

# Understanding Chemical Composition and Phase Transitions of Ash from Field Returned DPF Units and Their Correlation with Filter Operating Conditions

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## ABSTRACT

Current and future diesel engine oil categories have specifications that impose limits on SAPS (Sulfated Ash, Phosphorous and Sulfur) levels that help to minimize accumulation of ash in the DPF originating from oil consumption in the engine. Metallic species in the oil formulation, mostly from detergents and anti-wear additives, have a significant impact on ash behavior when subjected to high temperatures during active regeneration of the filter. Certain compounds in the oil, especially derivatives of ZDDP (Zinc Dialkyl Dithiophosphate), interact with filter substrate and sinter at temperatures that the DPF is exposed to during active regeneration. This phenomenon of sintering or 'ash wetting' leads to ash-bridges in the DPF that result in reduction of soot storage capacity, higher back-pressure and possibly reduced active surface area for catalytic conversion of engine-out emissions. Changes in ash chemistry when subjected to high temperature transient events is irreversible and necessitates wet cleaning of the DPF to recover most of the filter performance.

Ash samples were collected from field returned DPF's that were categorized into line-haul and a mix of 'stop and go' duty-cycles; these trucks had two different heavy-duty diesel engine types. Several techniques for materials and chemical characterization such as high-temp XRD (X-ray Diffraction), Raman Spectroscopy, ICP-OES, SEM-EDS amongst others were employed in the current study for an in-depth understanding of the composition, phase transition and crystal lattice structure of the samples. Additionally, DPF ash from two different oil formulations were evaluated for their wetting behavior on the filter substrate and changes in ash composition were documented. Ash that was rich in phosphorous compounds exhibited phase transitions which were different from the ash that was rich in calcium compounds. Crystallographic planes from phosphate compounds were identified and correlated with oil formulations and vehicle operating conditions.

Data generated in this study provides insights into ash morphology, chemistry and compositional changes when subjected to high temperatures in the DPF operating range. Analysis of ash from field returned DPF's can be helpful in understanding filter operating history (regeneration conditions, duty cycles, engine oil type etc.), which then could be used as inputs for recommending filter service intervals, specific cleaning techniques and even DPF calibration based on mileage and duty-cycles.

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## INTRODUCTION

Presence of DPF in the after-treatment system for vehicles equipped with diesel engines has been mandatory in order to comply with the engine-out PM emission requirements as enforced by EPA in North America. DPF is prone to loss of catalytic activity, increase in back-pressure and reduced long-term durability due to accumulation of ash in the filter [1, 2]. Most common type of DPFs used today are wall-flow ceramic monoliths made from cordierite, silicon carbide or aluminum titanate amongst other materials. There are alternating plugs at the ends of each channel and the exhaust gas is forced to flow through porous walls of the DPF, thereby trapping most of soot agglomerates. Filtration efficiency of wall flow filters depends on numerous factors, such as pore size distribution, porosity and geometric parameters of the substrate that include wall thickness, channel length, cells per square inch amongst others. Trapping of

engine-out soot takes place in two distinct phases: depth bed filtration and soot-cake filtration. In the first phase, deposition of soot in the filter wall changes the microstructure of the filter, leading to sharp increase in filtration efficiency and back-pressure; after these initial changes, soot collection occurs inside the channel forming 'soot-cake', which is a thick layer of soot. Soot cake leads to slight increase in back-pressure and close to 100% filtration efficiency [3, 4, 5]. These modes of soot filtration could be affected by the presence of incombustible ash species that accumulate in the filter channels and end-plugs over its useful life.

It's well-known that ash is primarily transported to the DPF by an oil consumption mechanism in the engine cylinder during piston-ring lubrication; cross-hatch pattern on the cylinder liner has to be designed optimally so as to provide adequate lubrication depending

on duty-cycles, while ring-pack geometry serves as a barrier for transfer of blow-by gases to the crankcase and to minimize oil consumption. Increased clearance between liner-piston rings due to wear in the long-term, could lead to exponential increase in oil consumption and oil degradation, resulting in higher ash accumulation rates per mile of the vehicle. Transport of metallic species in the oil along with soot dispersed in the crankcase (that has adsorbed oil-additives onto its surface) to the filter, influence chemical composition of ash. Ash-precursors are tightly bound in the structure of diesel soot agglomerates that get trapped in the filter wall or channels. Once these agglomerates are oxidized during filter regeneration, the ash precursors are left behind on the wall, that grow in size over time and in some cases sinter and bridge to washcoat deposited on the substrate [6, 7, 8]. Filters are generally oversized so as to increase ash storage capacity, extend service intervals and increase residence time of emission toxins for conversion.

