

THESIS

TWO-STROKE LEAN BURN NATURAL GAS ENGINE OXIDATION CATALYST  
DEGRADATION AND REGENERATION VIA WASHING

Submitted by

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## ABSTRACT

### TWO-STROKE LEAN BURN NATURAL GAS ENGINE OXIDATION CATALYST DEGRADATION AND REGENERATION VIA WASHING

Lean burn two stroke engines are used extensively for stationary applications including power generation, cogeneration and compression. Natural gas is abundant, relatively inexpensive, and combustion produces less CO<sub>2</sub>, particulate matter, and SO<sub>x</sub> than gasoline and diesel. However, the Natural gas industry continues to be impacted by increasingly stricter emissions limits. One approach to comply with these emission limits is outfitting engines with an oxidation catalyst. Oxidation catalysts are proven to reduce hydrocarbon and carbon monoxide emissions, but surface poisoning due to lube oil carry over diminishes performance. Zinc, phosphorus, and sulfur found in oil additives poison the catalysts surface, and readily leach into an acidic environment.

Two commercial catalyst modules were aged at a field site on a slipstream of a GMVH-12 engine until they no longer met the National Emissions Standards for Hazardous Air Pollutants (NESHAP) formaldehyde limit. The oxidation catalyst modules underwent a washing process of immersion into caustic soda, neutral water, and acetic acid baths. The surface chemistry of samples was analyzed on a scanning electron microscope (SEM-EDS) and X-ray photoelectron spectroscopy (XPS). Catalytic performance testing was carried out by a slipstream of a laboratory Cummins QSK-19G engine, five gas analyzer and Fourier transform infrared spectroscopy (FTIR). The washing process removed the majority of surface poisons and improved the catalytic performance. The modules were then aged again until non-compliance

with emissions limits occurred. The modules were periodically tested for poison accumulation and catalytic performance to determine the rate of degradation post-washing. These results were used to compare with that of a new catalyst to estimate the increase in lifespan from washing. The results of the experiments reported here should encourage the use of washing as a low cost partial regeneration procedure for oxidation catalysts.

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## 1. Introduction

Large bore natural gas engines are extensively used for compression, power generation and cogeneration as natural gas is a relatively clean and inexpensive fuel. Over 8000 large bore natural gas engines are in service, with most operating under lean conditions. Natural gas combustion produces low particulate matter (PM) compared to other fuels but other harmful compounds including carbon monoxide, volatile organic compounds (VOCs), and formaldehyde are still produced in significant concentrations [1]. Several air quality standards issue and enforce strict emission limits: The National Ambient Air Quality Standard (NAAQS), New Source Performance Standards (NSPS), and National Emissions Standards for Hazardous Air Pollutants (NESHAP) issue limits based on size and location of the engine. The specific standard can be a maximum allowed concentration or minimum catalytic reduction efficiency. For example, a 4-stroke lean burn engine greater than 500 hp in non-remote locations must meet a 47ppm CO limit or have a catalytic reduction efficiency of 93% or greater [2]. To meet the increasingly stricter emissions limits operators are utilizing several exhaust after treatment technologies including: exhaust gas recirculation, secondary air injection systems, selective catalytic reduction, and oxidation catalysts. Oxidation catalysts are proven to reduce carbon monoxide, formaldehyde, and VOC emissions even under lean equivalence ratios [3]. Overtime catalysts degrade until they can no longer meet the emissions limits and will either need to be replaced or regenerated to stay within compliance. Surface poisoning due to lube oil carry-over is a significant mode of deactivation, but is reversible through chemical washing. This project aims to evaluate the effectiveness of regeneration via chemical washing. Regeneration is thought to be an economical method to increase the lifespan of the catalyst. This project also looks into the rate of degradation after washing in order to evaluate the increase in lifespan to better assess the economic benefits of regeneration through chemical washing.

## 1.1 Exhaust After-treatments

Several exhaust after-treatment systems have been developed to allow operators to adhere to emissions limits. Secondary air-injection, exhaust gas recirculation, selective catalytic reducer, and oxidation catalysts are common methods of abating carbon monoxide, hydrocarbon and NO<sub>x</sub> emissions. Secondary air injection oxidizes hydrocarbons and carbon monoxide by injecting excess air into the exhaust stream. In an exhaust gas recirculation system (EGR), 10-15% of the engines exhaust is recirculated back into the combustion chamber. The re-injected exhaust lowers the adiabatic flame temperature within the combustion chamber which aids in limiting the formation of nitrogen oxides (NO<sub>x</sub>). EGR systems, however, result in decreases engine performance [4]. Selective catalyst reducers (SCRs) work by injecting a reductant solution into the exhaust and flowing the mixture through a catalyst to reduce NO<sub>x</sub> emissions. The catalyst is typically a ceramic substrate with titanium or vanadium being the catalytic element; the solution is either ammonia or urea. When the exhaust/solution mixture passes over the catalyst NO<sub>x</sub> is reduced to diatomic nitrogen and water [4]. Oxidation catalysts convert carbon monoxide and hydrocarbons into carbon dioxide and water. They are constructed out of a substrate material and a wash coat containing the catalyst elements. Precious metals such as platinum, palladium, and rhodium are common catalyst elements. Oxygen will bond with the precious metals forming metallic oxides. Exhaust gasses are oxidized as they diffuse to the surface and react with the bonded oxygen [5].

## 1.2 Degradation Mechanisms

### 1.2.1 Thermal Effects

Oxidation catalysts are frequently subjected to high temperatures for long periods causing sintering of both the wash coat and the precious metals. Oxidation catalysts are surface sensitive devices designed in a way to maximize the surface area exposed to the exhaust gas stream. Sintering effectively reduces the surface area of both the wash coat and the precious metal nano-particles. The precious metal nano-particles are able to migrate and coalesce with other nano-particles. When multiple nano-particles coalesce, the surface area to volume ratio decreases and catalytic performance is lost [6-10]. The wash coat, typically alumina, also undergoes a sintering process in which the wash coat compacts, increasing density at the loss of surface area and catalyst sites [8]. The construction of the catalyst modules is also conducive to sintering. Thin films of ceramic wash coat containing the catalytic metals is adhered to a base support of steel. The edges of the ceramic film do not respond well to sintering. Edge effects and differences in Poisson's ratio of the wash coat and substrate cause a lesser degree of sintering at the edge and a density gradient forms near the edge. This uneven sintering forms high internal stresses that lead to cracking and breaking of the ceramic film [11].

Engines being used for compression and power generation often see intermittent use based on demands for natural gas and electricity. This results in the catalyst modules undergoing large temperature fluctuations. The wash coat interface with the steel substrate experiences stresses due to different coefficients of thermal expansion. Fluctuating temperature effectively fatigues the interface and will eventually lead to an attrition of the wash coat thereby negatively impacting performance. Mechanical attrition of the wash coat is an irreversible process [11].

### **1.2.2 Surface Poisoning**

Thermal deactivation modes have a less dramatic effect on performance compared to surface poisoning [8]. Surface poisoning is the loss of active catalyst sites and is due to either physical blockage of the site or altering the site due to chemical reactions with the various poisons [6-10, 12-14]. Poisons chemically reacting with the catalyst sites have a larger adsorption coefficient than the reactants in the exhaust. This limits the number of sites that the reactants have access to [8]. Sulphur, found in sour natural gas, is a main contributor to loss of performance [6-10, 12-14]. Phosphorus and zinc are concentrated on the surface of the catalyst and tend to be found in greater amounts at the front of the catalyst module [8]. Zinc, especially, tends to form an over layer or glaze that blocks active sites [9]. Sulphur tends to be concentrated at the rear of the catalyst module [8] and tend to diffuse into the bulk of the wash coat [12]. Sulphur in the form of  $\text{SO}_2$  and  $\text{SO}_3$  reacts with the active catalyst metals altering the site. For this reason, alumina ( $\text{Al}_2\text{O}_3$ ) is more favorable than  $\text{SiO}_2$  as the wash coat material as silicon dioxide has a greater affinity to absorb sulfates and sulfites [8-12].

### **1.3 Poison Sources**

Oxidation catalysts used with natural gas engines are poisoned mainly by phosphorus, sulfur, zinc and calcium found in oil additives [6-10, 12-14]. Many different compounds are added to engine oil in order to increase the oils performance including dispersants, detergents, acid-base neutralizers, anti-corrosion, and anti-wear agents. These additives typically contain the main catalyst poisoning elements (P, Zn, S and Ca) in significant concentrations and are added in varying quantities based on the type of oil [15]. Zinc dithiophosphate (ZDDP) is a common anti-wear compound that contains high concentrations of phosphorus, zinc and sulfur. ZDDP is added depending on the lubrication needs of the engine; engines under higher loads or those that have

stiff valve springs require an oil with more anti-wear compounds. Detergents and dispersants are added to clean and neutralize any impurities in the oils while also keeping the impurities in suspension as to prevent buildup on the engine walls and in the oil sump. Calcium is typically found in the detergent additives. Phosphorus buildup can be directly influenced by the amount of oil introduced to the catalyst. Up to 70% of the phosphorus introduced is found on the surface [8].

Engine oil additives are the main source of catalyst poisons but are necessary for the engine to operate properly. These additives are added in varying amounts to tailor the oil for the type of engine and desired properties. Sulfated ash, phosphorus and sulfur (SAPS) is the result of oil additives burning and creating ash. Oils are often grouped based on their ash content. Ash helps protect valve faces and as such high ash oils (2% ash by weight) are used mainly for four-stroke engines or those with significant valve face wear [15]. Low ash oils (<0.5% ash by weight) are more often used for two-stroke engines and a catalyst installed on an engine running low ash oil will be exposed to less poisoning elements.

Along with the lube oil, fuel can be a potential source of sulfur. Natural gas often contains hydrogen sulfide and other sulfur containing compounds such as tert-Butylthiol, ethanethiol and tetrahydrothiophene. Hydrogen sulfide concentrations in natural gas is usually quite small (<4 ppm) with the other compounds being in even smaller concentrations.

The last major potential source for poisons comes from engine coolant. Engine coolant contains elements such as silicon, potassium, sodium, molybdenum and iron that can also poison the surface of a catalyst. Normally the coolant system is isolated from the exhaust, but gasket failures create a pathway for coolant to enter into the combustion chamber. The coolant, once

combusted, forms silicates that accumulate in a hard crust on the catalyst often blocking channels and limiting mass transfer of exhaust gasses [15].

## **1.4 Regeneration Processes**

There is little that can be done to reverse the thermal deactivation modes, though re-dispersion of the active metals can be achieved [12]. Thermal treatments to the catalyst can lead to the redistribution of active metal nano-particles. Partial regeneration of catalysts can be achieved by removing the surface poisons. Methods include washing the catalyst modules in acidic solutions, hydrogen gas treatment and exposure to a methane rich reducing environment.

### **1.4.1 Washing**

Phosphorus, zinc and sulfur are readily dissolvable in an acidic environment [6-10, 13]. Stronger acids are more effective at removing the poisons from the surface but damage to the wash coat and active sites is likely to occur. Weaker acids, (citric, acetic or oxalic) should be used as they are less likely to damage the wash coat but can still remove the poisons [6-10, 13]. The acid dissociation constant,  $pK_a$ , is a measure of an acids ability to donate protons and is independent of concentration. A lower  $pK_a$  corresponds to a stronger acid. Oxalic acid has been shown to be more effective at removing phosphorus and zinc, however oxalic acid ( $pK_a = 1.27$ ) is still quite stronger than citric acid ( $pK_a = 3.13$ ) and acetic acid ( $pK_a = 4.76$ ), and some discourage the use of it as it may be too strong and cause damage to the wash coat [6-10, 13]. Extraction rates and amounts of the poisons removed is dependent on the aging of the wash coat. The extraction rate was slower and less poisons were removed from catalysts that had been degraded for longer periods of time [9]. Agitation or stirring of the wash coat increases the rate of extraction [6-10]. Increasing the concentration of the acid in solution removes more poisons

and in a shorter amount of time. However this behavior is asymptotic, and eventually a maximum removal yield is achieved in a 5 wt.-% acetic acid solution [10]. Time in solution and poison removal yield is also an asymptotic relationship and eventually the catalyst benefits little from being in solution longer. One study found that after 2 hours in an acetic acid solution, the removal yield of phosphorus was nearly constant [9]. Heating of the acidic solution can aid the removal of poison [10]. Arapatsakos et.al. used an organic solvent (tetrachloroethylene) to dissolve oil, soot and fuel residue cleaning the catalyst surface and improving catalyst activity. Immersion times ranging from 10-60 minutes were tested. It was found that 30 minutes was adequate and improved reduction efficiencies by more than 25% compared to the degraded catalyst [16].

#### **1.4.2 Hydrogen Treatment**

Exposing the catalysts to a hydrogen gas mixture was proven to increase the performance after aging [12]. In this method the catalysts are installed in a reactor and exposed to a flow that is a mixture of 10% hydrogen gas with argon balance. Hydrogen has a strong affinity to react with sulfur species on the surface of the catalyst and remove them [12]. A nitrogen gas treatment was tested, but hydrogen gas was found to be more effective at regeneration. The regeneration effectiveness of this method was heavily reliant on temperature. The temperature at which the catalyst degraded effected the regeneration in that higher degradation temperatures lead to a lower regeneration effectiveness. Increases in the hydrogen/argon temperature had the effect of increasing the regeneration effectiveness [12]. One study used a hydrogen gas pre-treatment before washing in acid. Exposing the active metal, platinum, to hydrogen converted the platinum from oxide to metallic form. Platinum in metallic form is believed to be more resistant to acid



than in an oxidized state and thus reducing the risk of removing the active metal from the catalyst [10].

### **1.4.3 Methane Treatment**

A methane treatment has also been developed and tested and was found to be more effective than hydrogen treatment [10]. Similarly to the hydrogen treatment, catalyst are installed in a reactor and exposed to heated mixtures of methane and other gases. This process involves temperature programmed combustion (TPC) and temperature programmed reduction (TPR) to periodically alternate from methane combustion (both lean and rich combustion were tested) to a wet methane reducing atmosphere (0.5% CH<sub>4</sub>, 2% H<sub>2</sub>O, balance He). Partial regeneration occurred under lean combustion of methane with excess O<sub>2</sub>, but high temperatures were necessary [12, 13]. By changing from lean to rich methane conditions sulfates are quickly reduced and released from the catalyst. Rich methane conditions resulted in regeneration at lower temperatures compared to lean conditions [12, 13].

### **1.5 Previous Work and Project Aims**

A previous study conducted at the Engines and Energy Conservation Laboratory aged two small oxidation catalyst modules in the slipstream of a large bore natural gas engine. This work combined long-term field and intermittent laboratory testing from spring 2014 to summer 2015. The modules were periodically installed for durations of about 2 months before being retrieved for laboratory testing. Samples were taken from one module for surface chemistry analysis to investigate the amount of poison being deposited over time while the other module was installed on the exhaust of a laboratory engine for performance testing. The modules were aged and tested for performance until they were non-compliant with the NESHAP formaldehyde

emissions limit. The purpose of the study was to investigate the effects of lube-oil carry over and the relationship it has with the degradation rate.

The natural gas and pipeline industry has expressed a considerable desire to find methods to extend the life of oxidation catalysts, as they are quite costly to purchase and need replacement quite frequently. Chemical washing is the most economical way to restore performance to a catalyst module and has become the industry standard. Few studies have been conducted on the effectiveness of washing and no study to the author's knowledge has addressed the long term degradation after washing. This study combines the same long-term field testing and periodic laboratory evaluation testing to evaluate the effectiveness of the washing treatment on the previously degraded modules and the rate at which the washed modules degrade compared to new modules.

## 2. Experimental

### 2.1 Degraded modules

Two new DCL 4A0C-3 catalyst modules were aged in a previous study conducted in the Engines and Energy Conversion Laboratory until they no longer complied with the formaldehyde emission limit and were declared degraded. The catalyst modules were aged in parallel on a slipstream of a GMVH-12 integral compressor engine. Two modules were used. One was disassembled to extract samples for elemental analysis and, the other was left intact for performance testing as shown in Figure 1.1.



*Figure 2.1: Catalyst modules. Intact module on left for performance testing and partially disassembled module on left for elemental analysis*

## 2.2 Elemental Analysis

### 2.2.1 Spectroscopy Equipment

X-ray photoelectron spectroscopy (XPS) and a scanning electron microscope outfitted with energy dispersive spectroscopy (SEM-EDS) are used to analyze the surface and measure the atomic percent of each element present on the surface. XPS is known to be a surface sensitive technique capable of scanning only a few nanometers into the sample surface. XPS is also known to be a more quantitative method than SEM-EDS as it is capable of a higher resolution [16, 17]. A Physical Electronics PHI-5800 ESCA/AESA XPS instrument at the Central Instrument Facility at Colorado State University was used. The instrument uses an x-ray source operating at 35 kW and 15 kV to radiate the samples with x-rays. The x-rays hit the sample and eject electrons to be collected by a hemispherical analyzer. The analyzer records the counts and the voltage of each electron. A spectrum of intensity (counts per second) versus energy is generated and used to determine which elements are present based on the energy associated with each peak [16]. A short 10 minute long survey scan is taken of each sample. This survey scan is done at a pass energy of 186.5 eV with a resolution of 1.6 eV. The purpose of the survey scan is to quickly determine the elements and the rough quantities of each on a sample. The survey scan also provides the range of binding energies associated with each elemental peak. These binding energy values are then used for a high resolution scan. The high resolution scan is taken to achieve more accurate data. The scan is performed at 23.5 eV pass energy and a resolution of 0.1 eV.

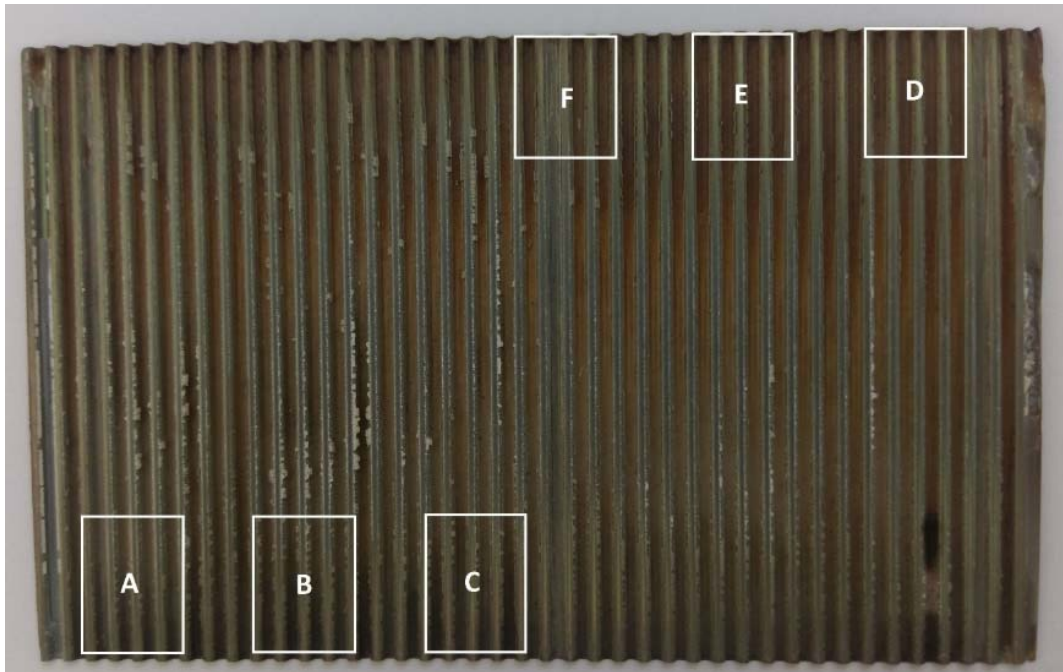
The scanning electron microscope used was a JEOL JSM-6500F at the Central Instrument Facility. An electron beam rasters over the sample at 10-30 kV. The electron beam excites core electrons in the sample. The excited electron rises to a higher energy orbit. An

electron from a higher energy orbital will fall into this vacated orbital and release an x-ray. The x-ray energy is measured and quantized to determine which element it derived from [17]. A beneficial use of the SEM-EDS is that it is capable of generating maps of element intensity and can overlay the maps on an image of the scanned area. Locations of high intensity show brighter and are areas where more poisons have accumulated [17]. These intensity maps are used as a qualitative way to show poison trends. XPS data is used to report the atomic percent of each poison while the SEM-EDS was used to discern trends in poisons distribution.

### **2.2.2 Sample Preparation**

Of the two catalyst modules used for the project one module is disassembled for the extraction of a full corrugated sheet. Smaller samples approximately 1cm<sup>2</sup> are then cut from 6 different locations on the catalyst sheet such that spatial trends in poison accumulation and removal can be identified. A full catalyst sheet is shown in Figure 2.2 with the locations for samples A-F marked. These spatial trends can be used to verify trends other studies have previously noted, such as high sulfur accumulation near the outlet and high phosphorus accumulation near the inlet [6-8].

Complications arose when trying to analyze samples after they had been aging for a period of time. A layer of organic carbon forms on the catalyst surface from lube-oil carry over. This carbon layer builds, becoming thicker overtime. Eventually the carbon layer formed thick enough that it masked poisons from being detected with the XPS instrument. A baking procedure was developed to remove the excess carbon without removing any of the poisons. Samples were baked at 425°F for two hour periods before analyzed for carbon and poison quantities. This temperature is slightly lower than what was used in another study [19]. Samples undergo baking cycles until the change in carbon and poison levels is 1% or less.



