon.

Cooler #	Volatile			Nonvolatile	
	25-120° C	120-350° C	350-600° C	EC	Residue
1	7.7	16.5	29.8	34.2	11.8
2	1.4	2.7	20.7	71.1	4.1
3	1.1	17.9	20.9	55.0	5.0
4	1.4	9.5	19.4	70.3	0.0
5	0.7	10.9	1.5	4.0	83.0
6	0.8	4.3	8.2	34.0	52.7
7	17.2	6.5	14.0	4.6	57.6
8	2.3	6.3	13.6	57.1	20.7
9	6.1	10.7	32.2	31.3	19.7
10a	2.3	19.6	14.9	54.7	8.5
10b	2.1	19.8	14.3	53.8	9.9

With three exceptions, the water content of all the deposits was less than 2.5% and most of this mass loss occurred below 80°C peaking around 45°C. Coolers #1 and #9 had high water loss likely due to the presence of hydrated metal sulfates which will dehydrate during heating. The high water content of cooler #7 was probably caused by water adsorbed on to silicates in the deposit. Above 120°C, coolers #2, #4, and #6 -

#8 had at least twice the mass loss in the heavy hydrocarbon region than the light hydrocarbon region which indicates that little unburned or partially burned fuel was present in these deposits. Above 350°C, volatilization is due mostly to partially oxygenated hydrocarbons, heavy hydrocarbons typical of lubricant, and polycyclic aromatic hydrocarbons (PAHs) present in all diesel particulate matter. For coolers #1 and #9, volatile mass percentage above 120°C was mostly governed by the decomposition of Fe₂(SO₃) to Fe₂O₃ and so does not accurately reflect the nature of the carbonaceous portion of the deposit. Coolers #3, #5, #10a and #10b had significant hydrocarbon devolatilization between 120 and 350°C which suggest the presence of fuel components in these deposits. Of particular note is cooler #5 which devolatilized almost entirely in the light hydrocarbon temperature range.

Figure 3 compares the derivative weight change in argon of the lightest deposit from Figure 1 (#2) to the heaviest deposit (#3). The highest mass loss rate for cooler deposit #2 occurred above 500°C, much higher than cooler deposit #3 which had its highest mass loss rate at 216°C. This suggests that most of the mass of cooler deposit #3 is from unburned fuel.

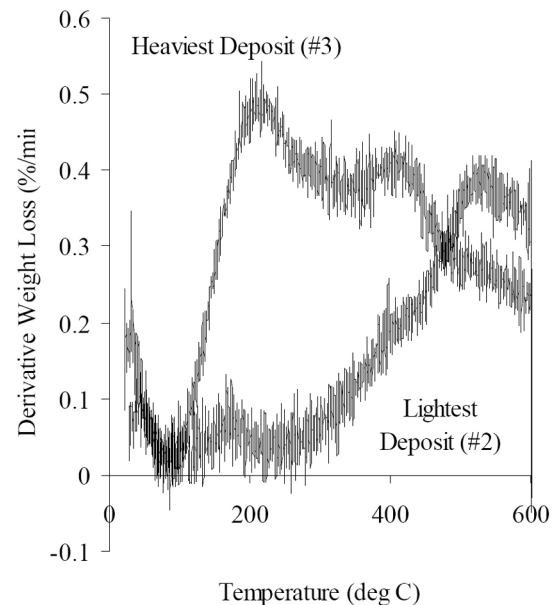


Figure 3. Derivative weight loss in percent per minute versus temperature (°C) while heating in argon for the lightest (#2) and the heaviest (#3) cooler deposits.

Two methods were developed to image the microstructure of the deposit. The first was to mount the deposit in epoxy and polish the cross-section. Epoxy mixed with a fluorescent dye (which provided contrast between the epoxy and the deposit) was poured over the 3/4-inch sections of tube without pulling a vacuum so as to preserve the deposit structure. The mount was then ground on one side until the outer tube was gone