As filter traps most of the material in the exhaust stream, composition of ash is highly complex and varies with type of engine oil, engine hardware design, fuel type and intake air impurities amongst others. Several studies in the literature have found that most of the ash originates from metallic species in the engine oil while a small portion of it comes from wear, corrosion by-products and inorganics from coolant formulation, impurities in fuel and intake air. Detergent components (from Ca & Mg compounds) and anti-wear/extreme-pressure/anti-oxidant additives (ZDDP derivatives and others) used in the oil make up for most of the ash composition. It is important to note that volatility of 'ash forming' metallic species is crucial in predicting ash accumulation rates rather than volatility of bulk engine oil as most of the oil consumption includes hydrocarbon base stocks. Current diesel engine oil formulations have gone away from high volatility ZDDP compounds while replacing them with low volatility compounds and in some cases ashless low-phosphorous additives [9, 10, 11]. Phosphorous wouldn't be eliminated from oil formulations in the near future due to significant benefits it offers vis-à-vis engine durability while being cost effective; a caveat to this unfortunately is phosphorous poisoning, which is well-known phenomenon that poisons catalyst by deactivating reactive sites. Low-volatility ZDDP compounds are designed in a way that their volatility is significantly lower as compared to the base compounds while maintaining their antiwear, corrosion resistance and antioxidant properties [12, 13, 14]. Likewise, dispersants and over-based detergents could make up more than half the amount of additive package as they're a part of deposit control additives. Sulfonates, phenates and carboxylates are commonly used polar groups in the detergent, while excess base in the core of the detergent structure is a metal carbonate or a hydroxide. These types of detergents are effective for long-term engine durability, however they're also the primary source of ash in the DPF forming  $\text{CaSO}_4$ ,  $\text{CaO}$  amongst other compounds [15, 16].

Ash accumulation in the filter occurs over long time scales and is sensitive to the temperature existing in the DPF bed; temperatures at the face of filter could be different from the temperature existing in the channels. Amount of soot trapped, fuel HC's present and catalytic activity are primary factors that determine resultant temperatures during active regeneration in the channels. Although temperatures below  $700^\circ\text{C}$  are seen by the filter through most of its useful life, there are instances where filter could see temperatures around

$900\text{--}1000^\circ\text{C}$  occurring over a span of few minutes which is sufficient for ash compounds to bridge and sinter [2]. Metal phosphates and pyrophosphates are the most susceptible to phase change and sintering, at temperatures around  $700\text{--}800^\circ\text{C}$ ; while metal sulfates tend to be stable upto  $1000^\circ\text{C}$  before changes in phase and composition leading to 'ash wetting'. Regeneration strategy and exhaust conditions of flow and temperature determine distribution of ash in the filter channels; several studies have shown that filters subjected predominantly to passive regeneration exhibit a thick layer of ash on the channel walls, and minimal amount of ash in the channel end-plugs, while filters that use higher frequency of active regenerations have a thicker ash end-plug and minimal ash on the wall [17, 18, 19]. Although operating in passive regeneration regime could see lower amount of fuel burnt for active regeneration, the ash distribution in the channel walls behave as a secondary filter, present on top of the channel walls, leading to exponential increase in back-pressure with soot accumulation, triggering more frequent active regenerations in the long run. The ash layer present on the wall could also reduce the amount of active catalytic sites available for passive regeneration and  $\text{NO-NO}_2$  conversion. On the other hand, using more active regenerations helps compact ash at the end of channels leaving more space for soot and ash collection over-time; there could be a higher probability of filter seeing high-temperature transient events occurring that exacerbates 'ash wetting' of the filter. There is a trade-off in both scenarios where fuel penalty due to excess active regenerations have to be compared with excess back-pressure triggered frequent active regenerations in the longer run along with down-time of the vehicle for servicing the filter.

This study assesses chemical composition of ash recovered from field returned DPF units that were fitted on two different types of heavy-duty diesel engines which used different filter regeneration strategies. Composition of the recovered ash was correlated with filter operating conditions; experiments were conducted to map changes in phase of ash when subjected to temperatures that are seen in filter channels during active regeneration. Ash wetting of the filter strongly correlated with the amount of metallic phosphates and/or pyrophosphates that originate from ZDDP derivatives in the engine oil. Filter service intervals and appropriate cleaning techniques are recommended from the findings in the study. Efforts are made to understand the effect of ash-accumulation on back-pressure ( $\Delta P$ ) in DPF's via flow-sweep tests.