*Figure 1.2: Full catalyst sheet removed from one of the modules.*

### **2.3 Performance Testing**

To effectively evaluate the washing process, the catalytic performance, the catalyst's ability to oxidize exhaust species, is tested before and after washing. A 4-stroke Cummins QSK19G engine is used to generate exhaust gasses; Table 2.1 contains the specifications for this engine. A 4-stroke engine is used as they operate at higher temperatures than a two stroke engine. This increases the maximum exhaust temperature that can be reached during the performance testing. A portion of this exhaust is diverted to a slipstream where catalyst module is installed. The slipstream is outfitted with a liquid/gas heat exchanger and valves such that the gas temperature and velocity can be controlled to precise values. The catalyst housing has thermocouples and pressure ports to measure the inlet and outlet temperatures and the pressure drop across the catalyst module as shown in a slipstream schematic in Figure 2.2. A Fourier transform infrared spectrometer (FTIR) is used to analyze the concentration of each exhaust

species before and after passing through the catalyst. The FTIR spectrometer is only capable of measuring a single sample stream at a time; a valve is installed to alternate the stream from pre-catalyst to post catalyst on a timed basis. The sample stream alternating valve is programmed to open for 1 minute to analyze the pre-catalyst stream to get average pre-catalyst species concentrations. The valve then switches to post-catalyst for 5 minutes to collect outlet species concentrations. The valve will alternate in this sequence throughout the duration of both the temperature and space velocity sweeps as shifts in the inlet concentrations for various species can occur and could cause errors in the calculated reduction efficiencies if inlet concentrations are assumed constant.

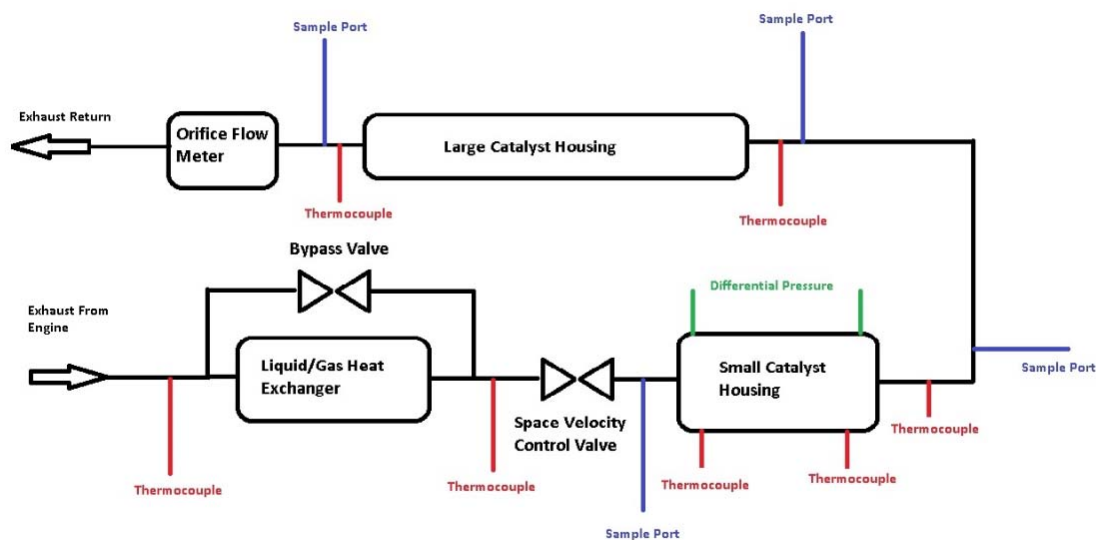


Figure 2.3: Schematic of the laboratory slipstream

*Table 2.4: Laboratory Engine Specifications*

Engine Specifications: Cummins QSK19G	
Displacement	1159 in <sup>3</sup> (19 L)
Bore	6.25" (159 mm)
Stroke	6.25" (159 mm)
Rated Power	470 hp (351 kW) at 1800 rpm
	450 hp (336 kW) at 1500 rpm
Fuel	Pipeline Natural Gas

During the temperature sweep the space velocity control valve is adjusted such that the exhaust gas space velocity is held constant at 150,000 hr<sup>-1</sup> while the bypass valve on the heat exchanger slowly closes, diverting more of the flow through the heat exchanger, to transition through a temperature range of approximately 300-800°F. During the space velocity sweep the bypass valve is adjusted to hold the exhaust temperature constant at 550°F while the space velocity valve opens to give a range of approximately 25,000-200,000 hr<sup>-1</sup>.

The reduction efficiency for each species is calculated with the following equation:

$$\eta = 1 - \frac{C_o}{C_i}$$

Where:

$\eta$ : reduction efficiency

$C_o$ : species concentration after passing through the catalyst



$C_i$ : species concentration before passing through the catalyst

The reduction efficiencies are evaluated for the temperature and space velocity sweeps, as both parameters impact the reduction efficiency.

## **2.4 Field Degradation**

Catalyst degradation is a relatively slow process, requiring multiple days of exposure to exhaust gas flow, or “on stream,” as poisons slowly accumulate. Kinder Morgan’s Watkins Stations just outside of Denver Colorado has offered the use of one of their several large bore two stroke compressor engines. This compressor station both pumps natural gas through the pipeline but also blends air into it to control and adjust the Wobbe index of the fuel. The engine being used to further aging the catalysts is the same one as the previous study; a Cooper Bessemer GMVH-12 engine used for compressing air into the natural gas. Table 2.2 summarizes the engine specifications. The slipstream is of similar construction to the slipstream used for performance testing. It is equipped with thermocouples, differential pressure ports and a pitot tube. A blower was installed to increase the gas velocity and data loggers are used to record data points every five minutes. Figure 2.3 is a schematic and picture of the field site’s slipstream and hardware. The washed modules are reinstalled into the same GMVH-12 slipstream and left for months to accumulate runtime before being retrieved for laboratory testing. After testing the modules are returned to the field for further aging.

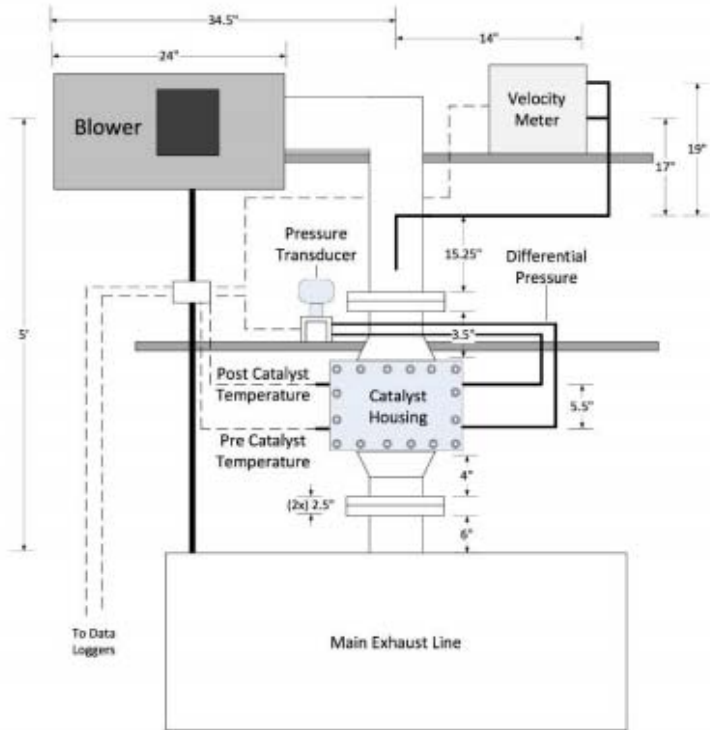


Figure 2.4: Picture of the field slipstream (left). Schematic of the field slipstream (right)

Table 5.2: Specifications for Watkin Station's GMVH-12 engine

Engine Specifications: Cooper Bessemer GMVH-12	
Displacement	2135 in <sup>3</sup> (35 L) per cylinder
Bore	14" (355 mm)
Stroke	14" (355 mm)
Rated Power	2700 hp (2013 kW) at 330 rpm
Fuel	Pipeline Natural Gas

Direct time on stream is not being used for tracking degradation as it does not take into account the engine operating parameters. Catalyst exchanges are used instead, which is the number of catalyst volumes of exhaust gas at standard temperature and pressure that have passed through the catalyst. Space velocity is defined as standard catalyst volumes treated per unit time and is used to calculate the total number of catalyst exchanges.

$$SV = \frac{\dot{V}}{V_{cat}}$$

$$CatExch. = SV * t$$

Where SV= Space Velocity

$\dot{V}$  = Standard volumetric flow rate.

$V_{cat}$  = Envelop volume of the catalyst module.

t = time on stream.

## 2.5 Washing process

Dresser Rand Engineuity in Fort Collins Colorado is a vendor that offers a catalyst washing service. Catalyst washing is chemical regeneration and their process involves soaking the catalyst module in 3 different chemical baths, which are: caustic soda, de-ionized water, and a glacial acetic acid. Modules are first inspected upon arrival to look for blocked channels and for catalysts that are too far degraded to benefit from washing. Modules are first lowered into the caustic soda solution which removes coke as well as poisons. The modules are then rinsed of residual caustic soda with a de-ionized water bath before going into the acetic acid bath. The acetic acid bath further removes poisons as well as any rust and organics. The modules are then

air dried on a rack overnight. All three baths are at room temperature and no stirring/agitation is used. Figure 2.4 shows photos of the washing setup and procedure and properties of each bath can be found in table 2.3.



*Figure 2.5: Collage of photos of the washing process. Left: Catalyst modules being blown with compressed air. Middle: Modules on a rack lowered into the acid bath. Right: the caustic soda, rinse water and acid baths*

*Table 2.3: Chemical bath properties*

<b>Bath Sequence</b>	<b>Soak Time</b>	<b>pH</b>	<b>Temperature (°F)</b>
Caustic Soda	4 hours	12.64	74.6
De-Ionized Water	1 hour	11.82	71.3
Acetic Acid	30 min	2.78	71.1
De-Ionized Water	30 min	11.82	71.3

## 2.6 Test Plan

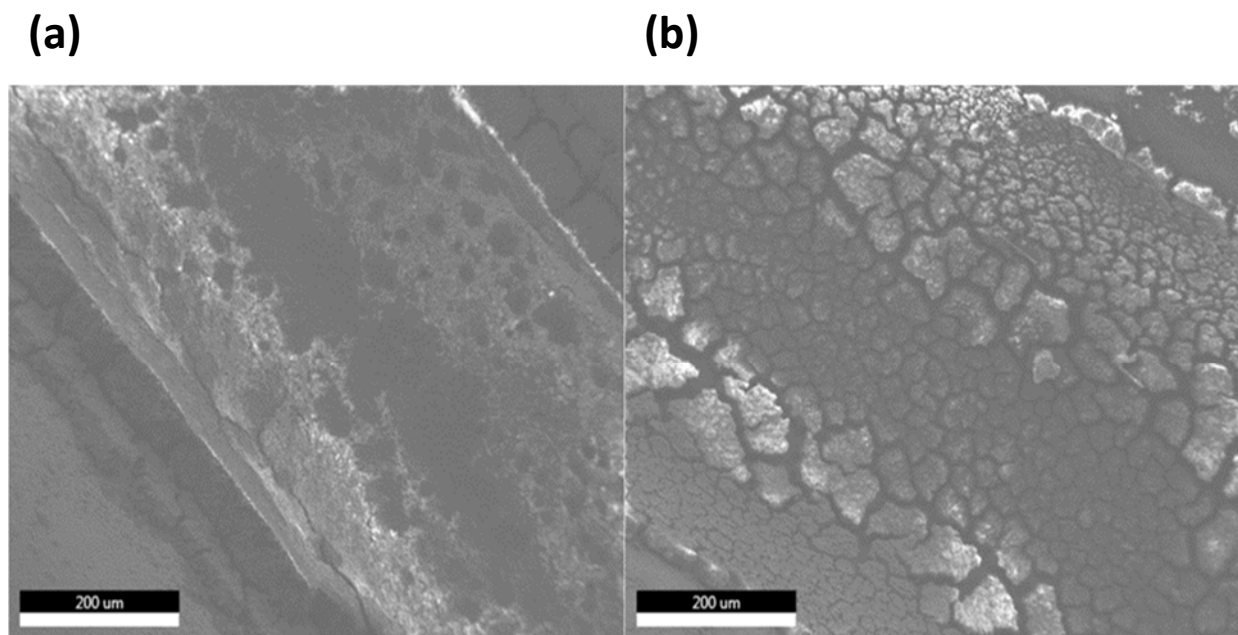
An initial materials analysis and performance testing was conducted on the two degraded catalyst modules. The modules then underwent the Dresser Rand washing procedure and were tested again to evaluate the effects of the washing process. Field degradation was conducted under the same procedure as the initial degradation test. The modules are installed in the field site slipstream and left there for approximately two months to age. The modules are retrieved and brought back to CSU for laboratory testing before being returned back to the field for another aging cycle. Table 2.4 shows the steps taken during testing, where steps 4-6 are repeated for each aging cycle until the catalyst modules no longer within compliance of the emission limits. Three aging cycles, approximately 2 months long each, were completed to evaluate the degradation rate after washing.

*Table 2.6: Testing procedure*

1.	Pre-Wash Testing
2.	Dresser Rand Washing Process
3.	Post-Wash Testing
4.	Re-install Modules
5.	Age for 2 months
6.	Re-test
7.	Repeat steps 4-6 until noncompliance is met

### 3. Chemical Washing

Throughout the project the modules had to be handled with great care because small flakes of the catalyst wash coat were found falling out of the modules. A sample of these flakes were collected and analyzed with the SEM and XPS. The chemical composition of the flakes matched the wash coat composition. Another strange observation was found from SEM images of the samples. Samples taken from near the outlet of the catalyst are very cracked and rough looking. Samples taken from near the inlet have a smoother less cracked looking surface. Figure 3.1 is two SEM images showing these differences.



*Figure 3.1: SEM image of inlet sample (a) and outlet sample (b)*

A baseline for the poison content before washing was difficult to obtain. The pre-wash samples had a thick layer of carbon that prevented poisons from being detected with XPS. The first samples scanned under the XPS contained 40% carbon and only 5% poisons. The samples had to be baked for several 2 hour long cycles before the carbon and poison levels remained

virtually constant. Samples were first baked at 450°C for one hour, but only a small amount of carbon was removed. As to reduce the number of iterations needed to bake away the carbon a slightly lower temperature of 425°F was chosen and samples were baked for 2 hours. After seven hours of combined baking time the carbon and poison atomic percentages have barely changed. The final average carbon content was 16% and the final total poison content was 18%. Using these results, samples were baked for 425°C for seven hours before being tested with the spectroscopy equipment. Figure 3.2 plots the carbon and poison content for each baking cycle.

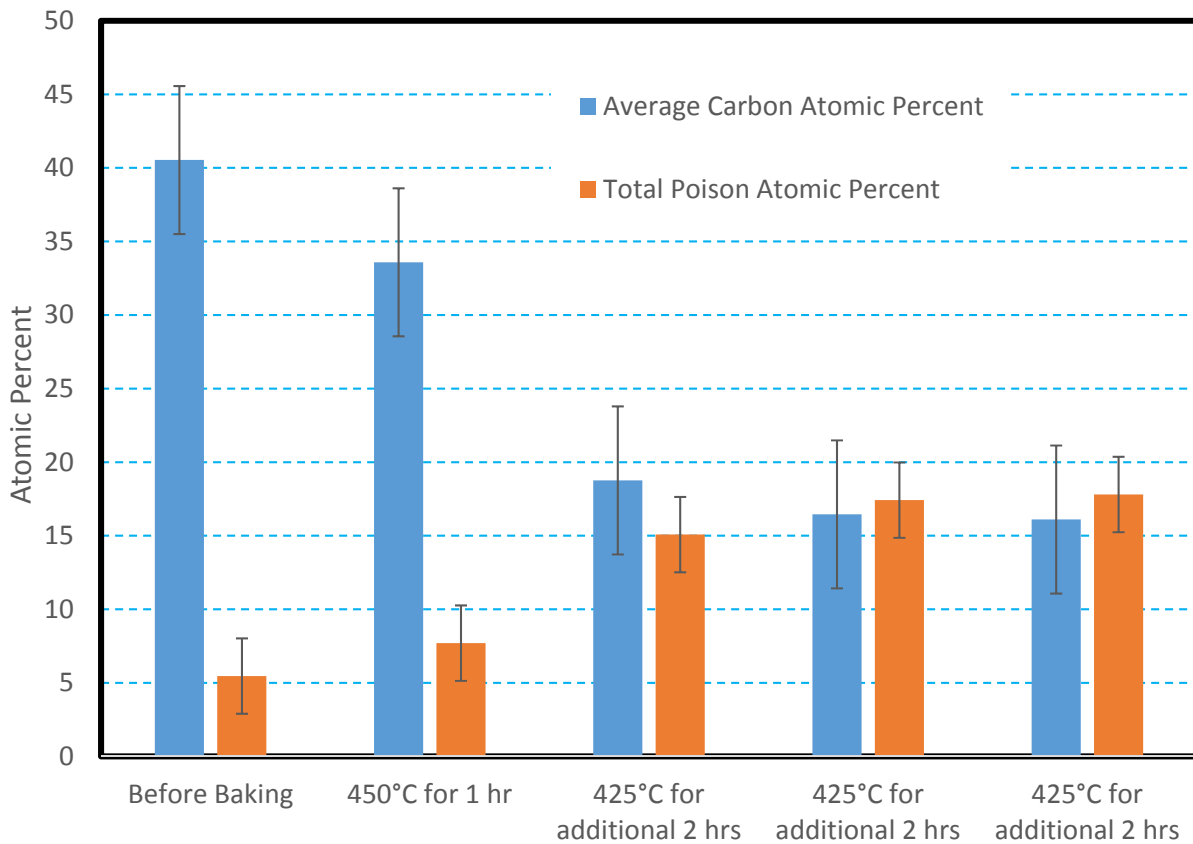


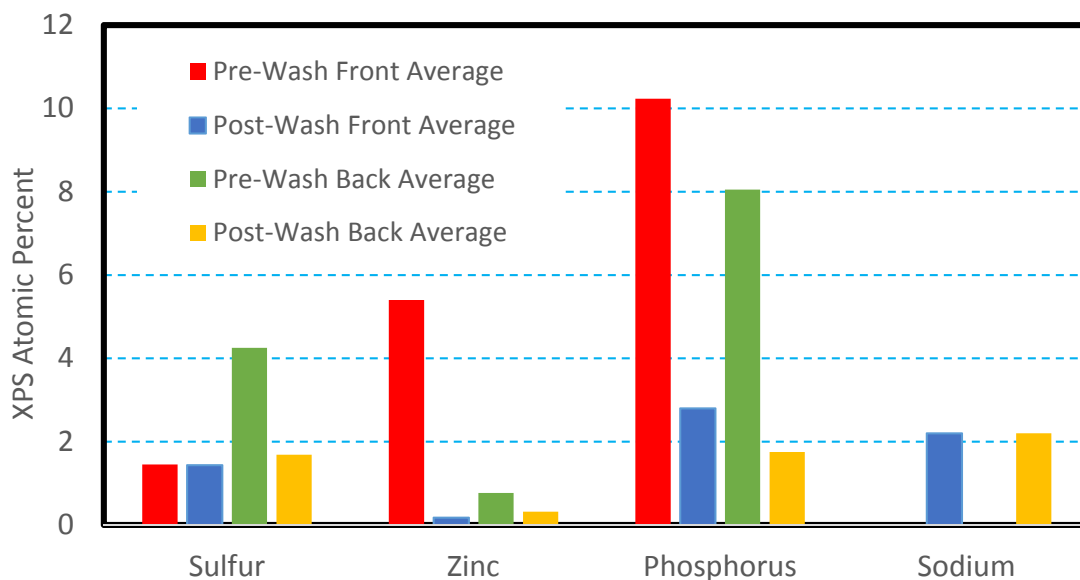
Figure 3.2: Carbon and poison atomic percent versus bake cycles

### 3.1 Poison Removal

Samples were tested for their surface chemistry before and after washing. Six samples were taken from spatial locations on the catalyst sheet and then each of these samples are scanned twice for a total sample size of 12 per test. First, a survey scan of each sample was taken. The survey scan quickly determines which elements are present and the rough quantities of each. A high resolution scan is then performed to gain more accurate data. Samples were scanned for long periods of time to achieve sufficient signal to noise ratios for peaks corresponding to catalyst poisons. This scan would take anywhere from 30-60 minutes depending on the signal quality. Atomic percent of each element was found by integrating the intensity of each element with its corresponding energy band gap and then taking the ratio of each element divided by the total to get an atomic percentage. XPS data is used to quantitatively measure and report the amounts of each element present while SEM-EDS data is used to more qualitatively support the results.

Figure 3.3 plots the average amount of each catalyst poison on the front and back both before and after the washing process. The front (inlet) data is the average from samples A-C while the back (outlet) data is the average of samples D-F. Large quantities of phosphorus and zinc were removed from both the inlet and outlet of the catalyst. Sulfur removal was measured primarily at the outlet of the catalyst, no sulfur removal occurred on the front samples. Average total poison content (sum of sulfur, zinc, and phosphorus) dropped from 18% to 4% due to the washing process.