## OVERVIEW

A total of 10 field returned DPFs were evaluated in the study. [Appendix A](#) specifies the duty-cycles, mileage at removal for the two engine types. Vehicles fitted with Engine A belonged to multiple fleets across the country and were independently maintained and serviced at various facilities. The filters recovered had a wide distribution for 'mileage at removal' and also comprised of duty cycles that were a mix of line-haul and regional 'pickup & delivery'. Filters recovered from vehicles fitted with Engine B comprised of line-haul duty cycles only. The truck fleet fitted with Engine B had a centralized maintenance and service facility that used the same brand of oil and had fixed intervals for oil change and other services. The engine oil used in all the vehicles conformed to API C4 performance category with SAE viscosity grade of 15W40. Both engines A and B

were heavy duty engines and had a power range from 283-447 kW. Both engines complied with EPA 2010 emissions regulation and were fitted with advanced aftertreatment system comprising of DOC, DPF, SCR and AMOX. Hydrocarbons were injected downstream of turbocharger during active regeneration. Both engines were fitted with variable geometry turbocharger, 4-valve per cylinder and intercooled EGR. The DPFs on both the engines were 22L in volume, cordierite at 300 CPSI with differences in PGM formulation and loading. Engine B used oil formulation that contained novel low-volatility ZDDP components, while no detailed information on oil formulation used in Engine A was known. Both oils were commercially available in the market. ICP-OES analysis results for oil used in Engine B are documented in [Appendix D](#). Fresh oil results are used as baseline and compared with data obtained from oil sampled at its mid-life and end of life (drain interval). It can be seen that there is a rise in concentration of wear metals, while the concentration of additive elements decreases with vehicle mileage or accumulated engine hours.

Filters recovered from the field were sent to a commercial cleaner for servicing. Cleaner used a mix of pneumatic, baking and wet cleaning techniques to rid of ash in the DPF and improve catalytic performance as well as lower back-pressure comparable to its initial values. Ash from 10 DPF units analyzed in this study were collected in the first stage of cleaning after filters were cleaned pneumatically, that employed high pressure pulsed-air for removing loose ash and ash-plugs (in most cases); recovered ash did not undergo any of the high temperature exposures during cleaning, that could've induced changes in ash chemistry. There are challenges associated with recovery of catalyst performance based on the cleaning processes employed for DPF ash removal; a more aggressive and robust cleaning that could remove most of the ash (loose ash as well as sintered and bridged ash), however this might negatively affect the washcoat performance. Ash cleaning intervals are specified by the OEM's; these recommendations are based on oil consumption rates, duty cycles and DPF volume and threshold  $\Delta P$  measurement amongst others.

## TEST PROCEDURES

This section describes the experimental setup and test procedures for chemical characterization of retrieved ash from the DPF. Protocol for engine-dyno tests to evaluate filter back-pressure pre and post cleaning is described.

### Chemical Characterization of Recovered Ash

Ash trapped in the filters that were serviced by the cleaner was retrieved and available in adequate quantity for an in-depth materials and chemical characterization. [Figure 1](#) illustrates as-received ash samples; note that ash samples could vary from white-beige color to dark brown or grey-black color in appearance. This is due to variation in ash chemistry as well as compositional changes during high-temperature exposures during vehicle operation. Ash samples had minimal or no soot content as the filters were deep-cleaned (active regeneration) before their removal from the trucks. Analytical

techniques such as packing density, ICP-OES, XRD, SEM, EDS, high temperature sintering behavior and Raman spectroscopy were performed. Details on these ash samples are provided in [Appendix A](#).



Figure 1. Ash samples as-received from DPF Cleaner.

### Packing Density Calculation

Packing density of ash samples was calculated by using a graduated glass cylinder. Weight of the sample that occupied  $1 \text{ cm}^3$  volume was noted and the resulting packing density (in  $\text{g/cm}^3$ ) was calculated. Three repeat measurements were done per sample and average values with error bars are reported. There was no compression applied to the sample during this measurement. True packing density of accumulated ash could slightly vary depending upon its location in the channels and regeneration conditions. To determine localized packing density, the channels have to be carefully dissected that might dislodge some of the material and/or contaminate the ash sample with washcoat or filter substrate, which may skew the packing density measurement.

### ICP-OES

Ash samples were digested in the sample matrix by subjecting them to acid treatment and subsequent digestion using a high-pressure microwave system. A variety of acid combinations were used to digest the ash samples; however Aqua-Regia (3:1 volumetric ratio of HCL and  $\text{HNO}_3$ ) was found to be the most effective in digesting all of ash components except silicates. A small amount of 'indigestible' material that was left behind (primarily comprised of silicates), was filtered out before analyzing with ICP; microwave digestion process lasted for about 60 minutes resulting in a peak pressure of 60 bars and temperature of  $220^\circ\text{C}$ . Wattage used for plasma was 1500 watts and sample flow rate was 1.5 ml/min.

### XRD

Ash sample was placed in the sample holder and effort was made to flatten the surface of the sample so as to avoid any discrepancies in the data. Bragg-Brentano reflection geometry was employed in the XRD. Scan range for  $2\theta$  was  $10-90^\circ$ . Tube voltage and current were at 40 kV and 44 mA respectively. Identification of compounds from the data was done using elemental data obtained from ICP, matching the peak positions & peak intensity values to those of model-

compounds in the ICDD crystal structure database. Approximate weight percent of the compounds present in the ash samples was calculated by the software using RIR, FWHM and other spectral parameters. The weight percent's of the compounds present might not be actual weight percent's as XRD doesn't pick up signals from amorphous material in the sample; also certain phase changes due to high temperature exposure during vehicle operation or cross-interaction amongst compounds could vary the peak intensities when compared to model compounds, which may slightly change the weight percent's that are calculated.

### High Temperature Sintering Setup

Two ash samples, one each from two different engine types, were picked to do an in-depth analysis to characterize sintering behavior when exposed to temperature ranges that are prevalent during active regeneration. Ash samples were placed on a fused silica glass slide capable of withstanding upto 1300°C; sample surface was flattened to get good x-ray reflection from its surface. Sample holder was placed in a heating furnace and temperature was ramped up from room-temperature to 1200°C at a rate of 30°C/min. X-ray scans were taken at increments of 50°C. Changes in phase or composition were mapped for every scan obtained. An additional scan was taken at 50°C after the sample was cooled from 1200°C to check for final composition of the sample. Same experiment was repeated using a substrate-washcoat combination of the current filter to correlate the sintering behavior to real-world observations. X-ray tube conditions and scanning parameters remain the same as described in the above section.

### SEM-EDS

Two ash samples that were subjected to high temperature XRD experiments were evaluated for changes in crystalline phases, grain boundaries before and after sintering. EDS was used to understand localized elemental concentrations.

### Raman Spectroscopy

Raman studies were conducted on the two ash samples that were studied to understand sintering behavior. Raman technique helps understand surface functionalities and identify certain phases in ash before and after being subjected to high temperatures. Data generated was correlated to the spectra originating from individual model compounds and cordierite substrate. 532 nm YAG laser was used that had a power of 5 mW and spot size of 0.6 µm. Photobleach time of 30 seconds was added to reduce fluorescence from the sample. Frequency range of 50-3350 cm<sup>-1</sup> was scanned with a total of 30 exposures per test. Spectral resolution of 3cm<sup>-1</sup> was obtained; grating resolution used in the detector was 900 lines per mm.

### Flow-Sweeps Tests on Engine-Dyno

Flow sweep tests were performed to understand the impact of ash on the pressure drop behavior across the DPF. Variation in amount of ash present in the filter as well as their distribution could lead to changes in ΔP values. Since presence of soot in ash loaded DPF leads to an exponential increase in ΔP, it was important to deep-clean the filter by passive and active regeneration for oxidation of soot, so that the

effects from ash only could be evaluated during flow-sweep tests. DPF's were subjected to temperature conditioning and stabilization before the measurements. Below is a brief overview of the experimental procedure for conducting a flow sweep:

- Run engine at 1000 rpm - 800 Nm for 180 seconds
- Ramp-up to 1900 rpm - full load in 200 seconds (throttle ramped in 5s to traverse full load curve)
- Stay at 1900 rpm - full load for 30 seconds
- Drop to 1000 rpm - 800 Nm in 5 seconds

## RESULTS AND DISCUSSIONS

Results presented in this study are roughly divided into two sections; the first section presents the data on chemical composition of the ash while the second section focusses more on sintering behavior of two different ash samples that were accumulated under different regeneration strategies, operating conditions and engine oil formulation. An overview of the results obtained from engine-dyno performance tests is presented.

### Ash Composition

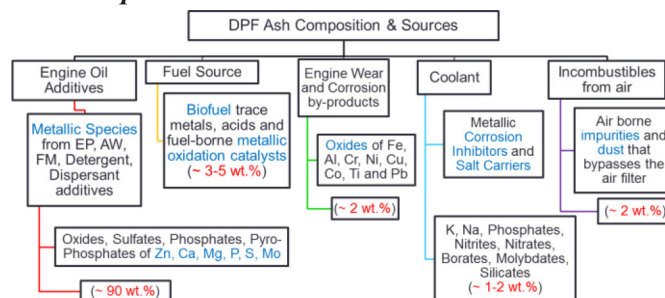


Figure 2. Flowchart representing the origin of DPF ash sources

Ash composition analyzed using ICP-OES and XRD is presented in the following section. [Appendix A](#) gives details of the 10 ash samples retrieved by the commercial filter cleaner while [Appendix B](#) breaks down weight percent's of compounds calculated from XRD spectra of the samples. Ash accumulated in the DPF is sum total of incombustible material left behind following active-regeneration in the DPF.