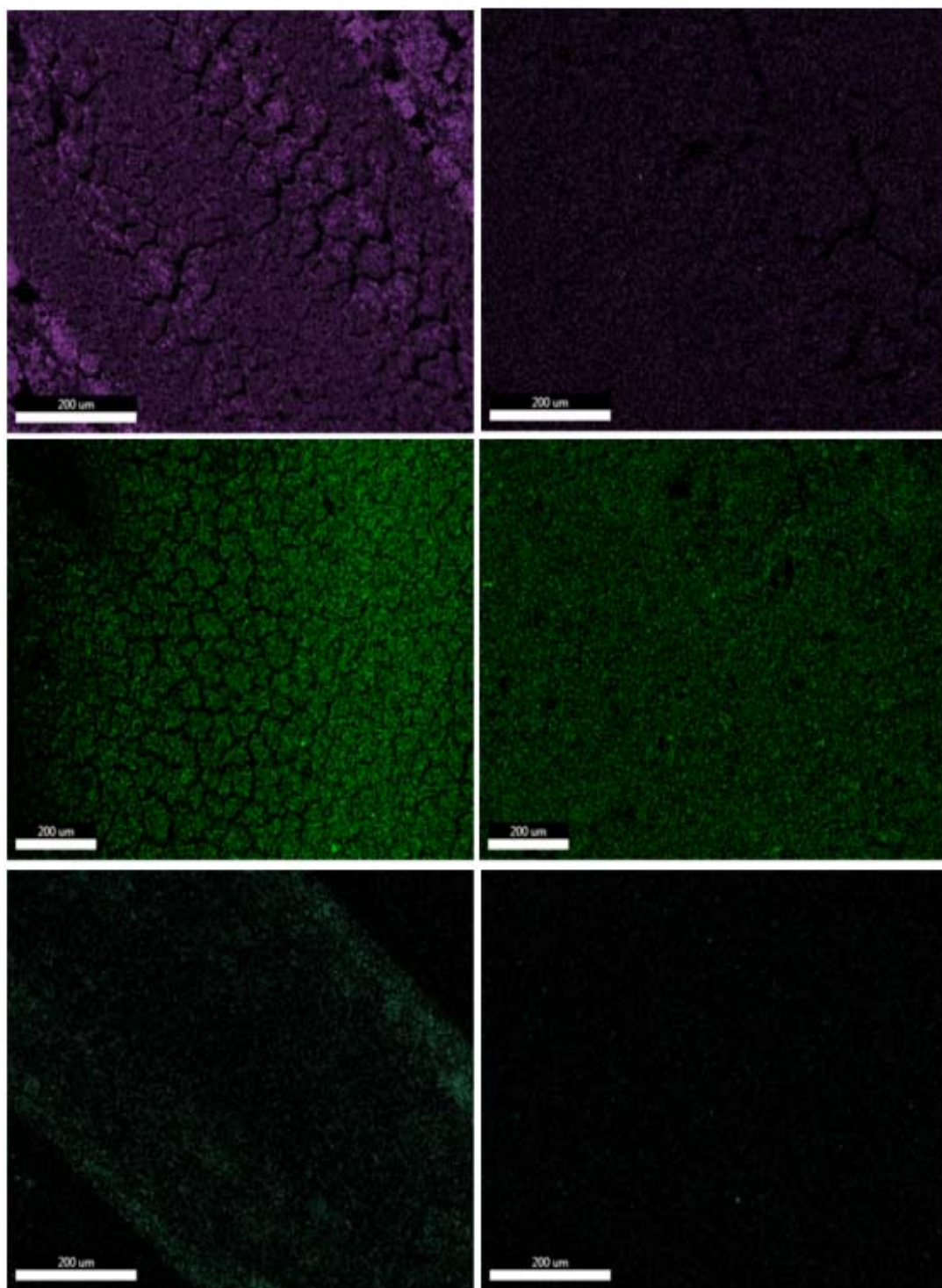
*Figure 3.3: Comparison of poison atomic percentages from pre-wash to post-wash for the inlet and outlet of the catalyst*

Post-wash samples are now showing small quantities of sodium on the surface. Sodium is present in engine coolant and has been identified as a catalyst poison [15]. The sodium does not appear to be from the coolant since, other poisoning elements commonly found in coolant (potassium, molybdenum, silicon and iron) were not detected. The sodium was most likely deposited onto the catalyst from the caustic soda (NaOH) solution during the washing process. The deionized rinse water had a very high pH of 11.82, indicating that it had been contaminated from multiple uses. The wash process may have been more effective if fresh de-ionized water was used.

SEM-EDS elemental intensity can be mapped and displayed over an image of the scanned area to provide a visual image of where each element is concentrated. The brightness of color indicates the concentration of that element, brighter colored regions correspond to a higher concentration. Figure 3.4 compares elemental intensity maps for sulfur, zinc and phosphorus

before and after washing. The pre-wash samples (left) are significantly brighter than the post-wash samples (right), visually indicating that poisons were removed in the washing process.

There was significant concern from other studies that the acid bath may leach the active catalyst metals [6-10, 13]. The precious metals used as the active catalyst material are highly dispersed on the catalyst surface but in very small quantities. The amount of precious metals contained in the projects two modules were below the limit of detection for both spectroscopy instruments. The effect of the acid on the precious metals was therefore unable to be determined.



*Figure 3.4: SEM-EDS element intensity maps for sulfur (top), phosphorus (middle) and zinc (bottom). The left-hand column are scans from pre-wash samples and on the right are post-wash samples.*

### 3.2 Performance Restoration

Light Off curves are plots of reduction efficiency of an exhaust species versus temperature. As degradation occurs and active catalyst sites are lost more thermal energy is required to meet the same reduction efficiency. The curves slowly shift to the right as degradation occurs, resulting in the need for higher temperatures. At higher temperatures thermal energy dominates and little to no loss in performance is seen as degradation occurs; however at lower temperatures large dips in reduction efficiency, as high as 30% can occur. This large decrease in efficiency effects two-stroke engines more than four-stroke engines. Two-stroke engines produce exhaust at much lower temperatures than four-stroke engines. Light off curves for the regulated exhaust species can be seen in Figure 3.5. The increased need for thermal energy shifts the light off curve further to the right as degradation occurs. Washing restored enough catalyst sites to active status thus reducing the need for thermal energy to oxidize the exhaust species. The light off curves shift back to the left after washing, but never reach the initial position of the new catalyst.

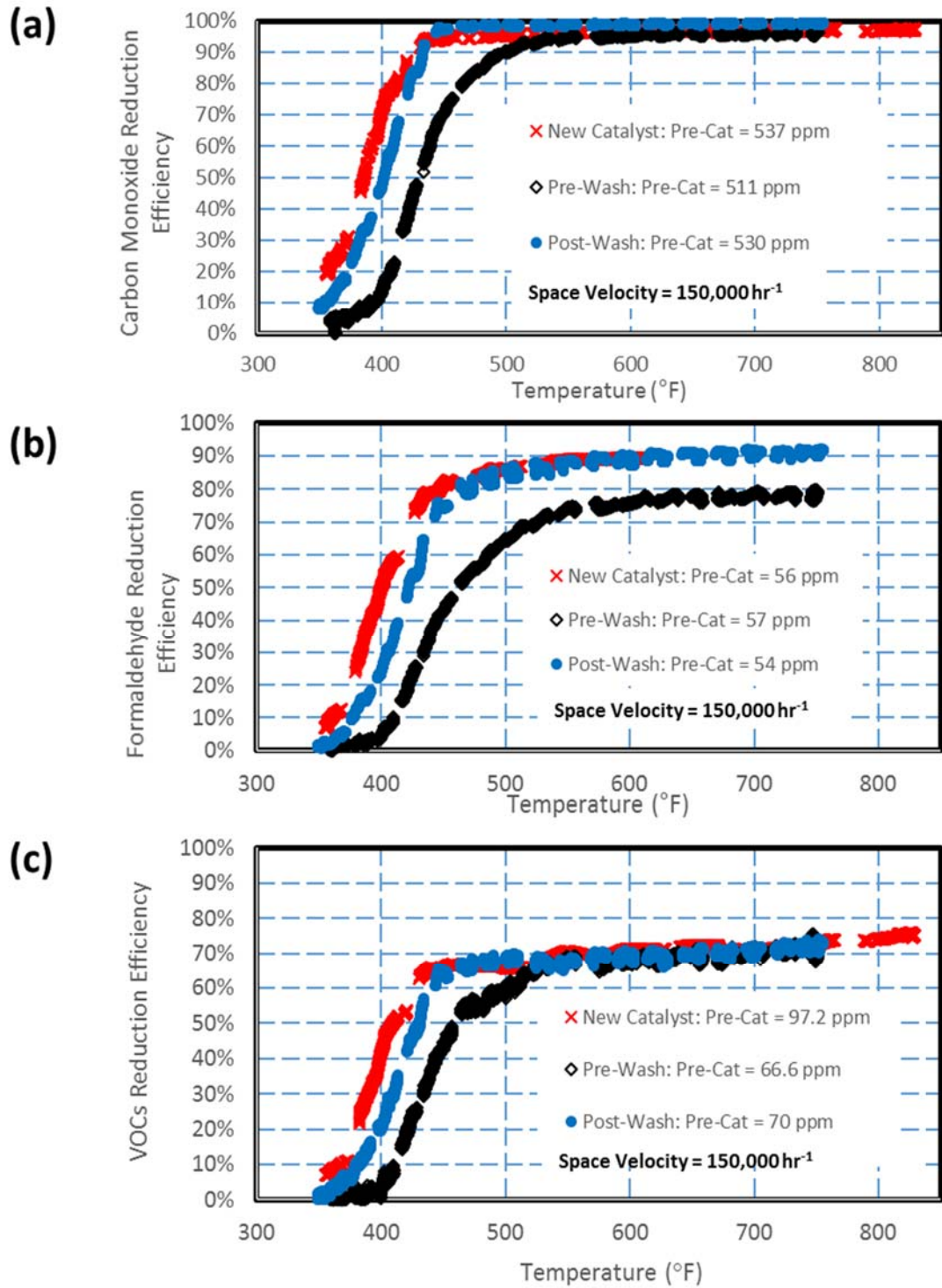


Figure 3.5: Light off curves for exhaust species for new, pre-wash, and post wash tests. Carbon monoxide (a), Formaldehyde (b) and VOC's (c).

Volatile organic compounds (VOC's) are non-methane, non-ethane and non-formaldehyde hydrocarbons. The VOC data is the summed quantities of propane, propylene and ethylene. The maximum reduction efficiency for VOC's is approximately 20% lower than that of carbon monoxide and formaldehyde. This is because VOC's are comprised of two very reactive alkene species propylene and ethylene, and propane, an alkane, which is less reactive. In fact, little to no reduction was seen for alkanes (methane, ethane, and propane) within this temperature range. Alkanes require higher energy to begin oxidizing. Alkenes are more reactive than alkanes due to bonding between the carbon atoms [20]. Alkanes contain only a sigma bond and alkenes are double bonded, containing one sigma and one pi bond. The pi bond in alkenes is weaker than the sigma bond and causes the orbitals to deform [20]. The deformation strains the orbitals making the bonds easier to break.

One metric used to record performance overtime is the light off temperature. The light off temperature is defined as the temperature at which 50% reduction efficiency is met. A trend in the light off temperature can be seen in figure 3.6. The baseline test and tests 1-7 were conducted during the initial degradation study [2, 22]. The light off temperature slowly increases overtime as the need for thermal energy increases with the loss of catalyst sites. The average light off temperature decreased by 31°F after washing, though the light off temperature for no species returned to that of a new catalyst.

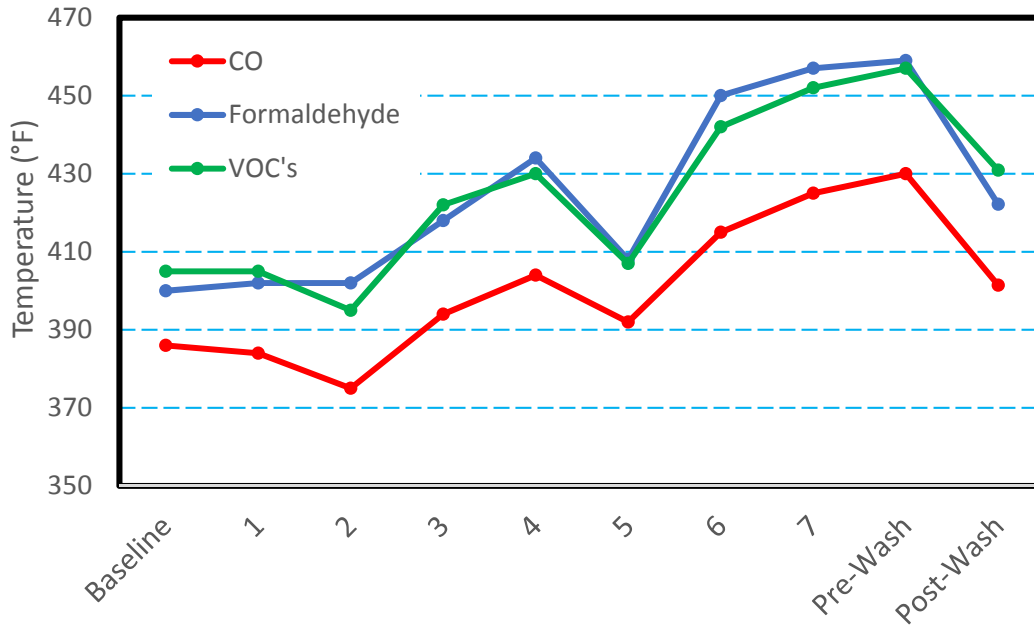


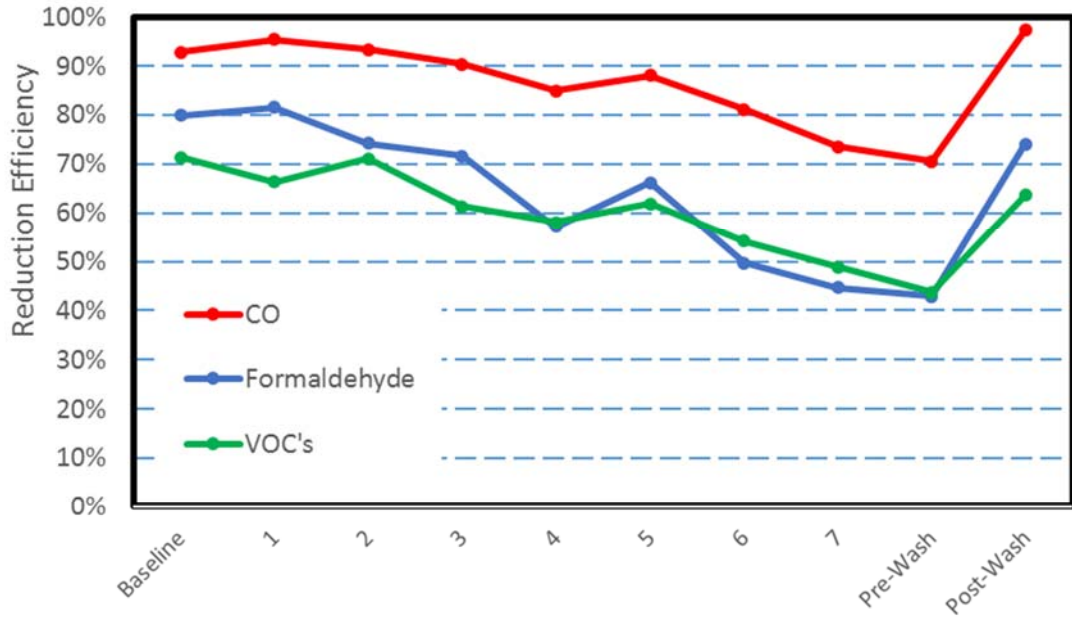
Figure 3.6: Light off temperatures overtime. Baseline being the new catalyst and data points 1-7 were from the initial degradation study with test 5 being an outlier.

A Similar yet opposite trend can be seen by tracking the reduction efficiency over time at a set temperature (Figure 3.7). The temperatures of 450°F (232°C) and 600°F (315°C) were chosen because they represent the range of exhaust gas temperatures for large bore two-stroke natural gas engines. Reduction efficiency slowly decreases with degradation but increased by an average of 25% from pre to post wash at 450°F. Reductions efficiencies are now equivalent to that of a new catalyst for temperatures  $\geq 450^{\circ}\text{F}$ .

The reduction efficiencies were also evaluated over a space velocity range. Higher space velocities correspond to lower reduction efficiencies due to a shorter resonant time for the exhaust gas. Reduction efficiencies steadily drop with space velocities as degradation occurs. The difference in efficiency between the various tests increases with an increasing space velocity. Figure 3.8 plots the reduction efficiencies versus space velocities for carbon monoxide, formaldehyde and VOCs.



(a)



(b)

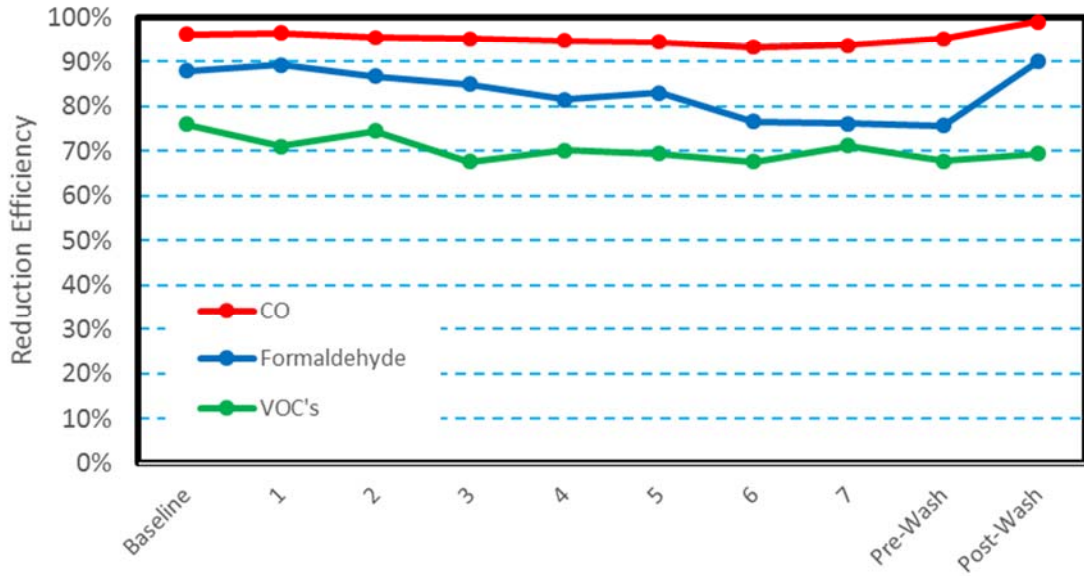


Figure 3.7: Degradation and regeneration of reduction efficiencies at 450°F (a) and at 600°F (b)



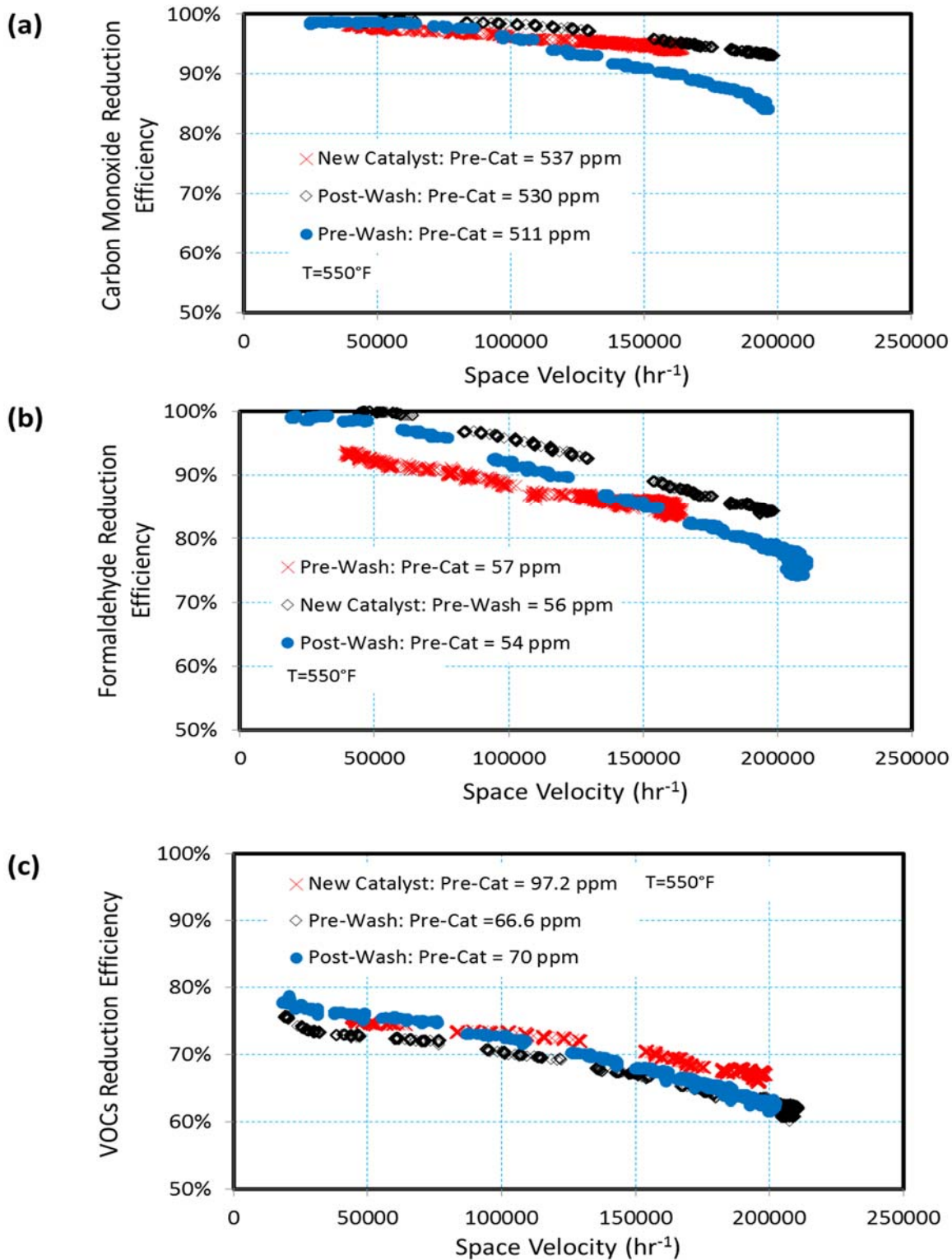


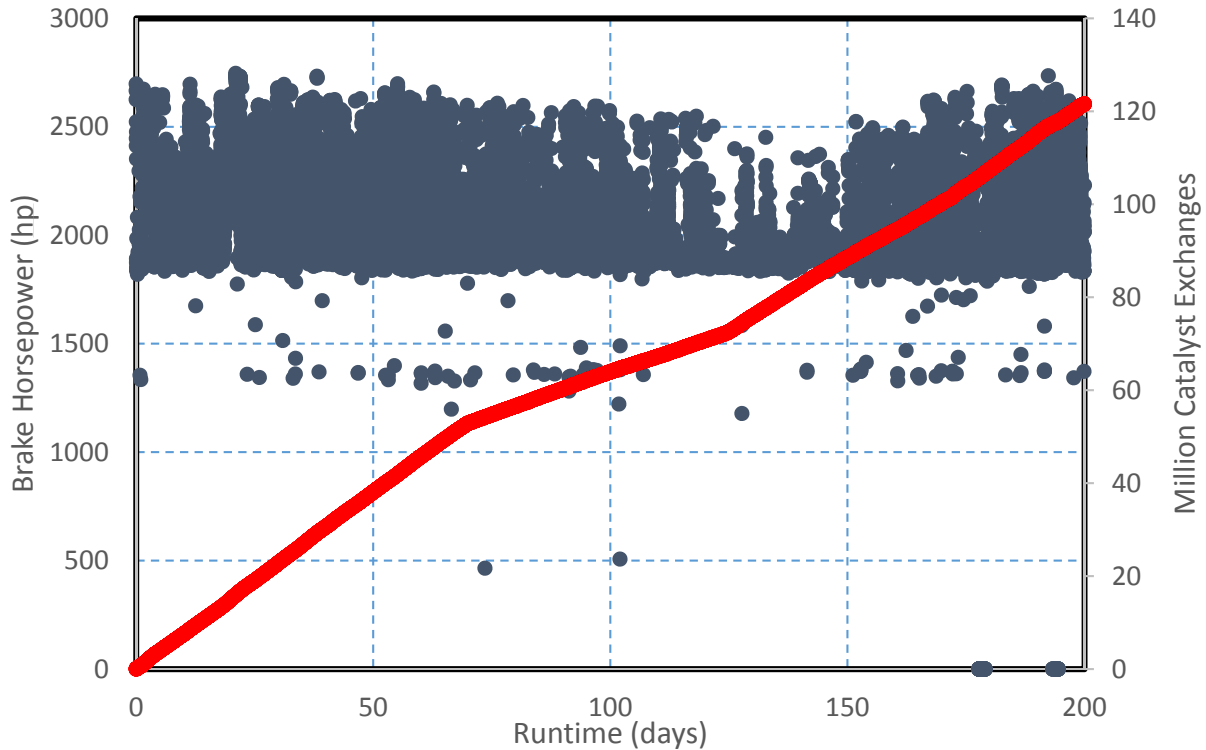
Figure 3.8: Reduction efficiency vs space velocity for carbon monoxide (a), formaldehyde (b) and VOCs (c)

#### **4. Post-Wash Degradation**

The second aim of the project was to evaluate the degradation rate of catalysts after chemical washing. Catalyst washing is supposed to be an inexpensive and effective way to restore efficiency and increase the lifespan of the catalyst. Increasing the lifespan of these modules is highly sought after as they can be costly to replace. Dresser Rand Engineuity estimates washing to be roughly 10% the cost of a new catalyst.

##### **4.1 Poison Accumulation**

The project's modules were installed and aged in the field site slipstream for three aging cycles. Each aging cycle was approximately 2 months long to allow for catalyst exchanges to accumulate. The field site engine saw infrequent use throughout the year based on demands for natural gas but still logged a significant amount of run time. The catalysts would log anywhere from 40-70 million catalyst exchanges during the two months based on the engine use. The engine loading fluctuated primarily between 1800 and 2700 hp during degradation. Catalyst exchanges accumulated slowly during this period and proportional to engine power (Figure 4.1). Each engine cylinder has two oil ports that provide lubrication on a timed basis. The engine is outfitted with a Trabon oil-injection system that is timed off the crankshaft to deliver a pulse of oil to each cylinder approximately every 30 crankshaft revolutions. Most of this oil will seep back into the oil sump to be recirculated, but a portion of oil will be burned then exhausted [21]. This small portion of burned oil, known as lube-oil carry over, is the primary mode of poison accumulation. The amount of oil in the exhaust eventually formed a thick layer and clogged the slipstream blower. The clogged blower slowed the rate of aging until it was cleaned by a site operator. The period of slow aging occurred roughly between 70 and 125 days on Figure 4.1.



*Figure 4.1: Engine horsepower and accumulation of catalyst exchanges over the total runtime. The rate of catalyst exchanges slowed in the middle of the project due to an oil clogged blower.*

The initial degradation project, previously conducted by the Engines and Energy Conversion Laboratory, tracked the poison accumulation on new modules [2, 22]. The modules completed several aging cycles before failing to meet the formaldehyde emissions limit. At this point, the modules were declared degraded with 24% of the surface being poisoned. The field site engine had three of its twelve power cylinders replaced after the initial degradation study. There was that the new components would alter the lube-oil carry over rate and affect the comparison of the degradation rates before and after washing. Figure 4.2 plots the accumulation of poisons against the amount of catalyst exchanges for both degradation studies. The rates for poison accumulation were similar for both degradation studies, though the post-wash rate was slightly higher. Therefore the engine overhaul did not significantly affect the lube-oil rate. Figure

4.3 is a similar plot, comparing poison accumulation with the total amount of oil passed over the catalyst. Once again the rates of accumulation are similar, but the post-wash rate slightly higher. Both Figures 4.2 and 4.3 show that the poison accumulation is linear in nature and proportional to the amount of oil exposed to the catalyst.

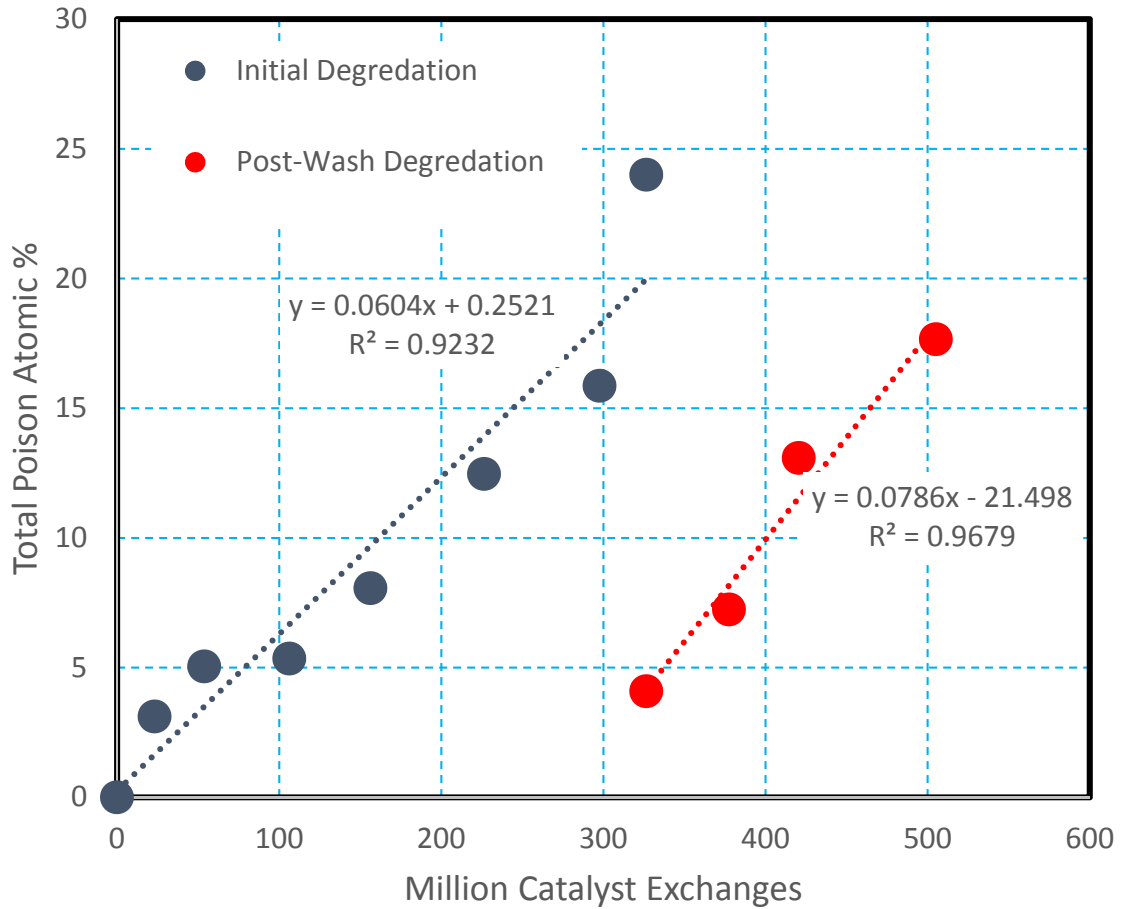


Figure 4.2: Total poison accumulation versus millions of catalyst exchanges for both degradation studies.

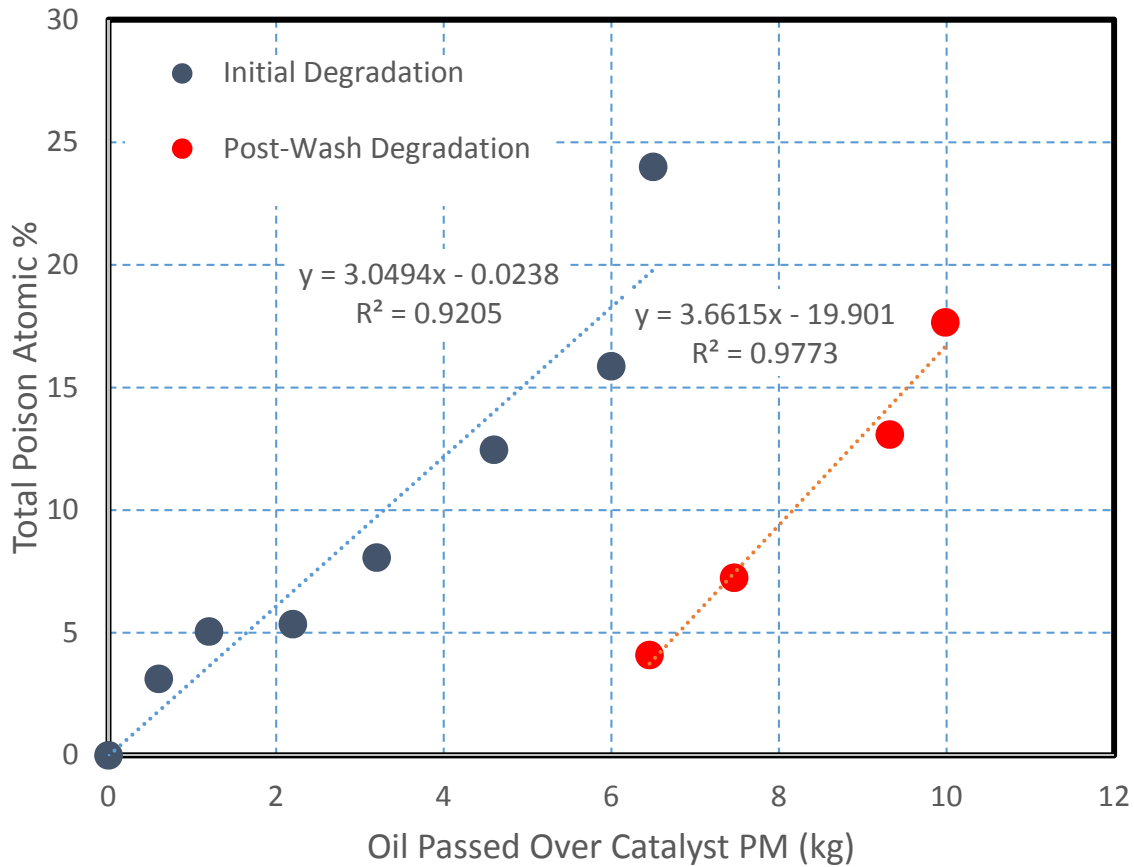


Figure 4.3: Total poison accumulation versus total amount of oil passed over the catalyst.

Taking samples from multiple locations in the catalyst has allowed for spatial trends in poison accumulation to be identified. The accumulation of sulfur on the front (inlet) and back (outlet) samples can be seen in Figure 4.4. Sulfur has been an interesting poison to track, as it tends to accumulate slowly and in higher quantities on the outlet of the catalyst module. Higher outlet accumulation of sulfur has been noted in another study [8]. Figures 4.5 and 4.6 are the same plots but for phosphorus and zinc respectively. Phosphorous and zinc were found to accumulate quickly and in higher quantities near the inlet than the outlet. Of the three poisons, phosphorus was detected in the highest quantity, followed by zinc and sulfur. Sodium was introduced in small quantities to the catalysts surface during the washing process. The small

amounts of sodium have stayed with the catalyst throughout the post-wash degradation (Figure 4.7). Trends in poison accumulation across the width of the catalyst were evaluated. The trend noticed was higher poisons accumulation in the center of the catalyst, but this was likely due to the velocity profile of the exhaust flow.

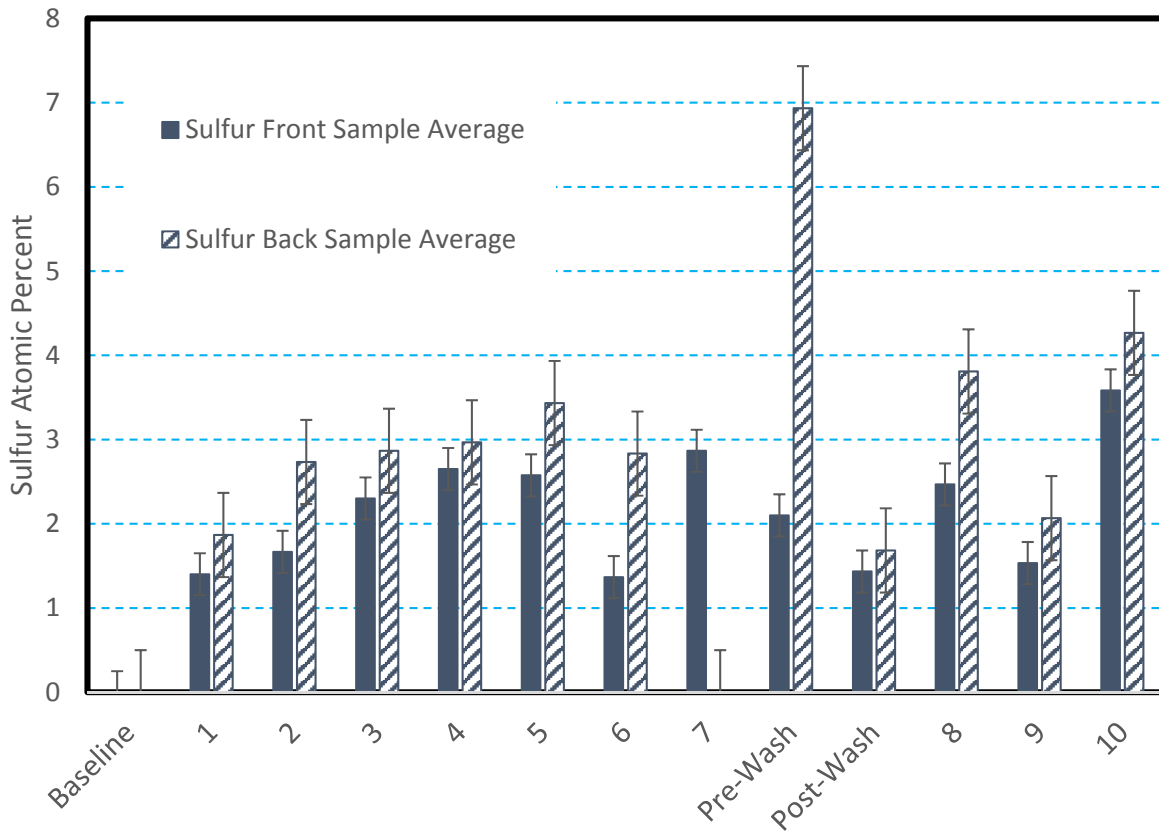


Figure 4.4: Sulfur accumulation for front (inlet) and back (outlet) samples

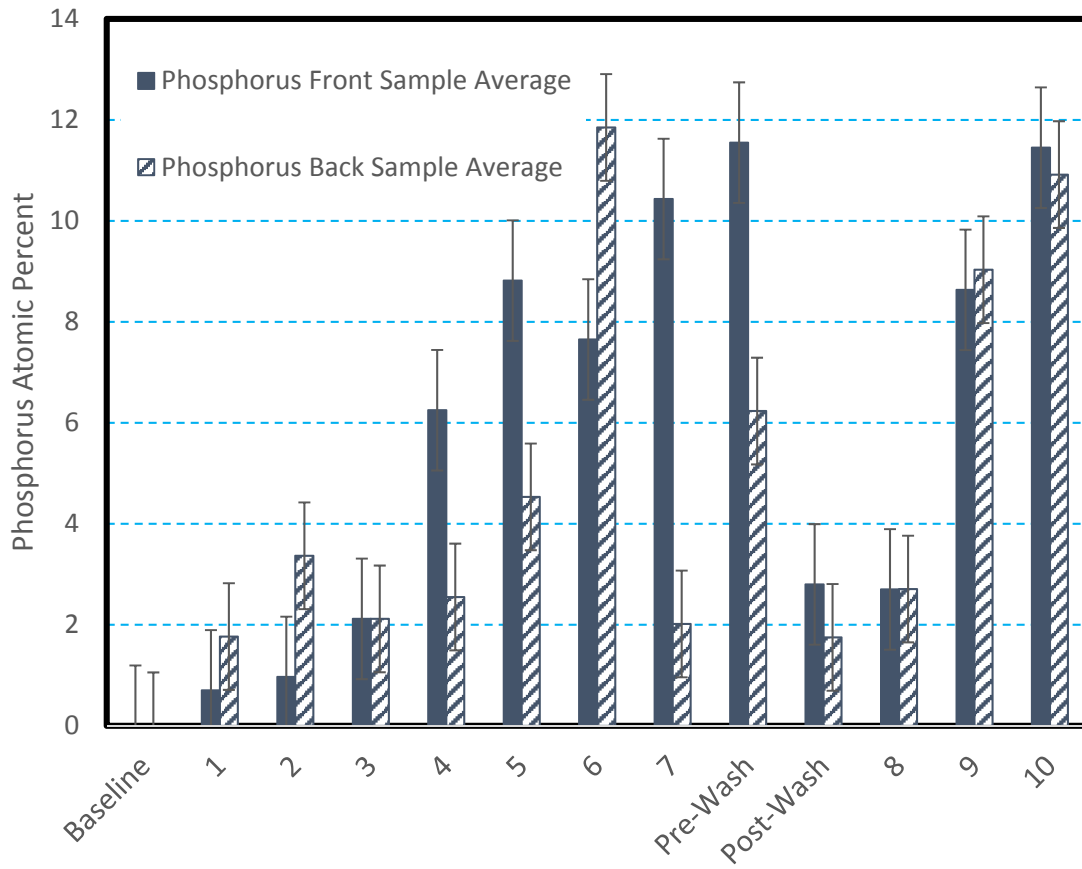


Figure 4.5: Phosphorus accumulation for front (inlet) and back (outlet) samples

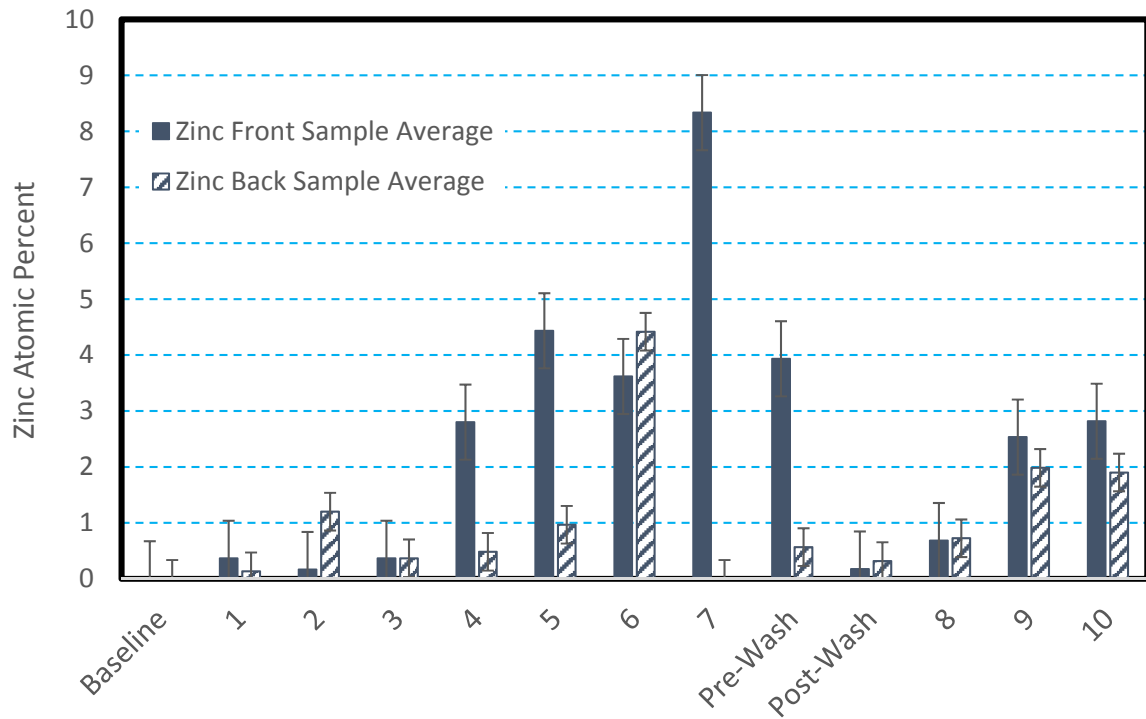


Figure 4.6: Zinc accumulation for front (inlet) and back (outlet) samples

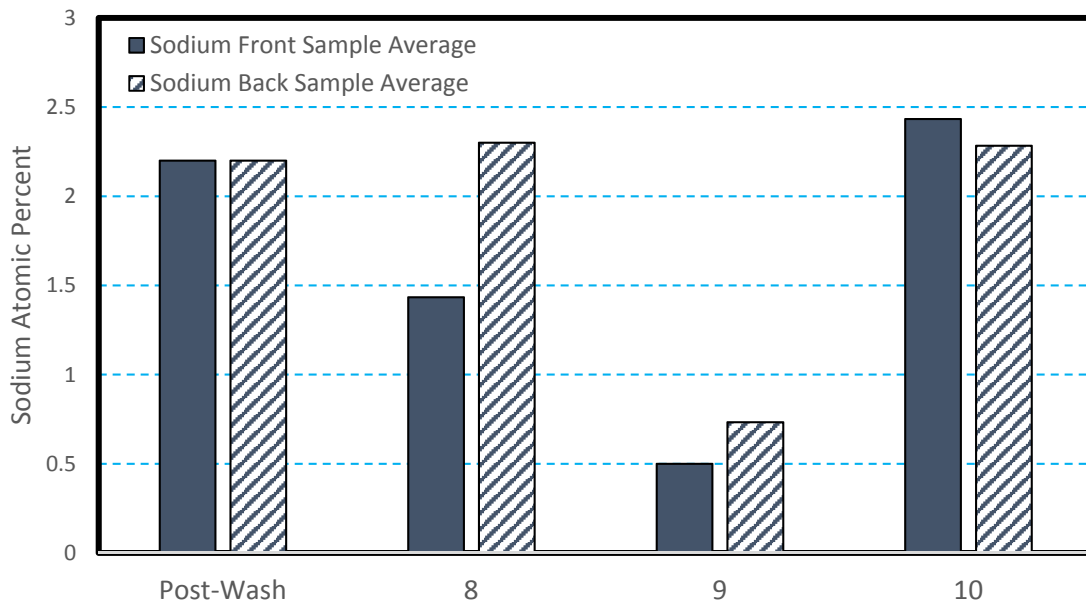


Figure 4.7: Sodium quantities following the washing process



## 4.2 Performance Degradation

As active catalyst sites are poisoned, more thermal energy is required to oxidize exhaust species. The effects of degradation also depend on the catalyst operating temperature due to the non-linear nature of the light off curves. Lower temperatures experience a greater effect of degradation as there are too few active catalyst sites. At higher temperatures degradation has little effect because thermal energy dominates and provides most the energy needed to oxidize exhaust species [6-10]. Figures 4.8-4.10 show the reduction efficiencies versus temperature for carbon monoxide, formaldehyde, and VOCs, respectively. All plots show the sharp rise in efficiency starting around 400°F (204°C) before leveling out to a maximum value. The increasing need for thermal energy pushes the curve to the right (direction of higher temperature). Additionally, the maximum possible efficiency lowers slightly as a function of time on stream. There are some oscillations in the data that can be attributed to slight variations in the natural gas composition. The laboratory engine runs off natural gas directly from the pipeline so these swings seen in the data can be considered to be representative of the effects natural gas composition can have on catalyst reduction efficiencies. This effect can even be seen in the VOC results for test number 8. The data for VOCs is the sum of propylene, ethylene and propane. Propylene and ethylene are very reactive while propane is not as reactive. The portion of propane compared to ethylene and propylene can have a significant impact on the reduction efficiency calculation. In test 8 the natural gas composition contained less propane and therefore boosted the reduction efficiencies by a few percent. Degradation of performance can be better visualized in Figures 4.11 and 4.12. These plots track the reduction efficiencies of carbon monoxide, formaldehyde, and VOCs for both degradation studies. Figure 4.11 shows the reduction efficiencies at 450°F (232°C) and Figure 4.12 plots reduction efficiencies at 600°F

(315°C). The plots show the effects of temperature but also compare the degradation rates before and after washing. The degradation rates were found to be very similar by comparing the average initial and post-wash degradation rates. The rates can be found in Table 4.1. The similar degradation rates indicate that the modules are being aged under similar testing conditions, and that the washing process does not substantially affect the rate of aging.