An overview of typical sources for ash components and their origin is illustrated in [figure 2](#); this categorization is valid for a vehicle fitted with diesel engine, which uses API CJ4 engine oil and ULSD fuel. More than 90% of the ash originates from engine oil metallic species while about 5% originates from wear or corrosion by-products, while the rest of ash could originate from fuel, coolants and other dirt [22, 23]. Detergents and ZDDP components in the engine oil are primary contributors of lubricant-oil generated ash in the filter. Volatility of metallic species in the oil is an important consideration in prediction of DPF ash rather than bulk volatility of engine oil. Due to the differences in NOACK volatility, additive chemistry formulations and the presence of additive sinks in the engine vis-à-vis tribofilms and thermal-films on the interacting surfaces of engine hardware, not all lubricant additives are consumed at the same rate as the bulk oil [24]. Ash derived from engine oil additives is composed of sulfates, sulfides, phosphates, pyrophosphates and oxides of

zinc, calcium, magnesium, while other elements such as iron, copper, aluminum and silicon originate from engine hardware & filter substrate [25]. Based on high temperature events occurring in the filter channels during active regeneration, some of the compounds mentioned above could oxidize further or change their phase and crystalline structure that is stable at elevated temperatures.

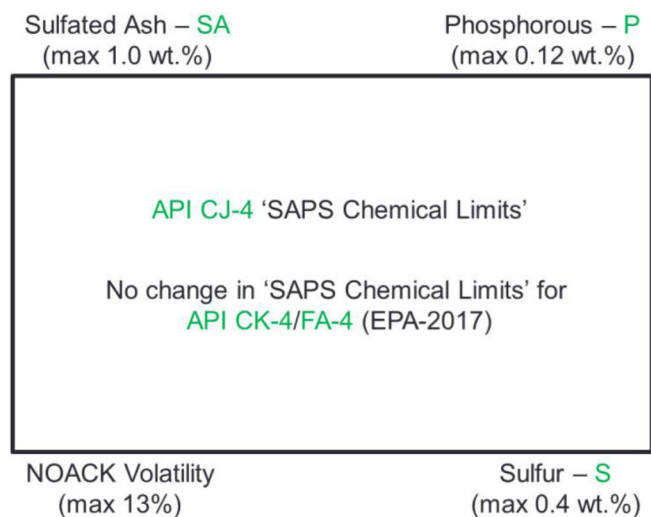


Figure 3. SAPS chemical limits for API CJ-4 and CK-4

SAPS limits as shown in figure 3, is a chemical box used by engine oil formulators to develop additive components that offer long-term durability of engine hardware, while maintaining after-treatment performance; phosphorous levels in the oil that have a major impact on catalyst performance could vary around the world. For instance, North America has max limits of 0.12 wt. % while Europe has 0.08 wt. % and Japan maintains 0.12 wt. %.

Figure 4 shows an overview of engine oil composition; the additive package could amount anywhere from 5-20 wt. % depending upon the application or duty-cycles of the engine. Base oil contributes to majority of the oil consumption occurring in the engine, however will not contribute to the ash in DPF. Viscosity modifiers and pour-point depressants are used to maintain the oil viscosity limits and cold-flow flow properties; they are 'ashless' and their consumption would not result in ash in the filter.

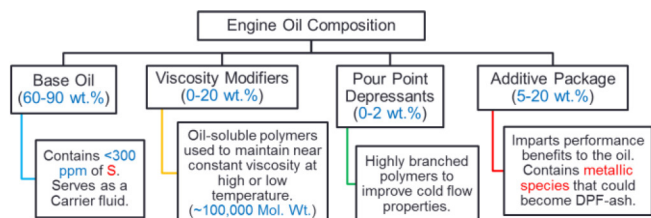


Figure 4. Flowchart showing typical engine oil composition

If the vehicle uses elevated levels of biodiesel blends (more than B20), a higher contribution of fuel-derived ash components could be seen in the DPF; metallic species from Group 1 and Group 2

metals (such as Na, K, Ca, Mg) that are used as catalysts during biodiesel manufacturing could be present in low concentrations (below 10ppm) in biodiesel. These metallic fuel contaminants are converted to oxides, sulfates, hydroxides or carbonates in the combustion process and form inorganic ash species in the filter. Alkali metals are well known poisons for catalysts and have been shown to negatively impact the mechanical properties of ceramic substrates [21]. Since consumption rates of fuel tend to be several times higher in magnitude than engine oil consumption, slight increase in fuel metallic species can lead to large amounts of fuel-derived ash collected in the DPF. Fuel borne catalysts that were used previously did contribute to more than 80% of the ash [26].