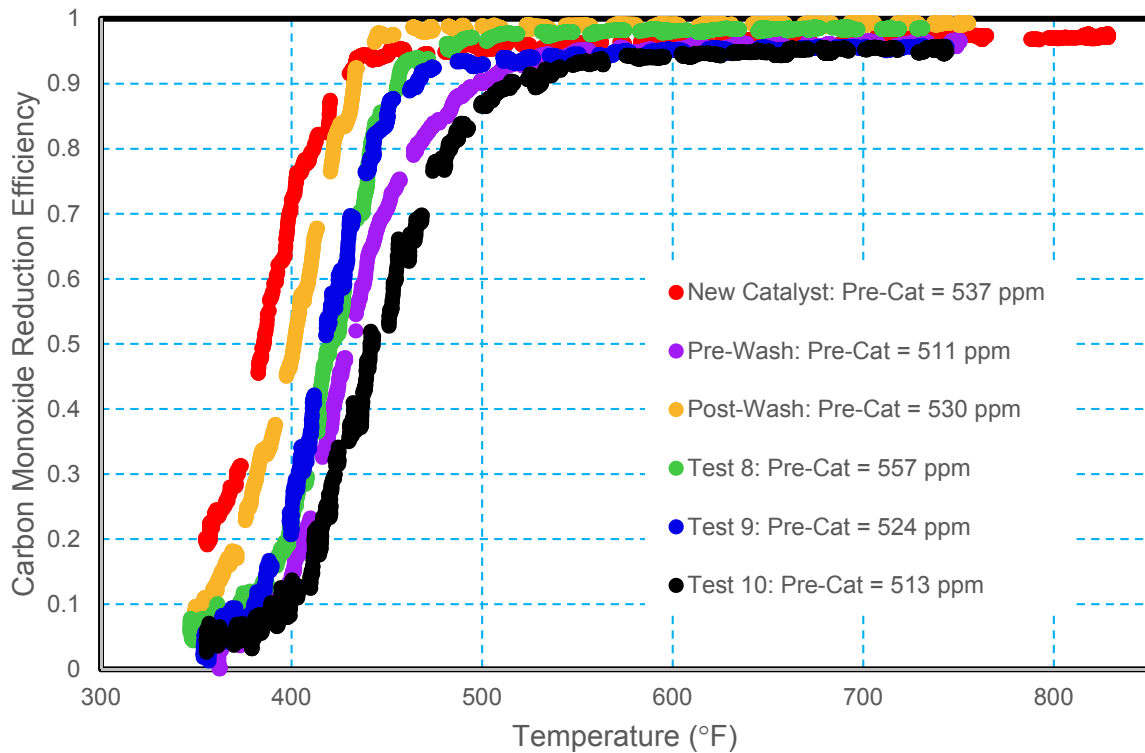


Figure 4.8: Reduction efficiency of carbon monoxide vs. temperature

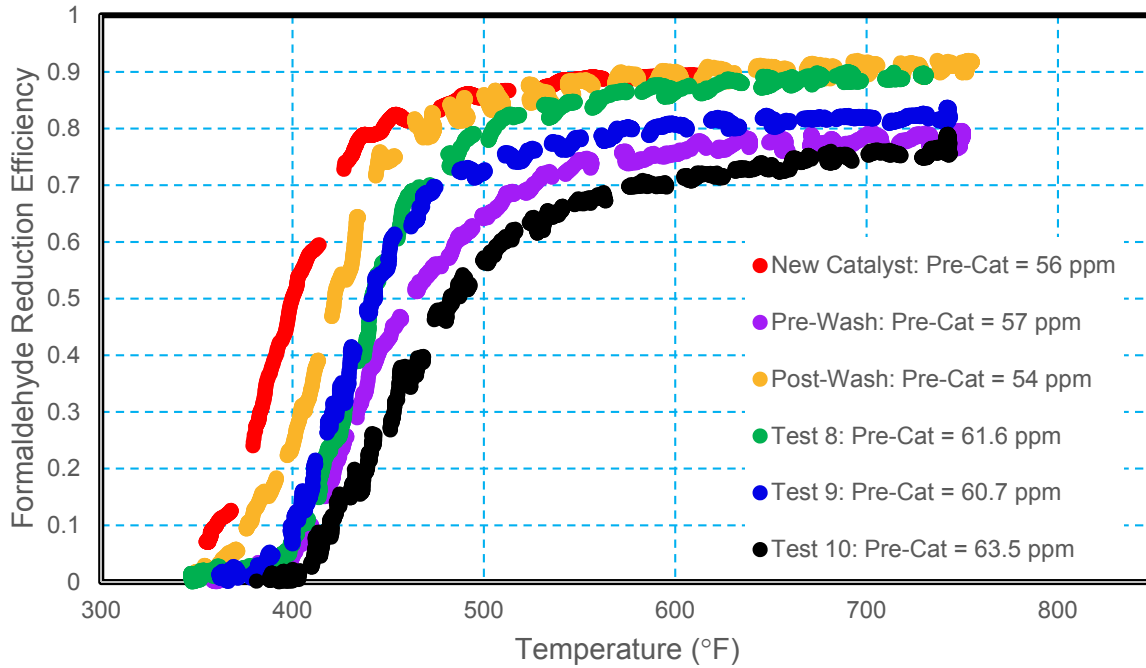


Figure 4.9: Reduction efficiency of formaldehyde vs. temperature

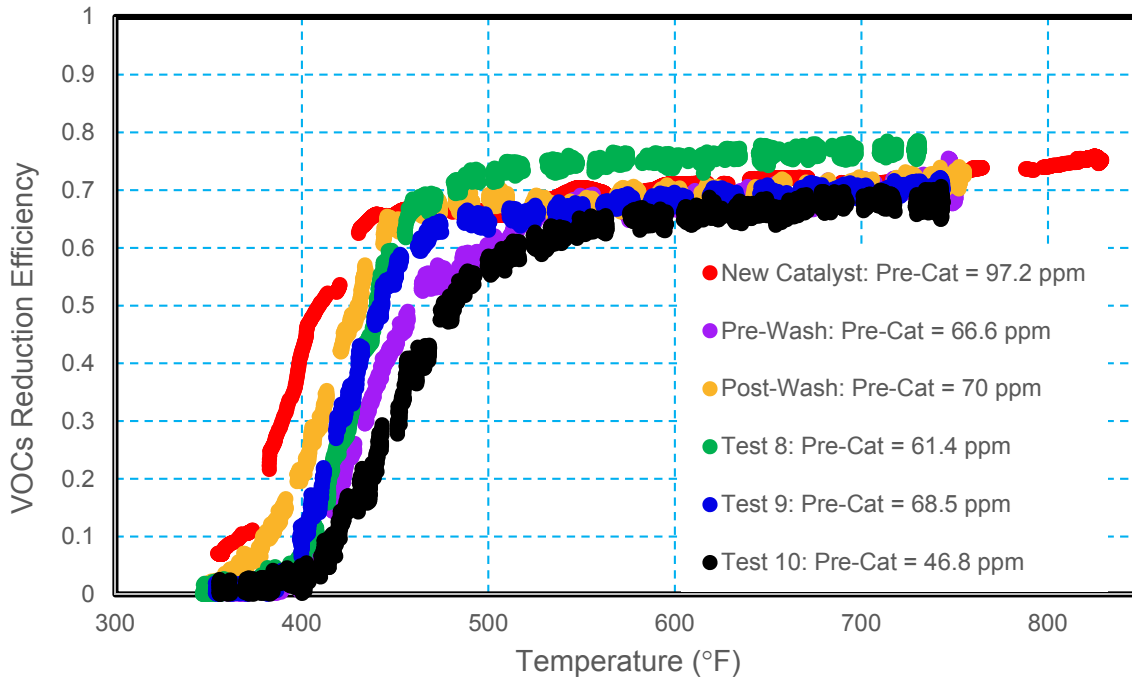


Figure 4.10: Reduction efficiency of VOCs vs. temperature

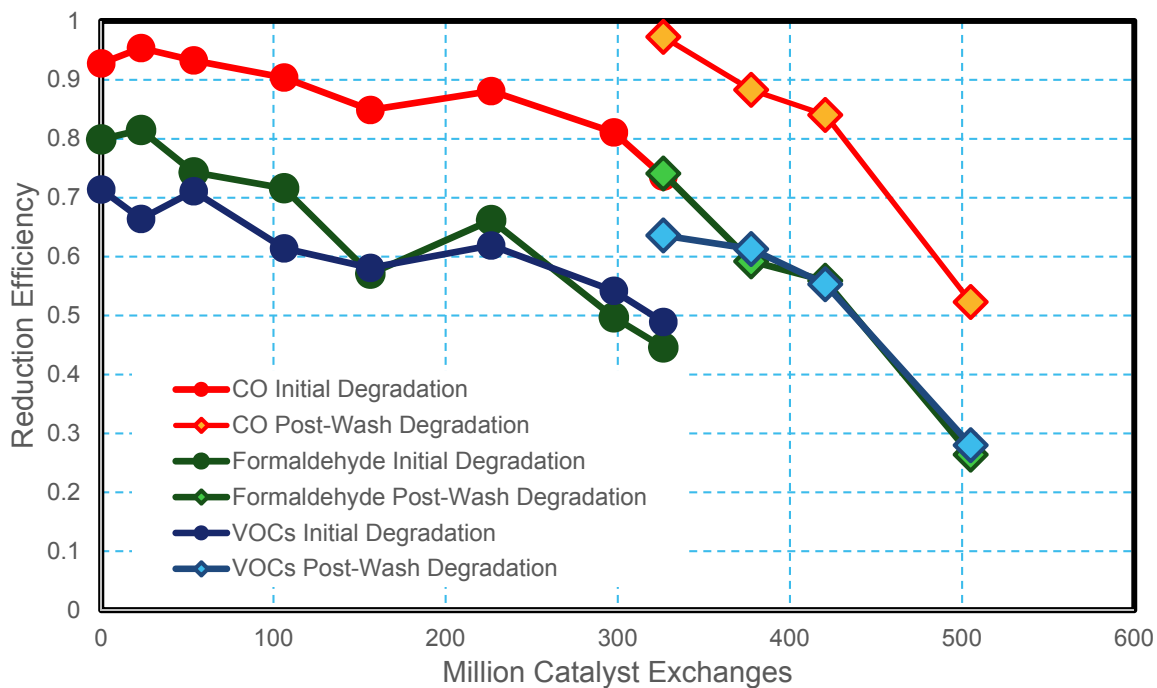


Figure 4.11: Reduction efficiencies versus catalyst exchanges at 450°F

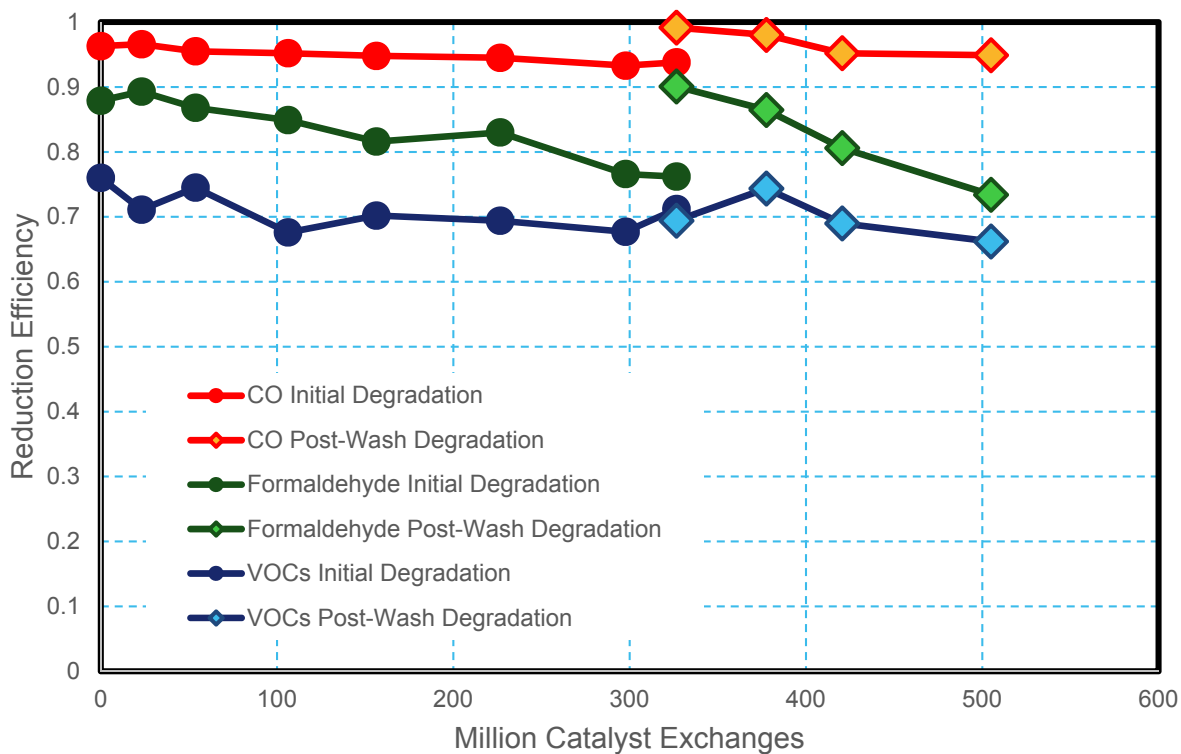


Figure 4.12: Reduction efficiencies versus catalyst exchanges at 600°F

*Table 4.1: Degradation rates before and after washing*

Temperature	Initial Degradation Average	Post-wash Degradation Average
450°F	-0.0025 %/Million exchanges	-0.0024 %/Million exchanges
600°F	-0.0002 %/Million exchanges	-0.00053 %/Million exchanges

### **4.3 NESHAP Limits**

Ultimately, the catalyst is degraded if it can no longer meet even just one of the emissions limits at its operating temperature. The field engine is lean burning, greater than 500 horsepower and is in a non-remote location. The NESHAP standards state that the maximum formaldehyde emissions for this engine is 12 ppm when standardized to dry 15% excess oxygen. The carbon monoxide limit is different as it is a minimum conversion efficiency for exhaust after-treatment. Any device installed to mitigate carbon monoxide must operate above or at a minimum efficiency of 58%. Degradation limits the catalytic performance and therefore overtime the concentration of formaldehyde increase until it approaches its limit of 12 ppm. In the initial degradation study, the modules surpassed the allowable formaldehyde limit at 450°F and around 300 million catalyst exchanges. Washing restored performance and reduced formaldehyde concentration to 8 ppm. The formaldehyde limit was surpassed shortly after starting the post-wash aging. Figures 4.13 and 4.14 plot the carbon monoxide reduction efficiency and the formaldehyde concentration versus the number of catalyst exchanges. Figure 4.13 is for a catalyst operating temperature of 450°F while figure 4.14 is at 600°F. At 450°F the catalyst eventually failed to meet the formaldehyde limit and then the carbon monoxide limit shortly after. Figures 4.13 and 4.14 again highlight the significant effect that temperature has on

reduction efficiencies. At 600°F the catalyst is still well above the minimum carbon monoxide efficiency and is just starting to approach the formaldehyde limit.

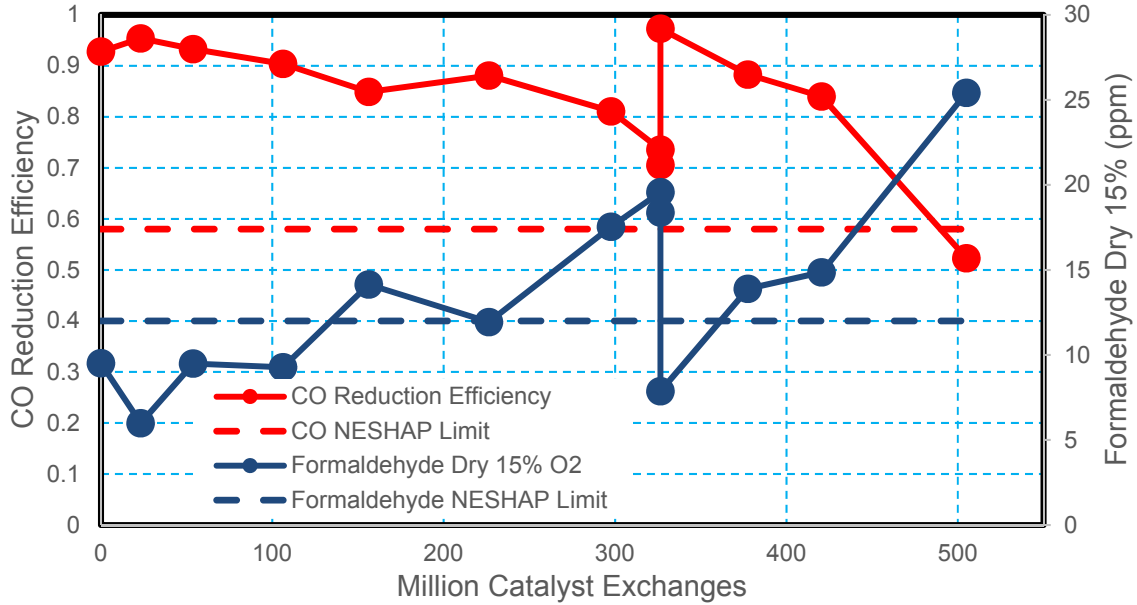


Figure 4.13: NESHAP limits for carbon monoxide and formaldehyde versus the number of catalyst exchanges at 450°F

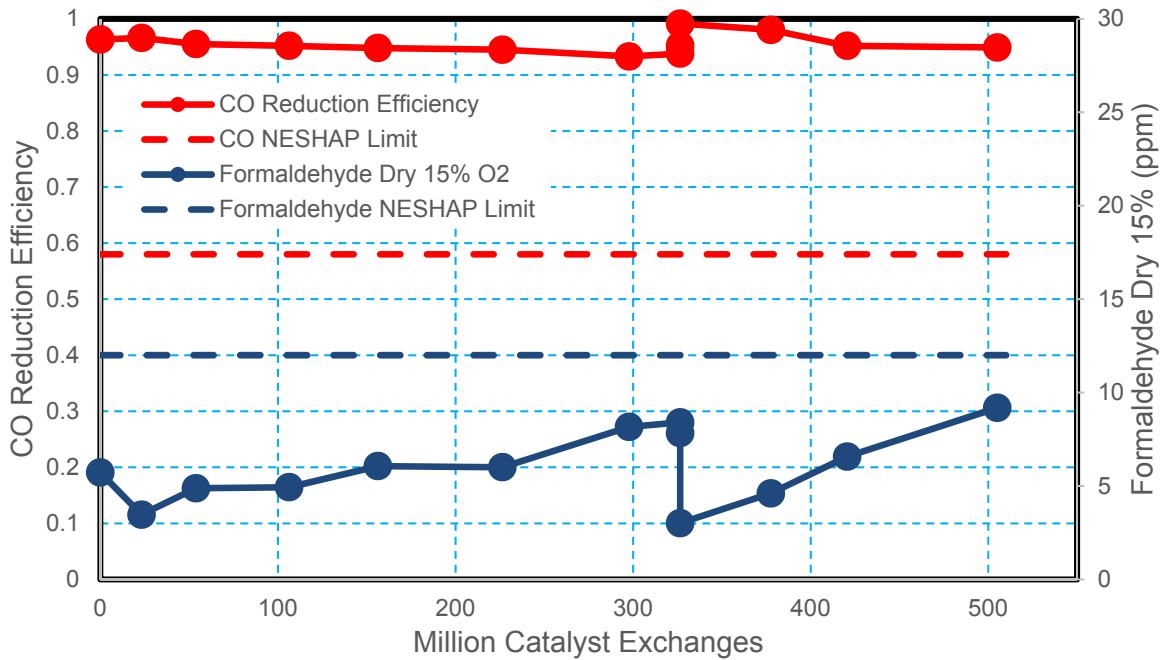


Figure 4.14: NESHAP limits for carbon monoxide and formaldehyde versus the number of catalyst exchanges at 600°F

#### 4.4 Lube-Oil Analysis

An analysis of two different lube-oils was conducted to investigate the amount of poisons in different oils. The two oils tested were Mobil Pegasus 701 and Mobil Pegasus 805. Samples of new oil and used oil (approximately 60 hours use) were analyzed to see if the poison content within the oil changed or not. All samples were provided by Kinder Morgan and were analyzed through Wagner Equipment's Fluid/Oil Analysis Laboratory. Pegasus 701 is the oil used in the field sites GMVH-12 engine. This is a low ash oil (<0.1 wt. %) designed for spark ignited two-stroke engines and natural gas compressor cylinders. Pegasus 805 has a higher ash content (0.5 wt. %) with better anti-wear properties than 701. Pegasus 805 was designed more for lean burn and stoichiometric four-stroke engines. Pegasus 805 is also marketed as catalyst friendly due to its low ash content. Figure 4.15 and 4.16 plot the content of the poisons within the oil. Both oils contained similar quantities of sulfur, phosphorus and zinc. The main difference between the two oils is that Pegasus 805 contains significantly more calcium than 701. Dispersants typically contain calcium. Pegasus 805 was designed for four-stroke engines, which require more dispersants. Calcium has been identified as a catalyst poisons though no calcium was detected on samples. The extremely low level of calcium in Pegasus 701 may be why no calcium has been detected. The amounts of all the poisons changed slightly with use, some increased while others decreased. No conclusion on the changing quantities can be made at this point.

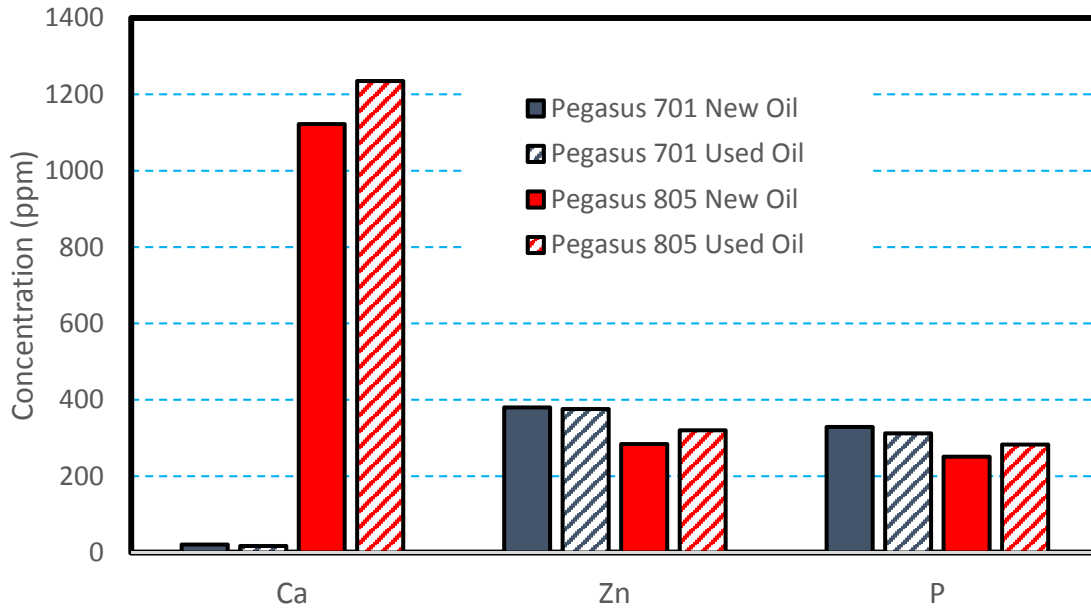


Figure 4.15: Oil additive analysis for new and used engine oils

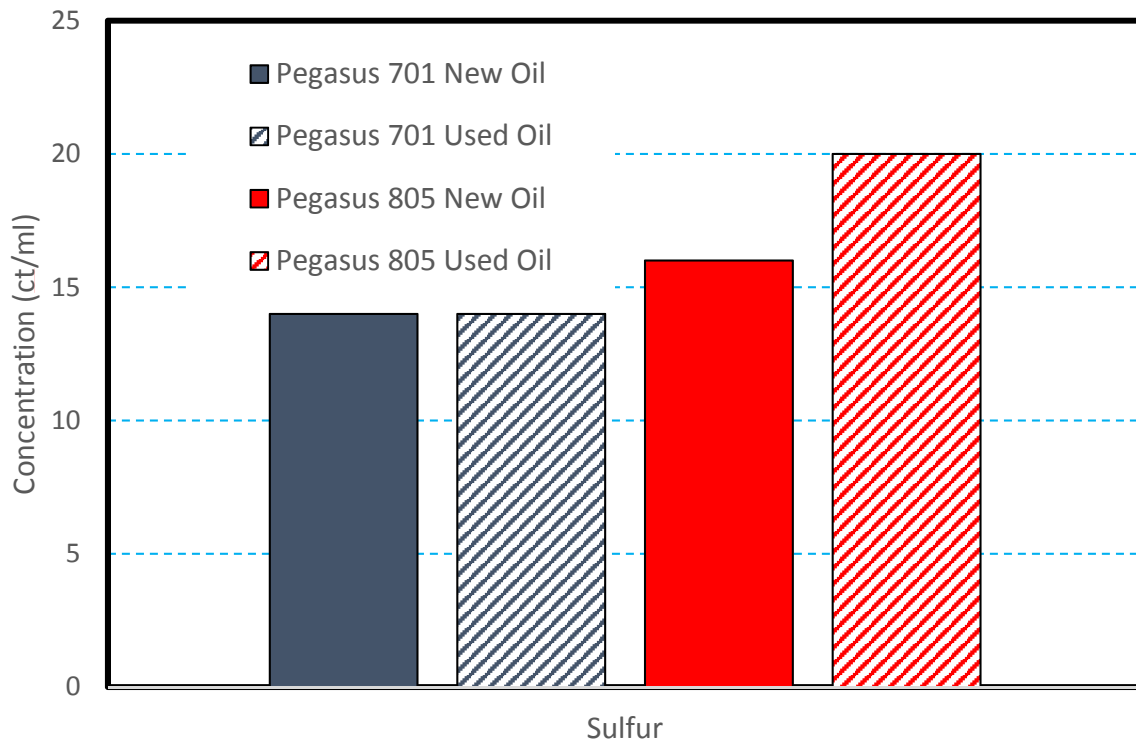


Figure 4.16: Sulfur content of the engine oils



## 5. Conclusion

The two catalyst modules used were previously degraded in a study performed by the EECL until they no longer met the NESHAP formaldehyde emission limit. The modules were laboratory tested for their surface poison content and catalytic performance before being washed to establish a baseline. The modules were washed at Dresser-Rand Engineuity following an industry standard washing procedure. The same laboratory testing was conducted again to compare the poison content and performance before and after washing. The modules were degraded again in the same slipstream and conditions as the previous degradation study. They were installed for periods of about 2 months before being retrieved for laboratory testing. Three aging cycles (each approximately 2 months in duration) were completed before the modules failed to meet the carbon monoxide and formaldehyde NESHAP limits at temperatures less than or equal to 450°F.

The washing procedure removed significant amounts of surface poisons and partially restored performance. Specific conclusions related to catalyst washing are as follows:

- Before washing approximately 18% of the catalyst surface was poisoned; washing reduced this to 4%.
- Light off temperatures were reduced by an average of 35°F through the washing process.
- At 450°F reduction efficiencies increased by an average of 30%; reduction efficiencies after washing were similar to that of a new catalyst for temperatures above 450°F.

- The washing process deposited small amounts of sodium; approximately 2% of the post-washed surface was sodium.

Washing only partially restored performance due to several factors. Thermal and mechanical degradation modes are virtually irreversible. Any sintering of the wash coat or precious metals will decrease performance as well as the loss of wash coat material. Throughout the project small flakes of wash coat material were noticed falling out of the modules during handling. The washing process removed most poisons, but there was still a small amount remaining on the surface. The added sodium could also be limiting performance as one source identified sodium as a poison.

The poison accumulation and degradation after washing was similar to that of a new catalyst. Specific conclusions related to the degradation process after washing are as follows:

- The new catalyst and washed catalyst both showed linear trends in poison accumulation; though the slope of the post-wash accumulation was slightly higher.
- Degradation rates (loss of efficiency per number of catalyst exchanges) were compared before and after washing at temperatures of 450°F and 600°F. The rates before and after washing were similar for both temperatures.
- Degradation was found to occur faster at 450°F than 600°F.
- The lifespan of the modules was increased by 45% from washing at a temperature of 450°F.
- At 600°F the modules are still within compliance of the NESHAP limits, but is approaching the formaldehyde limit.

Lube-oil carry over was found to be the leading cause of catalyst degradation and limiting the amount of oil in the exhaust could greatly improve the catalyst lifespan. Lowering the lubrication rate of the engine would decrease the total amount of oil in the exhaust. However, the lubrication rate must be enough to properly lubricate components and prevent wear. Oils with lower quantities of these poisoning elements can be used instead. Oils are often rated on their ash content; an oil with a lower ash content typically contains less additives and therefore less poisons. The amount of oil in the exhaust was seen when the blower on the field slipstream was clogged with a thick layer of oil residue. Filters or screens could be installed upstream of the catalyst to collect most of this oil before reaching the catalyst. The effects of degradation were found to be less severe at higher temperatures. Operators could reconfigure exhaust systems to place the catalyst further upstream where it would operate at a higher temperature.

Future work on improving the washing process is to be conducted at the EECL. Catalyst sheets taken before washing can be used to run small scale washing procedures testing different variables. The literature review indicated that elevated bath temperatures and stirring/agitation is more effective at removing poisons. Bath pH and soak time had an effect but to a lesser degree. These variables could be tested on small strips taken from the pre-washed sheets. Catalytic performance cannot be tested as a full module is required, but the strips could be tested for poison removal as a basis to justify any improvements in the process. The rinse water bath at Dresser Rand seemed to be contaminated from multiple uses due to its high pH of 11.8. This high pH rinse water may not have effectively rinsed the catalyst of the residual sodium. A repeat of the Dresser Rand procedure but with fresh rinse water should be evaluated.

## 6. References

- [1] Jim McCarthy, "Air Regulations Impacting the Natural Gas Transmission Industry: 2011 Air Quality Regulatory Update", Gas Machinery Conference, Nashville, TN, October 2011.
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## Appendix A: Elemental Analysis Data

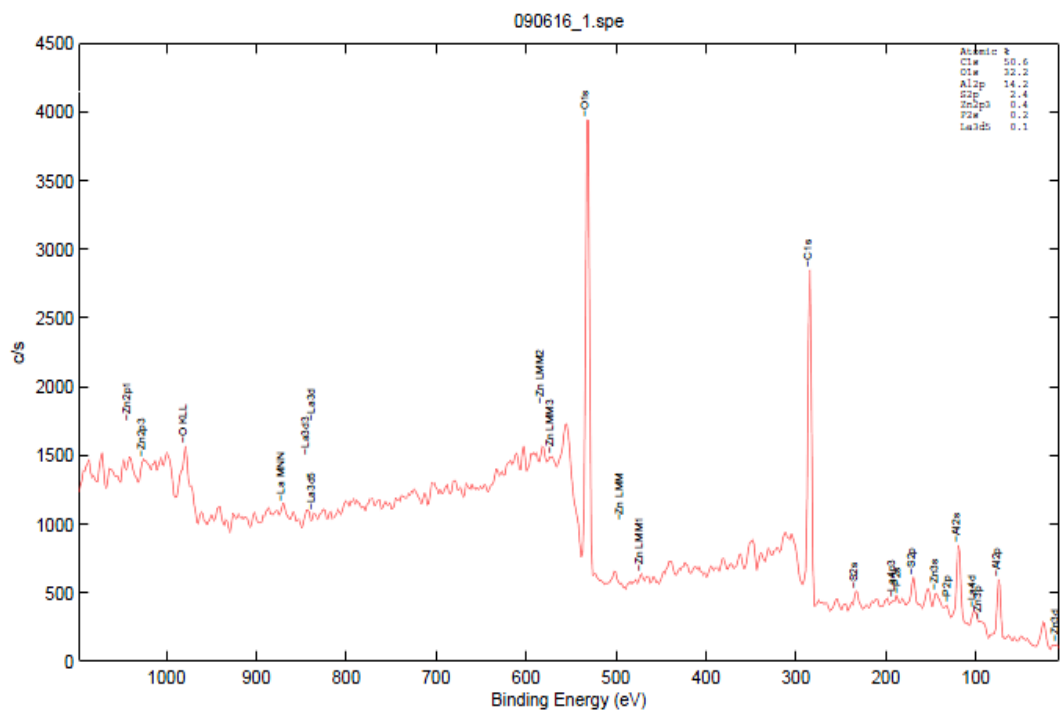


Figure A1: Survey Scan for pre-washed sample A.

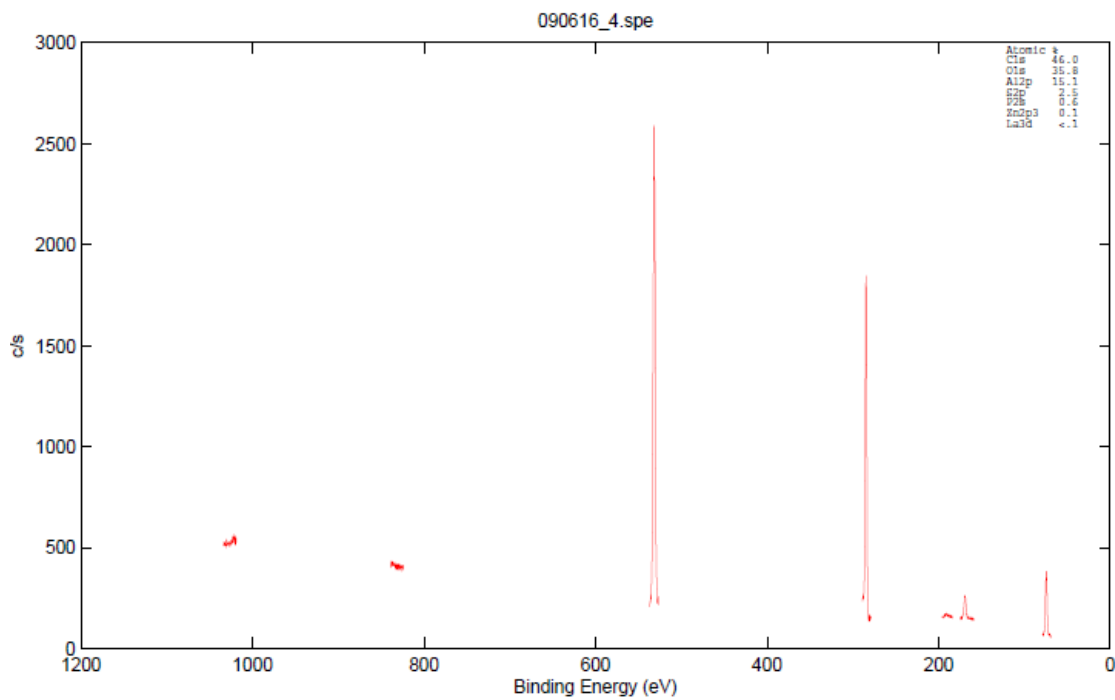


Figure A2: High resolution scan for pre-washed sample A.

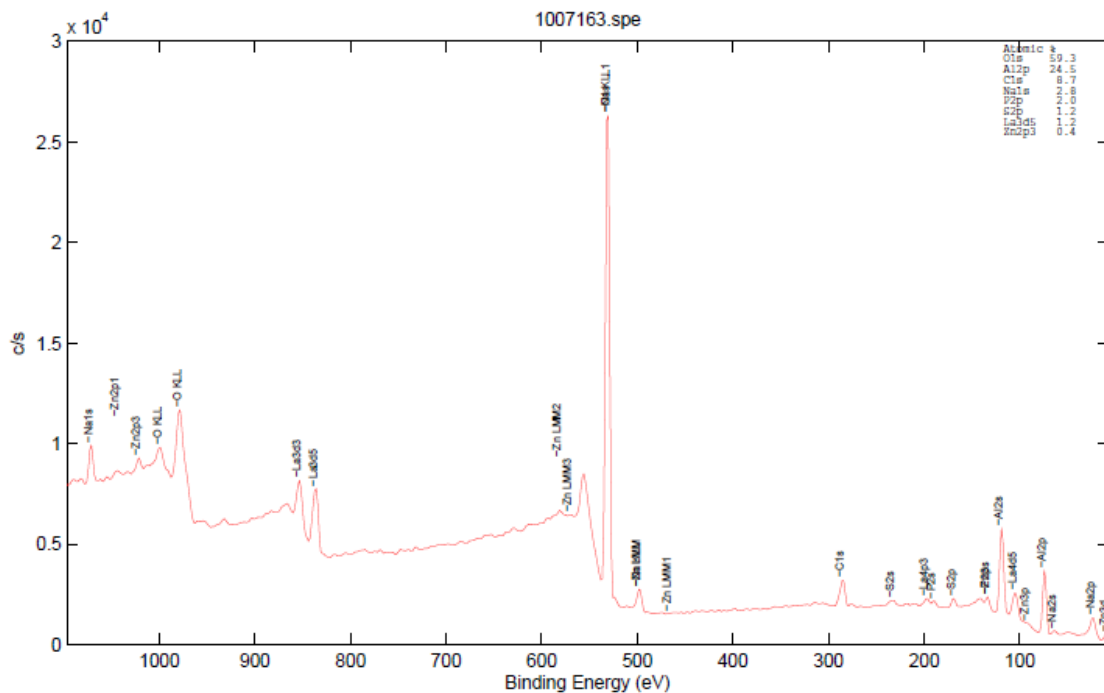


Figure A3: XPS survey scan for post-washed sample A.

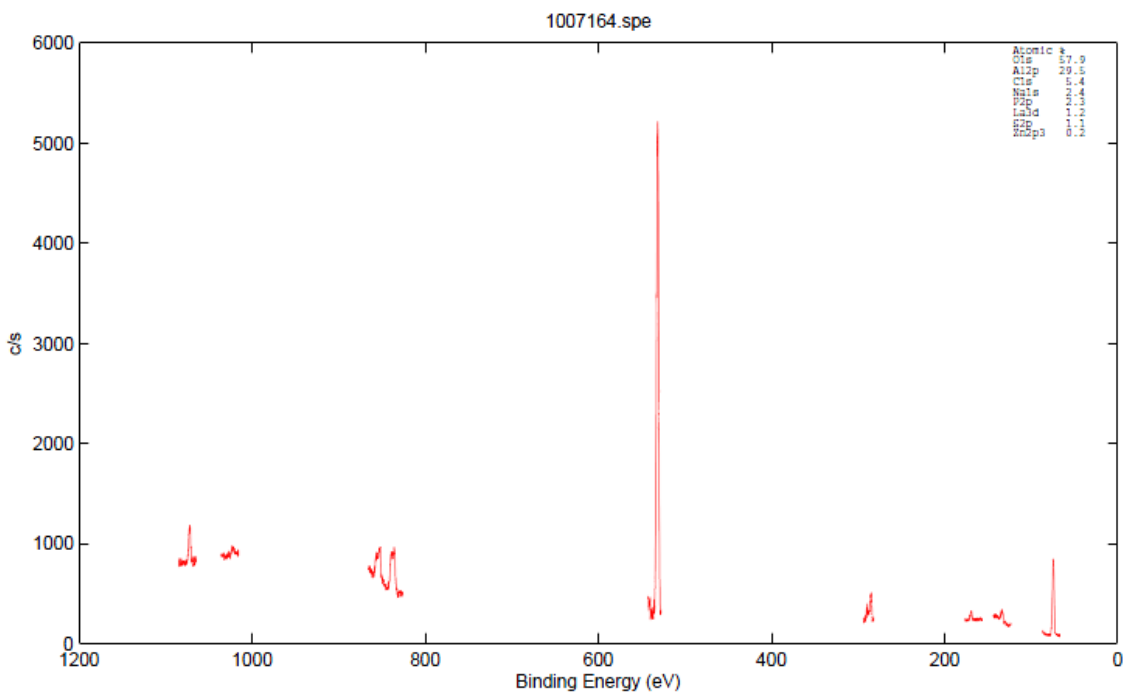
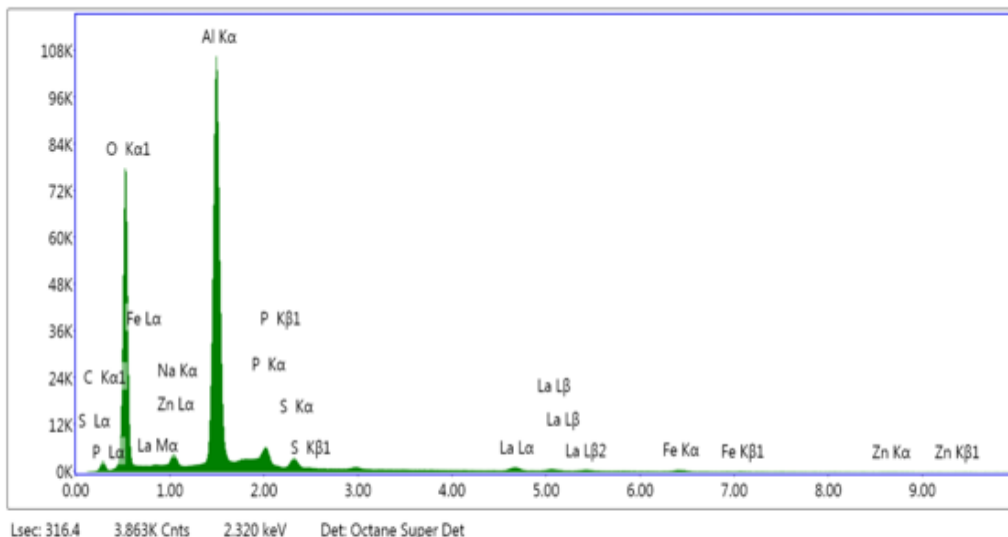


Figure A4: XPS high resolution scan for post-washed sample A.