### Elemental Concentration via ICP-OES

Figure 5 gives details on concentrations of elements such as Ca, Zn, P, Mg and S that predominantly originate from engine oil additives. Results from ash samples indicate the usage of two different additive systems in the oil irrespective of the oil brand being used; sample 1, 2 could be grouped into one category, while rest of the samples from both engine types (sample 3-10) could be broadly grouped in another category. Since Engine B was a controlled fleet that used centralized service facility with well-maintained oil drains and oil-type, the elemental concentrations do reflect the same; concentrations are tightly grouped for these samples. As mentioned above, vehicles with Engine A belonged to multiple fleets and were independently serviced; there was a higher probability of different engine-oil types being used throughout the study; additive platforms used in samples 1, 2 and samples 4, 6, 7, 9 had a different chemical makeup.

Elements such as Ca and Mg form an integral part of over-based detergent chemistry in the oil formulations. Most detergents used in a heavy-duty diesel engine utilize a calcium carbonate core-structure, that is encapsulated by soap molecules containing sulfonate or phenate as a polar head group [27, 28, 29]. Some formulations use a combination of Ca and Mg detergents as they've differences in depletion rates; hence one detergent pallet could last for 60% of oils useful life while another pallet could last longer and help protect engine hardware if in case oil-drains have to be extended. ZDDP forms an essential part of diesel engine oil formulation as it has multiple functionalities like anti-wear, extreme-pressure, anti-corrosion additive amongst others. P and S present in the structure help protect engine hardware; nonetheless they are detrimental to after-treatment components. It's been well-documented in previous studies about effect phosphorous poisoning [30, 31, 32]. Phosphorous compounds usually form a glassy 'masking' layer and in some cases crystalline deposits that lead to irreversible fouling. Phosphorous poisoning usually affects oxide components in the washcoat leading to a reduction in active catalytic area available for HC light-off and NO-NO<sub>2</sub> conversion. Phosphorous poisoning is effective at higher operating temperatures with relatively high amounts of oxygen and water content in the exhaust gas stream [33, 34].

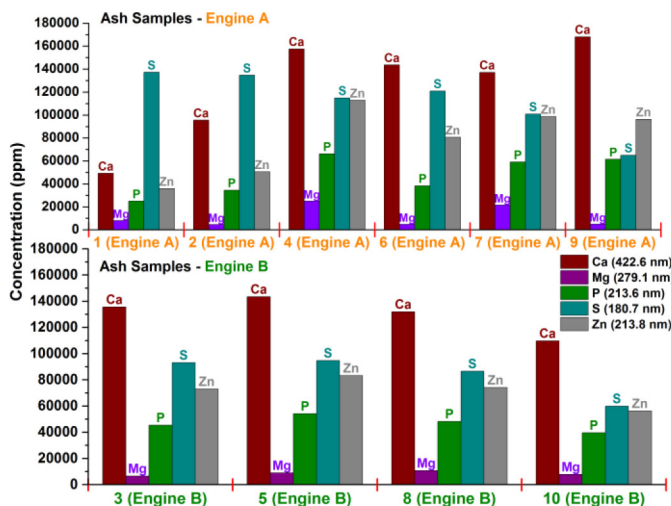


Figure 5. Additive elements concentrations in ppm

Figure 6 describes the concentrations of Pt and Pd from recovered ash. As y-axis scales are normalized, it was seen that ash retrieved from Engine B had almost twice the PGM content as compared to ash from Engine A. Two main factors behind these observations were: 1) The washcoat of filters (from Engine B) could have a higher PGM loading to begin with and 2) Ash distribution and morphology in the filters was fundamentally different for both engine types.

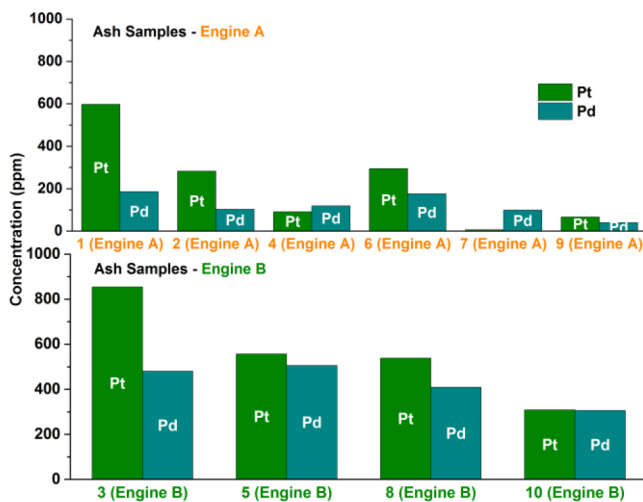


Figure 6. PGM elements concentration in ppm

DPF's from Engine A predominantly had an ash-plug at the end of the channels and relatively minimal or no ash over the length of the channels; while on the other hand DPF's from Engine B had ash distributed as a thin layer over the length of the channel and a small amount accumulated as ash plug. As a result, the filters where ash was distributed as a thin layer over the channel length could potentially have more contact area with the washcoat surface; while cleaning the DPF with a relatively aggressive technique, some quantity of washcoat could've been removed with ash from the filter, thereby contributing to higher levels of Pt and Pd in the ash. Some studies have shown that differences in filter regeneration strategies could lead to variation in ash-distribution in the filter channels [17, 19]. Filters that were subjected to higher active-regeneration frequencies exhibit ash-plugs at the end of

channels and minimal ash deposits throughout the channel length, while filters that rely more on passive-regeneration did exhibit thicker deposits along the channel walls.