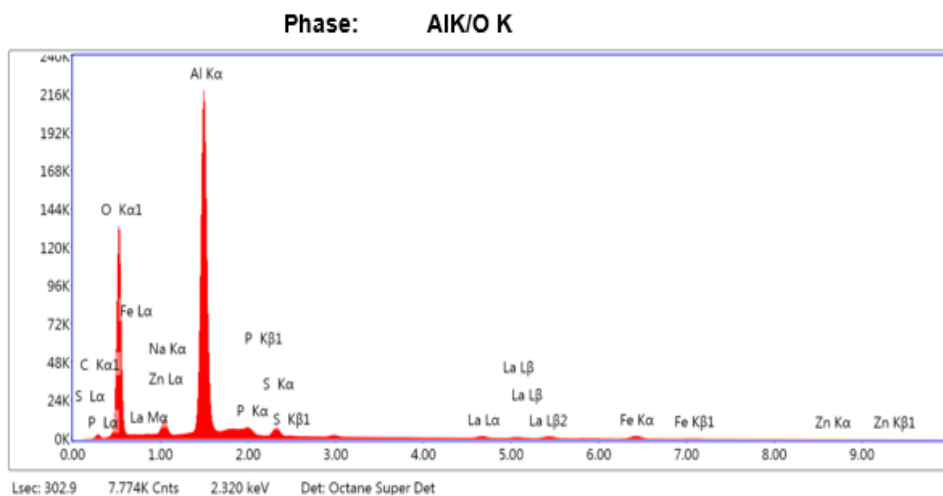
Phase: AIK/O K



**eZAF Smart Quant Results**

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	7.45	12.28	50.60	10.81	0.0135	1.1168	0.9525	0.1623	1.0000
O K	45.25	55.98	1549.10	6.91	0.2134	1.0643	0.9739	0.4432	1.0000
NaK	0.48	0.41	21.30	8.85	0.0024	0.9620	0.9993	0.5197	1.0074
AlK	35.86	26.30	2793.40	3.55	0.2659	0.9398	1.0133	0.7864	1.0035
P K	4.85	3.10	270.30	4.28	0.0336	0.9203	1.0255	0.7498	1.0059
S K	1.57	0.97	91.30	4.21	0.0120	0.9373	1.0309	0.8063	1.0073
LaL	2.97	0.42	33.40	8.42	0.0212	0.6252	1.2193	1.0630	1.0714
FeK	1.15	0.41	16.70	9.54	0.0100	0.7932	1.0590	1.0010	1.0854
ZnK	0.42	0.13	2.30	41.07	0.0037	0.7451	1.0443	1.0044	1.1953

Figure A5: SEM-EDS data for pre-washed sample F. The x-axis is x-ray energy (keV) and the y-axis intensity (counts per second).



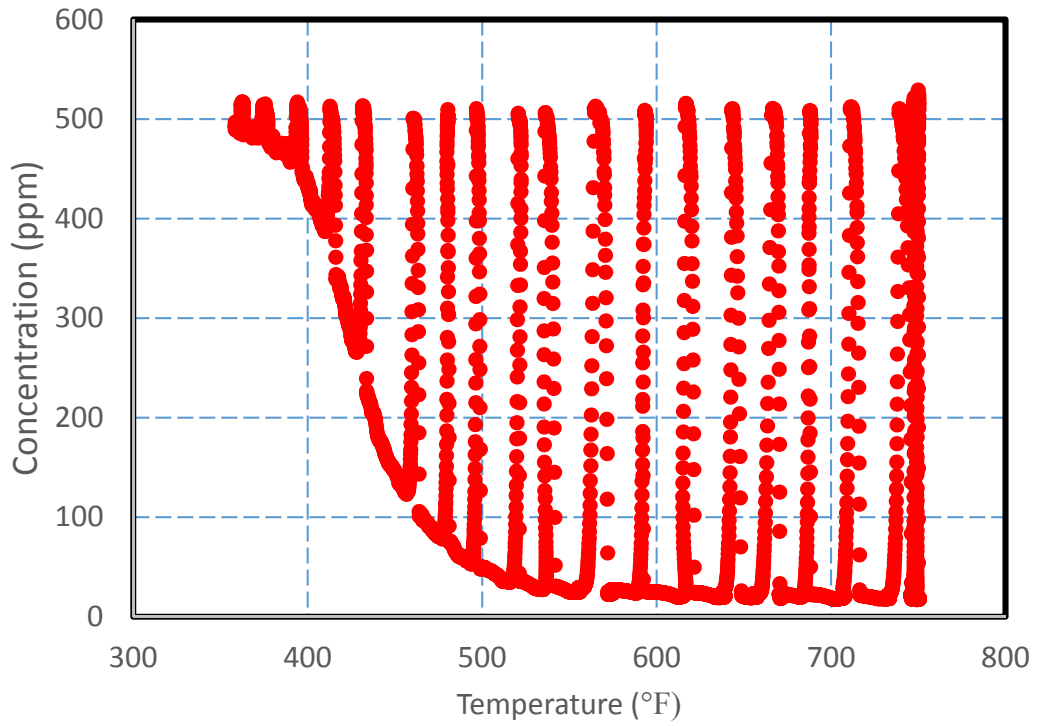
**eZAF Smart Quant Results**

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	4.11	7.08	48.20	11.04	0.0070	1.1264	0.9498	0.1502	1.0000
O K	42.34	54.75	2792.10	6.73	0.2081	1.0736	0.9714	0.4579	1.0000
NaK	1.82	1.64	155.10	6.88	0.0095	0.9705	0.9970	0.5302	1.0080
AlK	41.02	31.45	5960.00	3.52	0.3069	0.9481	1.0112	0.7869	1.0031
P K	3.71	2.48	374.80	4.49	0.0252	0.9285	1.0235	0.7279	1.0058
S K	1.81	1.17	193.20	4.14	0.0137	0.9457	1.0290	0.7939	1.0070
LaL	2.16	0.32	45.40	6.45	0.0156	0.6308	1.2178	1.0608	1.0797
FeK	2.83	1.05	76.10	4.40	0.0245	0.8004	1.0580	1.0010	1.0808
ZnK	0.20	0.06	2.00	57.19	0.0018	0.7520	1.0437	1.0036	1.1909

Figure A6: SEM-EDS data for post-washed sample F. The x-axis is x-ray energy (keV) and the y-axis intensity (counts per second).

## Appendix B: Performance Data

### Raw Emission Data: CO



*Figure B1: FTIR raw data for carbon monoxide from the post-wash performance test.*

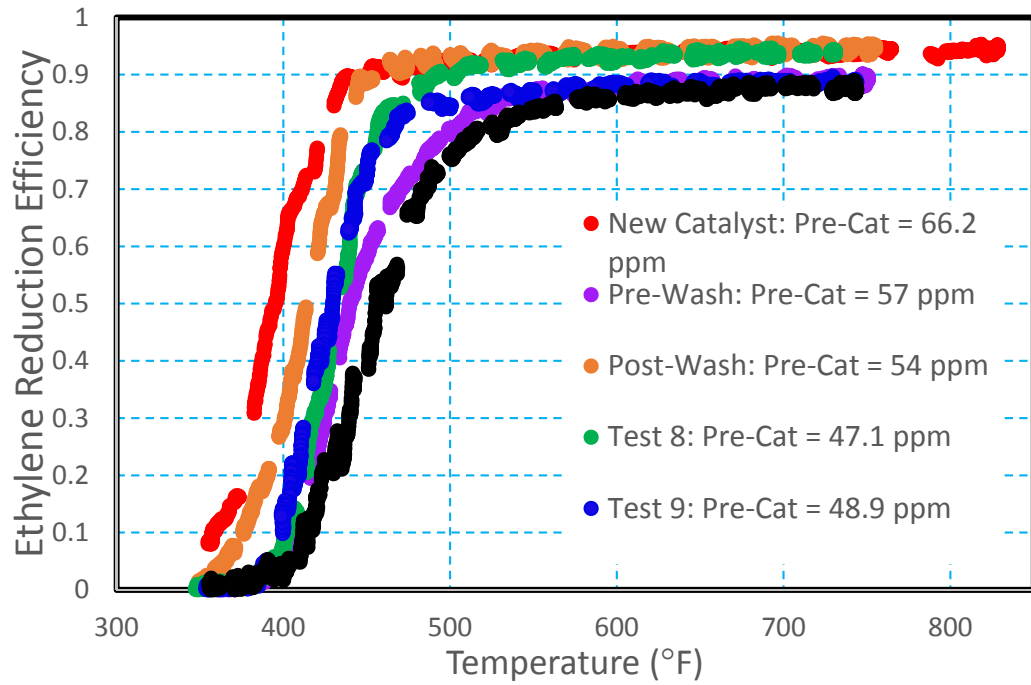


Figure B2: Reduction efficiencies versus temperature for ethylene.

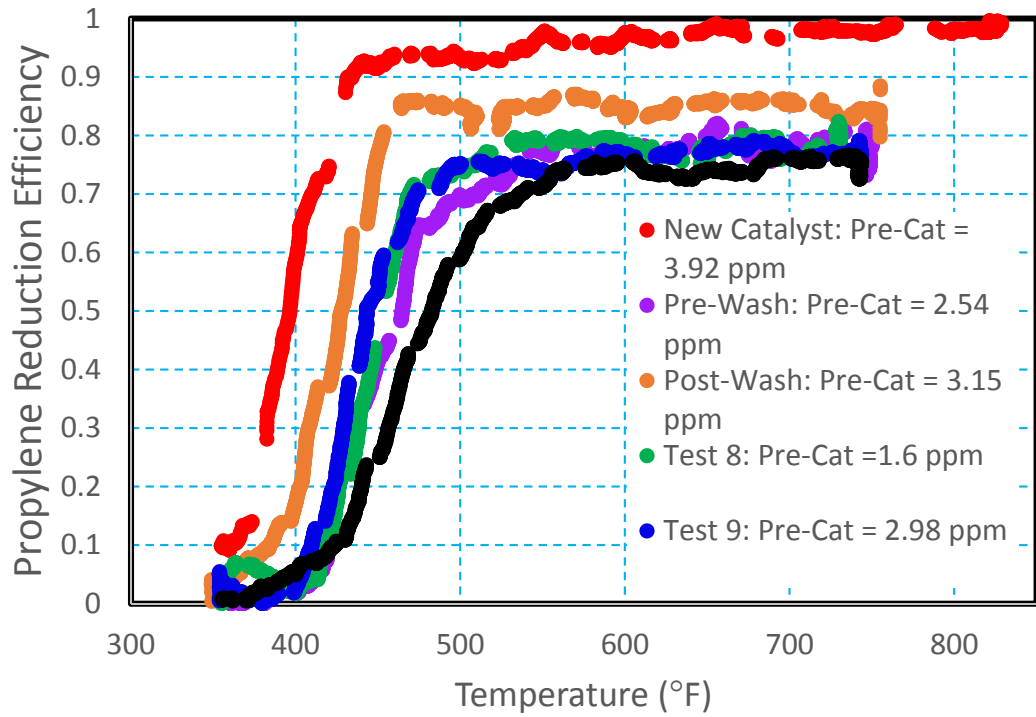


Figure B3: Reduction efficiencies versus temperature for propylene.

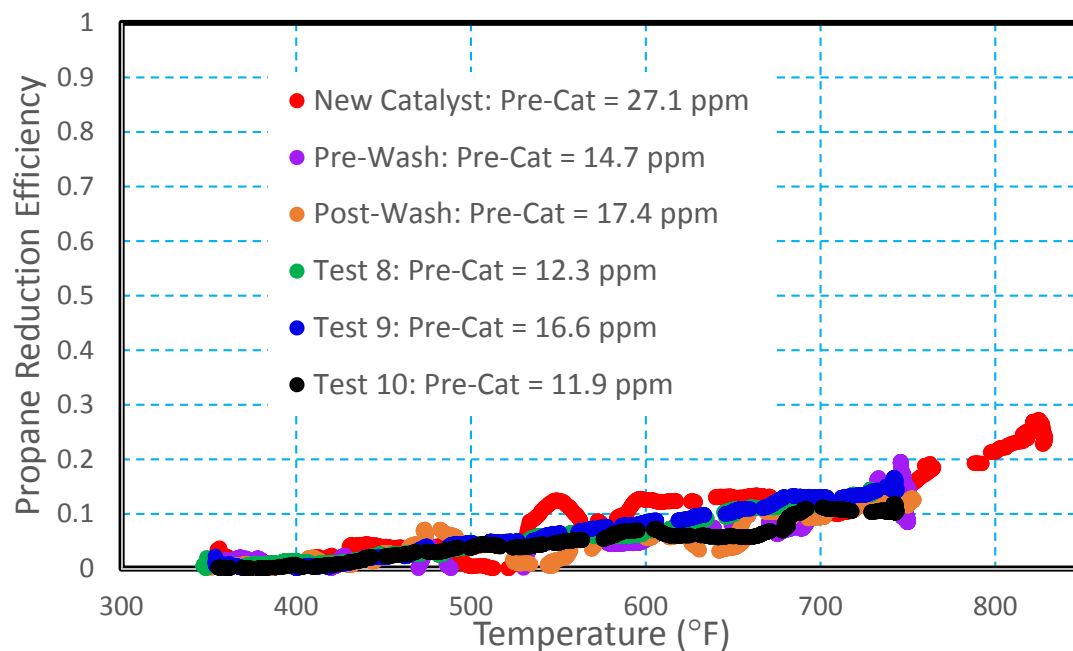


Figure B4: Reduction efficiency versus temperature for propane.

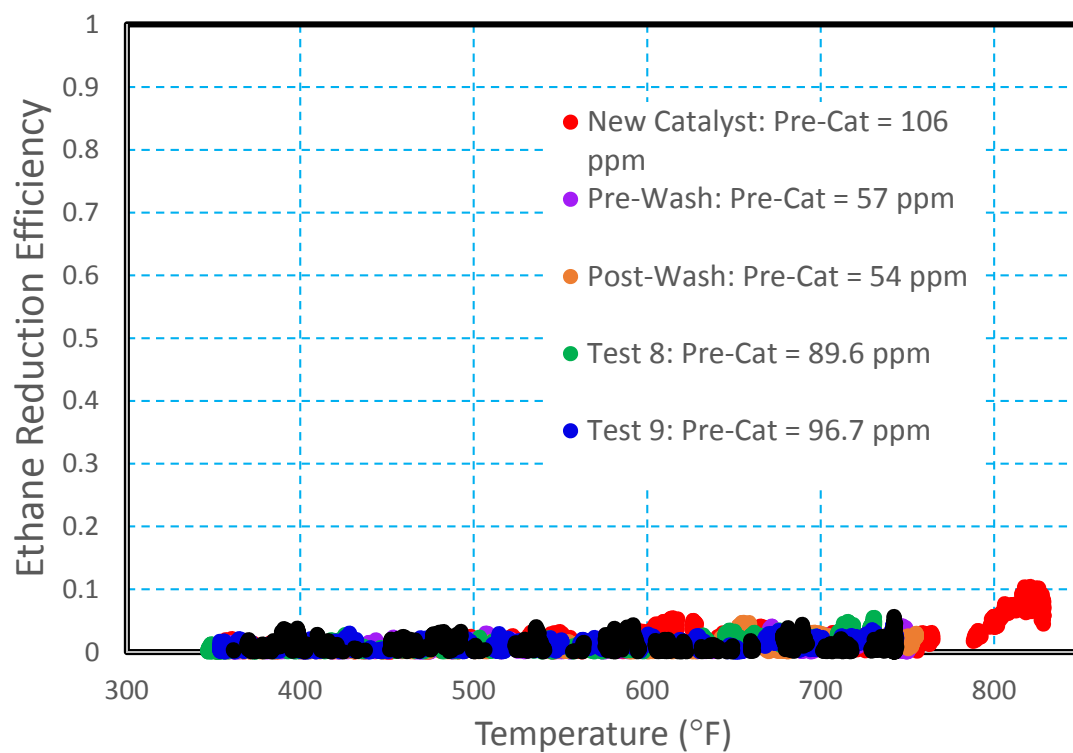


Figure B5: Reduction efficiencies versus temperature for ethane.

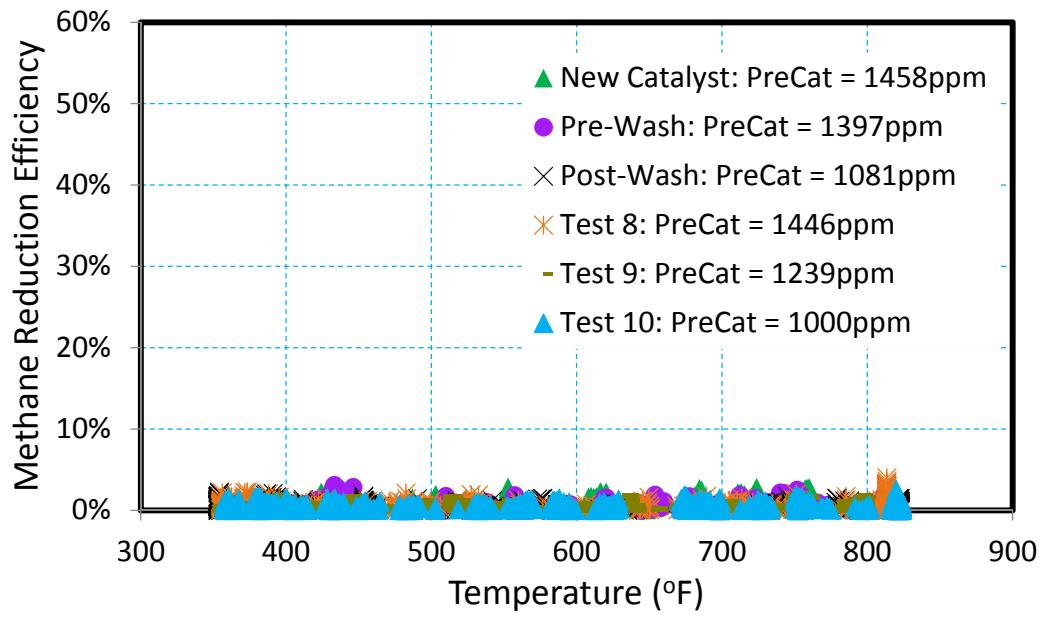


Figure B6: Reduction efficiencies versus temperature for methane.

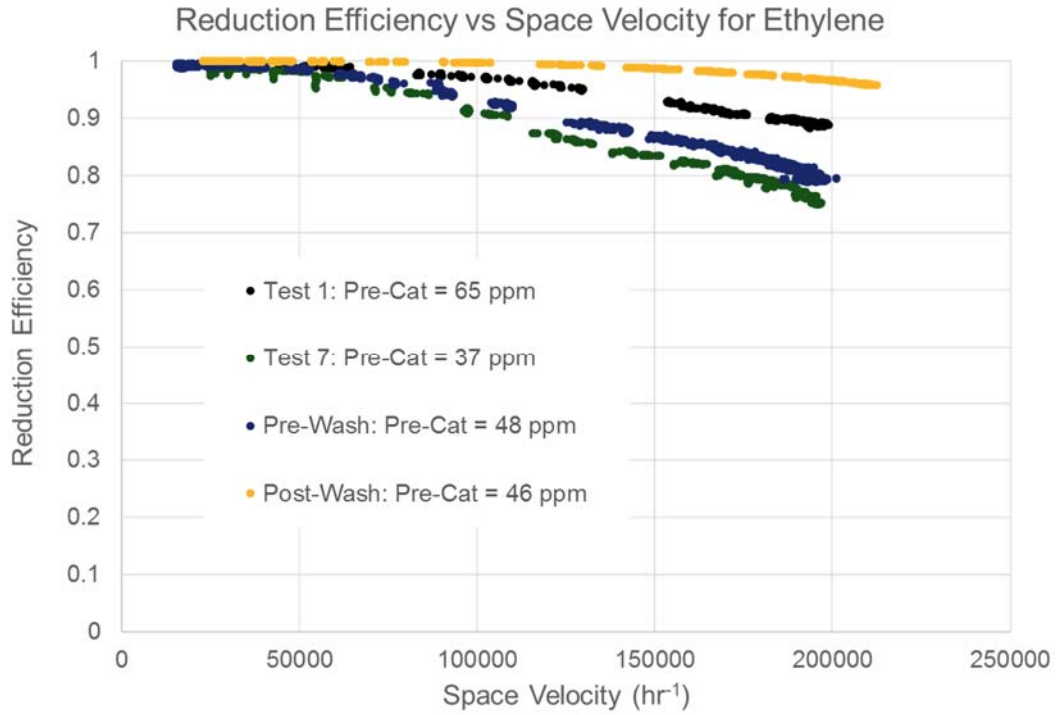


Figure B7: Reduction efficiency versus Space velocity for ethylene.

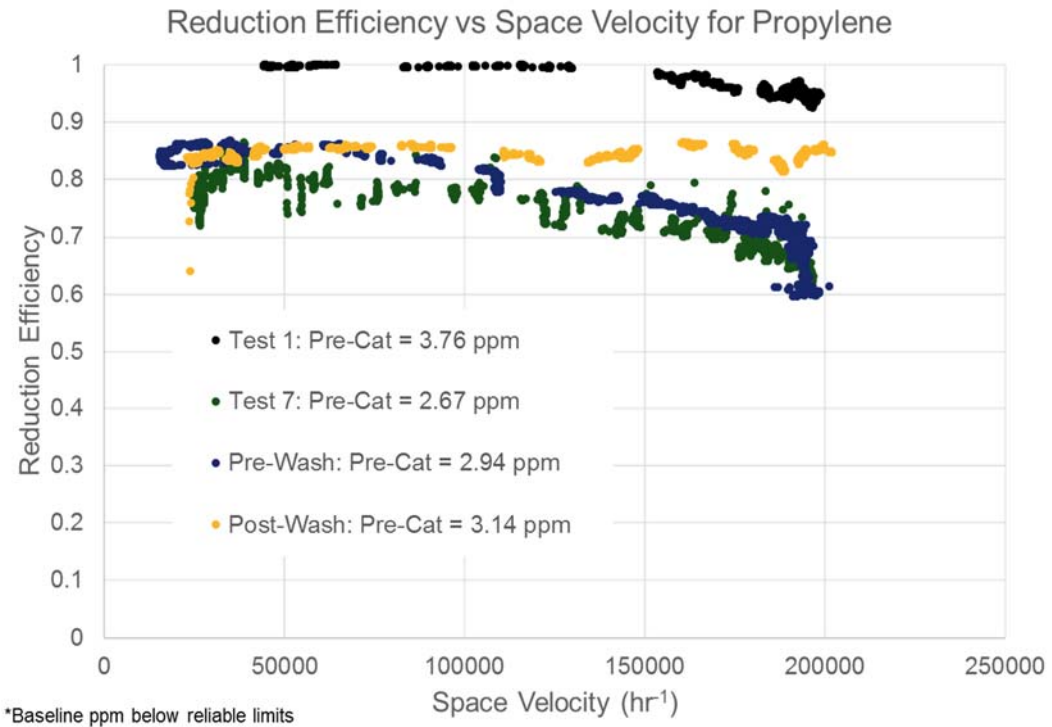


Figure B8: Reduction efficiencies versus space velocity for propylene.



### Reduction Efficiency vs Space Velocity for Propane

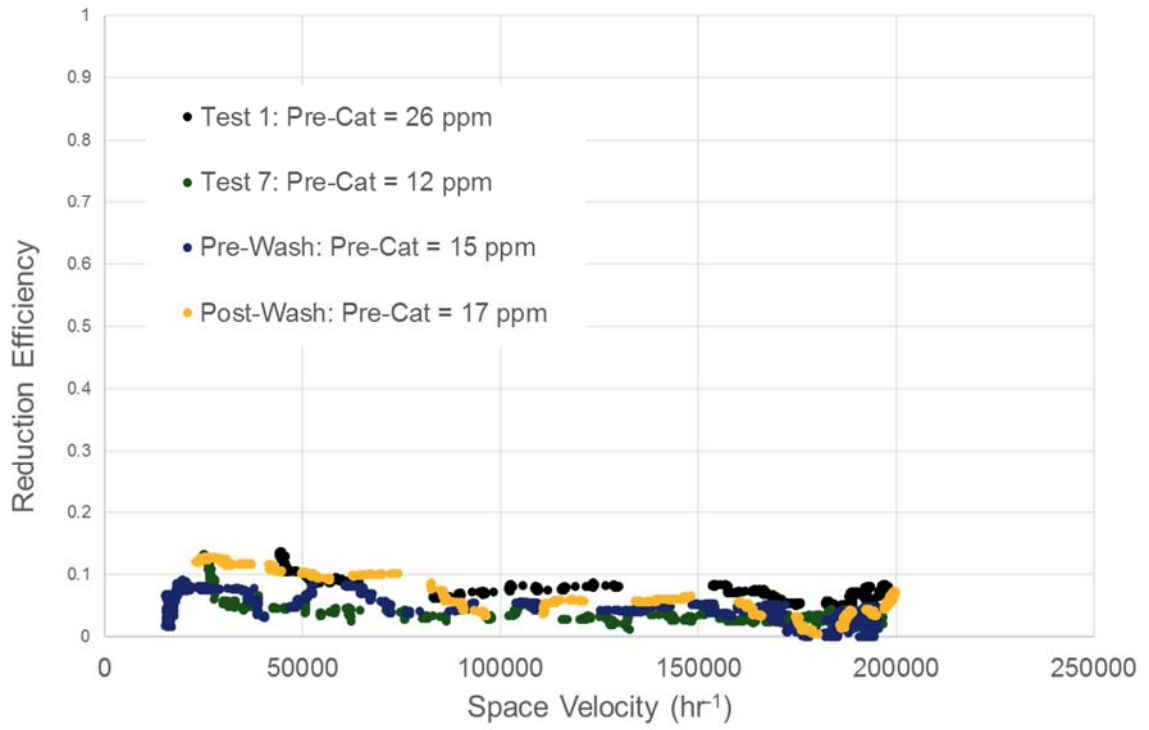
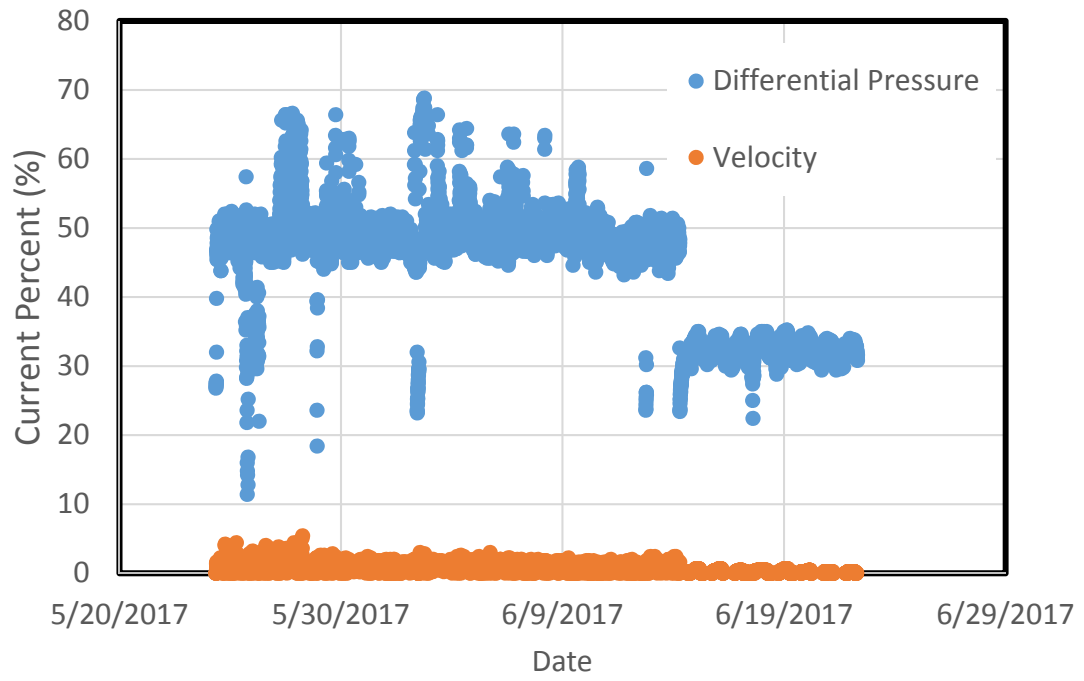


Figure B9: Reduction efficiency versus space velocity for propane.

## Appendix C: Field Slipstream Data



*Figure C1: Data sample of current percent from differential pressure and velocity transducers.*

## Appendix D: Oil Analysis Reports

COMPANY NAME : BRYAN HACKLEMAN  
 CUSTOMER EQUIP NUM : HACKLEMAN-GMVH-12  
 COMPARTMENT NAME : ENGINE NATURAL GAS  
 SERIAL NUMBER : HACKLEMAN-GMVH-12  
 MANUFACTURER : COOPER  
 MODEL : GMUH\_COOPER  
 JOB SITE :  
 EXT WARR NUMBER :

SHOP JOB NUM :  
 COMP SERIAL NUM :  
 COMPARTMENT MODEL :  
 COMP MANUFACTURER :  
 SAMPLE LABEL NUM :  
 FLUID BRAND/WEIGHT : PEGASUS805  
 FLUID TYPE :  
 EXT WARR EXPIRE DATE :  
 FUEL CONSUMED :

**WAGNER**  
**SOS Services Laboratory**  
**18000 E SMITH RD**  
**AURORA, CO 80011-35**  
**1 (303) 739-3165**  
**www.wagnerequipment**

FAX :  
 PHONE :  
 SAMPLE TYPE : **OIL**  
 SAMPLE SHIP TIME (days) : 6

LAB CONTROL NUMBER	SAMPLE DATE	PROCESS DATE	EQUIPMENT METER	METER ON FLUID	FLUID CHANGED	MAKE UP FLUID	MAKE UP FLUID UN
E250-47311-1155	01-Nov-2017	07-Nov-2017	0	500 HR	Unknown		
<b>No Action Required</b>	WEAR PATTERN IS ACCEPTABLE AT THIS TIME. RE-SAMPLE AT NORMAL INTERVAL COMPARED AGAINST BASELINE OF PEGASUS 805, VISCOSITY AND ADDITIVE METALS AND PRODUCT. OXIDATION IS WITHIN THE 20 UNIT LIMIT WE USE FOR CAT NATURAL GAS ENGINES. IF YOUR EQUIPMENT SUPPLIER HAS OIL SAMPLE GUIDELINES ESTABLISHED, FOLLOW THE LAB AMENDED REPORT WITH REFERENCE TO THE NEW OIL SAMPLE.						
E250-47264-1127	18-Sep-2017	21-Sep-2017	0	0	Unknown		
<b>No Action Required</b>	FIRST SAMPLE/NO TREND ESTABLISHED. MORE THAN ONE SAMPLE TODAY ON THIS COMPARTMENT. NEED HOURS USAGE FOR GOOD DATA EVALUATION. INCLUDE SERVICE SAMPLES. WEAR PATTERN APPEARS TO BE NORMAL ON A FIRST SAMPLE BASIS. RE-SAMPLE AT NORMAL INTERVAL TO ESTABLISH A TREND.						
E250-47264-1126	18-Sep-2017	21-Sep-2017	0	0	Unknown		
<b>No Action Required</b>	FIRST SAMPLE/NO TREND ESTABLISHED. MORE THAN ONE SAMPLE TODAY ON THIS COMPARTMENT. NEED HOURS USAGE FOR GOOD DATA EVALUATION. INCLUDE SERVICE SAMPLES. WEAR PATTERN APPEARS TO BE NORMAL ON A FIRST SAMPLE BASIS. RE-SAMPLE AT NORMAL INTERVAL TO ESTABLISH A TREND.						


Element (ppm)	Ca	Fe	Cr	Al	Pb	Sn	Si	Na	K	B	Mo	Ni	Ag	Cu	Mg	Zn	P
E250-47311-1155	0	2	0	0	1	0	2	0	2	0	1	0	0	126	14	300	283
E250-47264-1127	0	1	0	0	0	0	4	1	0	1	0	0	0	102	2	271	236
E250-47264-1126	0	1	0	0	0	0	4	1	0	5	1	0	0	104	8	278	238

ST	CM	NIT	SUL	W	A	V100	
E250-47311-1155	0	17	8	20	N	N	13.9
E250-47264-1127	0	11	5	16	N	N	13.0
E250-47264-1126	0	11	5	16	N	N	13.1

Ag = Silver, Al = Aluminum, B = Boron, Ca = Calcium, Cr = Chromium, Cu = Copper, Fe = Iron, P = Phosphorus, K = Potassium, Li = Lithium, Mg = Magnesium, Mo = Molybdenum, Na = Sodium, Ni = Nickel, Pb = Lead, S = Sulfur, V = Vanadium, Zn = Zinc, A = Antifreeze, F = Fuel, W = Water, P = Positive, N = Negative, T = Trace, E = Excessive, NIT = Nitration, CMI = Oxidation, ST = Soot, SUL = Sulfation, ISO = ISO Rating, PFC = Particle Counting Index, NaW = Salt Water, FL Pt = Flash Point, TAN = Total Acid Number, TBN = Total Base Number, HFO = Karl Fisher result, V100 = Viscosity@100C, V40 = Viscosity@40C, PVI = Particle

Notice: This analysis is intended as an aid in predicting mechanical wear. No guarantee, expressed or implied, is made against failure of this piece of equipment or a component thereof.

Figure D1: Oil analysis report for used Pegasus 805.

FAX		COMPANY NAME: BRYAN HACKLEMAN		SHOP JOB NUM		 <b>SOS Services Lab</b> 18000 E SMITH RD AURORA, CO 80011 1 (303) 739-3165 www.wagnerequip.com	
PHONE		CUSTOMER EQUIP NUM: HACKLEMAN-GMVH-12		COMP SERIAL NUM:			
SAMPLE TYPE: OIL		COMPARTMENT NAME: BULK OIL PEGASUS 805		COMPARTMENT MODEL:			
SAMPLE SHIP TIME (days): 6		SERIAL NUMBER: HACKLEMAN-GMVH-12		COMP MANUFACTURER:			
		MANUFACTURER: COOPER		SAMPLE LABEL NUM:			
		MODEL: GMUH_COOPER		FLUID BRAND/WEIGHT: PEGASUS805			
		JOB SITE:		FLUID TYPE:			
		EXT WARR NUMBER:		EXT WARR EXPIRE DATE:			
				FUEL CONSUMED:			

LAB CONTROL NUMBER	SAMPLE DATE	PROCESS DATE	EQUIPMENT METER	METER ON FLUID	FLUID CHANGED	MAKE UP FLUID	MAKE UP FLU
E250-47311-8002	01-Nov-2017	07-Nov-2017			Unknown		

**Monitor Compartment** FIRST SAMPLE/NO TREND ESTABLISHED. NO OBVIOUS PROBLEMS INDICATED ON A FIRST SAMPLE BASIS. PARTICLE COUNT DATA IS HIGH OVERALL, HOWEVER, ADJUST FOR MOST OILS EXCEPT HYDRAULIC OILS FROM MEETING ISO CODE 15/13. FOR ENGINE OILS, CAT ADVISES US TO FILTER THE OIL WITH 12 MICRON ABSOLUTE EFFICIENCY

Element	Cu	Fe	Cr	Al	Pb	Sb	Si	Na	K	B	Mo	Ni	Ag	Ca	Mg	Zn	P
E250-47311-8002	0	1	0	1	0	0	4	0	1	0	1	0	0	1122	6	264	251

Element	ST	OX	NIT	SUL	W	A	V100	ISO	4µ	6µ	10µ	14µ	18µ	24µ	36µ	50µ
E250-47311-8002	0	11	4	10	N	N	13.5	22/20/15	20249	8536	1318	27%	89	61	16	0

Ag = Silver, Al = Aluminum, B = Boron, Ca = Calcium, Cr = Chromium, Cu = Copper, Fe = Iron, P = Phosphorus, K = Potassium, Li = Lithium, Mg = Magnesium, Mo = Molybdenum, Na = Sodium, Ni = Nickel, Pb = Sulphur, V = Vanadium, Zn = Zinc, A = Antifreeze, F = Fuel, W = Water, P = Positive, N = Negative, T = Trace, E = Excessive, NIT = Nitration, OX = Oxidation, ST = Soot, SUL = Sulfation, ISO = ISO Rating, PQI = Particle Quantifying Index, NAW = Salt Water, FL PR = Flash Point, TAN = Total Acid Number, TBN = Total Base Number, H2O = Karl Fisher result, V100 = Viscosity@100C, V40 = Viscosity@40C, PVI = 1

Notice: This analysis is intended as an aid in predicting mechanical wear. No guarantee, expressed or implied, is made against failure of this piece of equipment or a component thereof.

Figure D2: Oil analysis report for new Pegasus 805.

COMPANY NAME: BRYAN HACKLEMAN  
 CUSTOMER EQUIP NUM: HACKLEMAN-GMV-12  
 COMPARTMENT NAME: ENGINE NATURAL GAS  
 SERIAL NUMBER: HACKLEMAN-GMV-12  
 MANUFACTURER: COOPER  
 MODEL: GMJH\_COOPER  
 JOB SITE:  
 EXT WARR NUMBER:

SHOP JOB NUM:  
 COMP SERIAL NUM:  
 COMPARTMENT MODEL:  
 COMP MANUFACTURER:  
 SAMPLE LABEL NUM:  
 FLUID BRAND/WEIGHT: PEGASUS  
 FLUID TYPE: PEGASUS 701  
 EXT WARR EXPIRE DATE:  
 FUEL CONSUMED:

SOS Services Lab  
 18000 E SMITH RD  
 AURORA, CO 80017  
 1 (303) 739-3165  
 www.wagnereq.com

FAX:  
 PHONE:  
 SAMPLE TYPE: OIL  
 SAMPLE SHIP TIME (days): 5

LAB CONTROL NUMBER	SAMPLE DATE	PROCESS DATE	EQUIPMENT METER	METER ON FLUID	FLUID CHANGED	MAKE UP FLUID	MAKE UP FL
E250-47311-1156	02-Nov-2017	07-Nov-2017	0	500 HR	Unknown		

NO ACTION REQUIRED  
 FIRST SAMPLING TREND ESTABLISHED. INCLUDE SERVICE METER READING ON ALL SAMPLES. WEAR PATTERNS APPEARS TO BE NORMAL ON A FIRST SAMPLE BASED TO ESTABLISH A TREND. VISCOSITY, ADDITIVE METALS, AND OXIDATION ARE ALL WELL WITHIN NORMAL LIMITS FOR THE PRODUCT IN USE. IF YOUR EQUIPMENT SUPPLY IS ESTABLISHED, PLEASE PROVIDE THEM TO THE LAB. AMENDED REPORT WITH REFERENCE TO THE NEW OIL SAMPLE.

Wear Index (ppm)	Cu	Fe	Cr	Al	Pb	Sn	Si	Na	K	B	Mo	Ni	Ag	Ca	Mg	Zn	P
E250-47311-1156	1	2	0	0	0	2	1	0	7	1	1	0	0	17	1	376	312

Oil Analysis	ST	OX	NIT	SUL	W	A	VHM
E250-47311-1156	0	12	4	16	N	N	128

Ag = Silver, Al = Aluminum, B = Boron, Ca = Calcium, Cr = Chromium, Cu = Copper, Fe = Iron, P = Phosphorus, K = Potassium, Li = Lithium, Mg = Magnesium, Mo = Molybdenum, Na = Sodium, Ni = Nickel, P = Sulfur, V = Vanadium, Zn = Zinc, A = Anthracene, F = Fuel, W = Water, P = Positive, N = Negative, T = Trace, E = Excessive, NIT = Nitration, OXI = Oxidation, ST = Soot, SUL = Sulfation, ISO = ISO Rate, PQI = Particle Quantifying Index, NaW = Salt Water, FL Pt = Flash Point, TAN = Total Acid Number, TBN = Total Base Number, H2O = Karl Fisher result, V100 = Viscosity@100C, V40 = Viscosity@40C, PWT =

Note: This analysis is intended as an aid in predicting mechanical wear. No guarantee, expressed or implied, is made against failure of this piece of equipment or a component thereof.

Figure D3: Oil analysis report for used Pegasus 701.

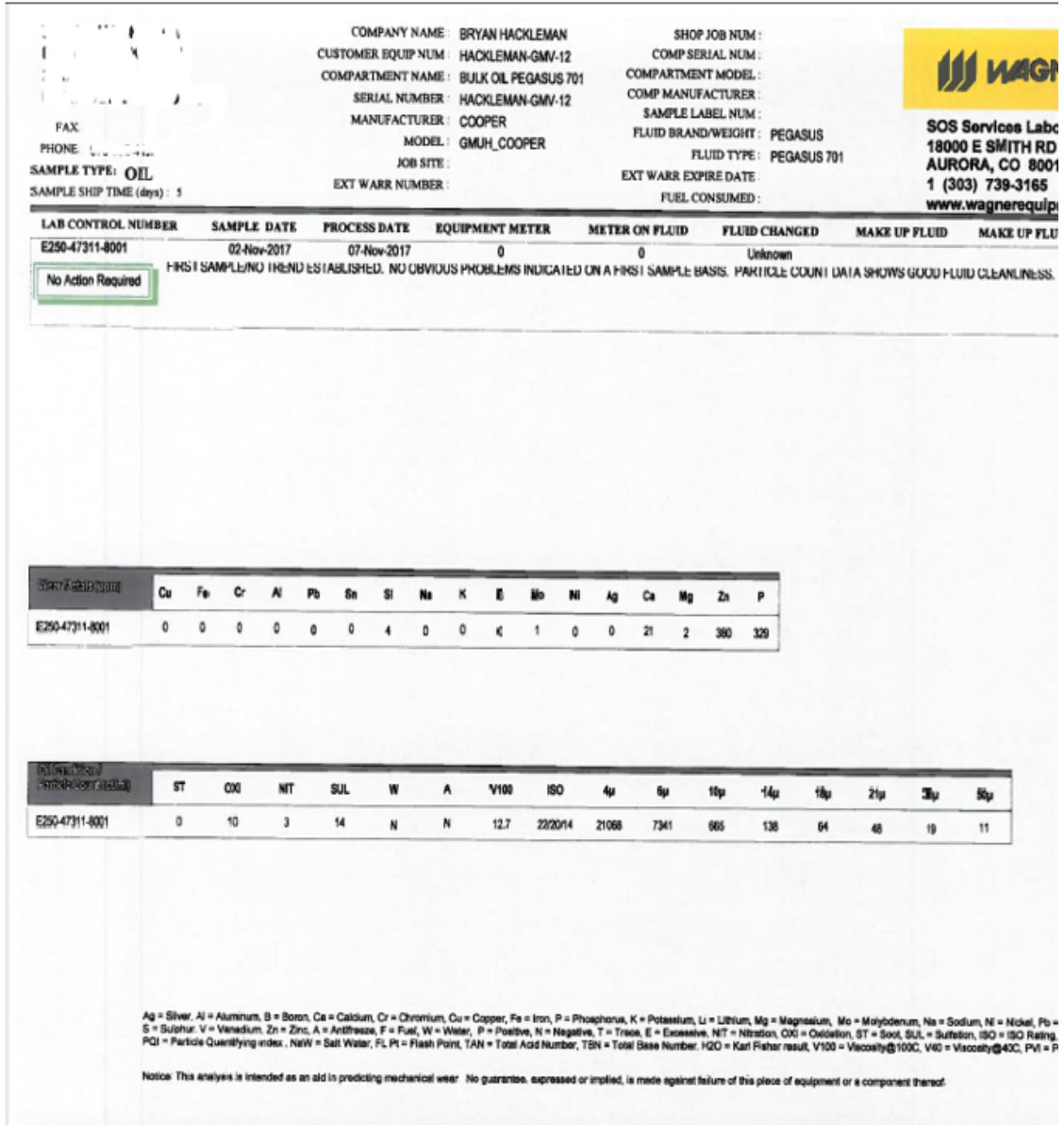


Figure D4: Oil analysis report for ne Pegasus 701.