### Ash Compounds Identification via XRD

Since ash from the DPF is a complex mixture of compounds that originate from multiple sources, it is important to identify the chemical make-up which could help in predicting operational history of the filter. Appendix B lists the compounds identified, chemical formula, densities of respective model compounds and their relative amounts in weight percent. Only crystalline components present in ash could be observed in the XRD spectra; quantification of components (in weight percent) based on RIR (Reference Intensity Ratio) should be cautiously used as it doesn't take amorphous materials into consideration, thereby not representing true weight of the sample. Equation (1) was used by the software package to quantify amount of compounds present.  $R_i$  is calculated based on ratio of intensity of the highest peak of the specific compound ( $I_i$ ) to the ratio of peak intensity of corundum ( $I_c$ ), when mixed with corundum ( $Al_2O_3$ ) in a 1:1 ( $W_i:W_c$ ) weight ratio [35].

For some compounds it could so happen that the most intense peak could overlap with other peaks in the spectra; in such cases another diffraction peak originating from the compound could be used.

$$\frac{W_i}{W_c} = (1/R_i)(I_i/I_c) \quad (1)$$

Figure 7 shows a stacked overview of diffraction spectra from Engine A samples; a reference spectra of Calcium Sulfate ( $CaSO_4$ ) and Zinc Phosphate ( $Zn_3(PO_4)_2$ ), were added and indexed as sulfates of Ca, and phosphates (of Zn, Fe and Ca) were seen to be major component in the ash samples. Origin of components in each of the ash samples are indexed by a color-filled dot on top of the peaks, that correspond to  $CaSO_4$  or  $Zn_3(PO_4)_2$ . Some of the peaks couldn't be identified due to a large number of unknown compounds trapped by the filter. Sample 1 and 2 showed a large number of unknown compounds present in the spectra. Diffraction intensity from certain crystallographic planes cannot be picked up as some planes diffract more strongly than others depending upon planar packing density; this could lead to signals from low diffraction intensity planes being merged into high diffraction intensity signals. Also lower amount of certain compounds results in lower diffraction intensity as less number of planes in a specific crystallographic direction are available for diffraction.

Figure 8 shows diffraction spectra from four samples obtained from filters installed on vehicles with Engine B. All the samples primarily exhibit presence of  $CaSO_4$  originating from detergent components in the engine oil. Oil used in Engine B was formulated with a 'low-volatility' ZDDP compound that resulted in lower phosphate or pyro-phosphate emissions. Although there is some amount of phosphorous that is detected in the elemental data from ICP, X-ray diffraction didn't show the presence of any phosphorous compounds that could originate from ZDDP derivatives. One explanation for this observation is that phosphorous compounds trapped in Engine

B filters were amorphous which couldn't be detected by XRD. This also might explain that different ZDDP formulations used in engine oil will result in slightly different phosphate compounds in the DPF which affect the sintering behavior and filter durability during long-term operation.

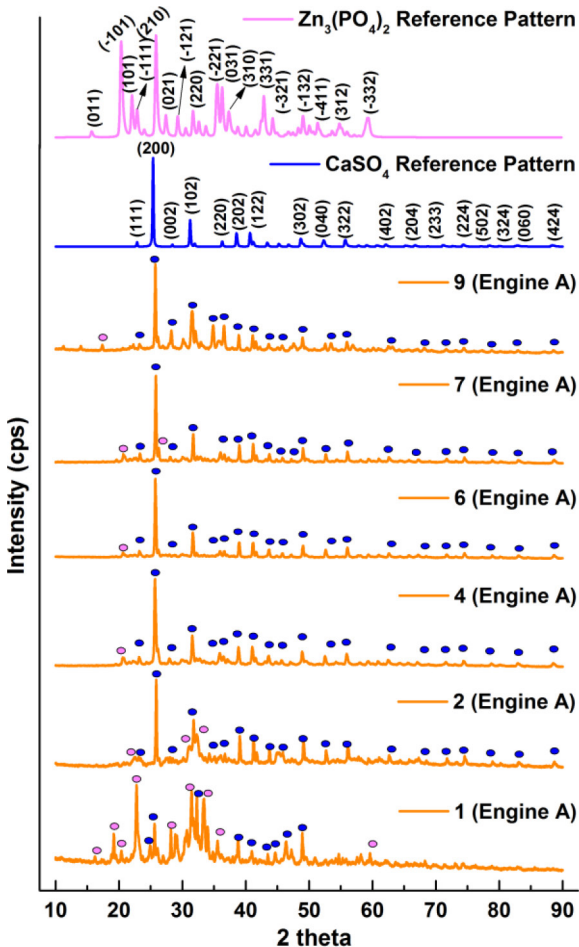


Figure 7. XRD spectra for phase ID of Engine A samples

Ash components in the filters from both engine types (A and B) were primarily comprised of Calcium Sulfate ( $\text{CaSO}_4$ ) and oxides of elements such as Zn and Fe. Presence of 'metal oxides' could be used as a "tell-tale" sign of high temperature excursions in the DPF during operation; this would have a profound effect on poisoning the washcoat and/or catalyst aging [17, 18]. Sulfates and carbonates of group 1 and 2 elements do oxidize under higher exhaust temperatures ( $>800^\circ\text{C}$ ) in the presence of oxygen to form metal oxides, while driving out sulfur and carbon in gaseous form. Ash recovered from Engine A filters had a wider distribution of compounds present, while ash samples from Engine B filters were fairly similar in composition. Presence of cordierite components in the ash could be correlated to removal of thin-layer of ash that is distributed along the length of channel walls. It was hypothesized that portions of sintered ash attached to the DPF wall, when cleaned with an aggressive cleaning technique could remove washcoat/substrate. Uniformities in ash composition suggest similarities in between engine oil additive chemistries, oil consumption rates and DPF regeneration strategies.

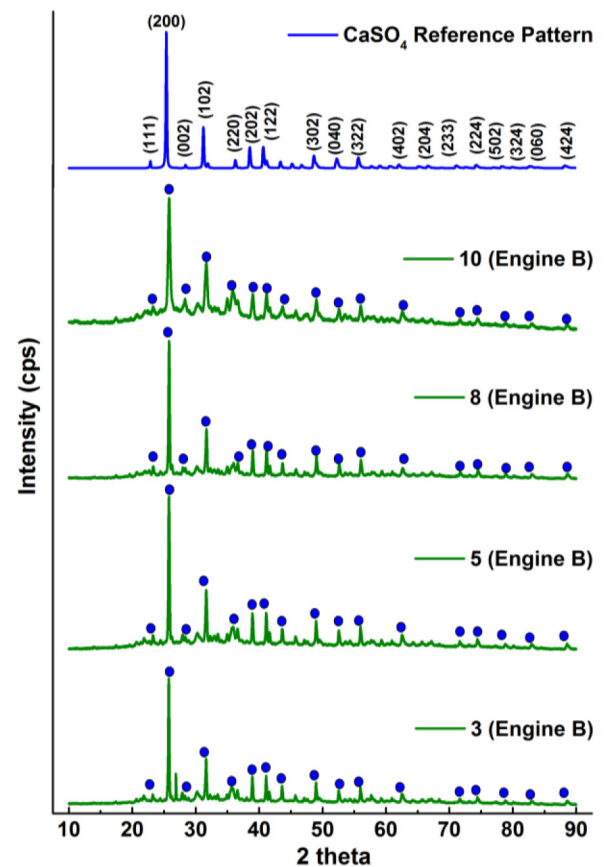


Figure 8. XRD spectra for phase ID of Engine B samples

### Packing Density Calculations

Packing density of ash is an extrinsic property of the sample and is related to particle size, packing efficiency, agglomerate shape or structure. Packing density influences permeability, porosity of the ash layer and back-pressure of the filter. Measurement of packing density gives insights on filter operating history; if the filter channels experience temperatures above  $800^\circ\text{C}$  over the course of DPF's total service life, certain phosphate compounds that sinter starting  $700^\circ\text{C}$ - $750^\circ\text{C}$ , result in a more compact mass in the filter that has low permeability, low porosity and high packing density [17, 36].

Figure 9 shows packing densities of ash samples recovered from Engine A and B filters. Most values reported in the literature fall in the range of  $0.16$ - $0.54 \text{ g/cm}^3$  [17, 36, 37]. Densities for Engine A samples are higher than those for Engine B samples. Since Engine A filters used a regeneration strategy that relied on higher number of active regenerations per unit time, the possibility of ash being exposed to temperatures above  $750^\circ\text{C}$  was higher; as mentioned above, type of oil used in Engine A was uncontrolled and in some cases could have contained a ZDDP compound with slightly higher volatility as compared to the low-volatility ZDDP formulation used in Engine B oil. Higher volatility of ZDDP derivatives in the oil leads to higher amount of phosphate components in the ash that sinter at lower exhaust temperatures ( $>750^\circ\text{C}$ ). This helps explain the packing density observation seen for Engine A samples. On the other hand Engine B samples had lower amount of phosphate components in the