

Characteristics and Effects of Lubricant Additive Chemistry on Ash Properties Impacting Diesel Particulate Filter Service Life

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ABSTRACT

Ash accumulation in diesel particulate filters, mostly from essential lubricant additives, decreases the filter's soot storage capacity, adversely affects fuel economy, and negatively impacts the filter's service life. While the adverse effects of ash accumulation on DPF performance are well known, the underlying mechanisms controlling these effects are not. To address these issues, results of detailed measurements with specially formulated lubricants, correlating ash properties to individual lubricant additives and their effects on DPF pressure drop, are presented.

Investigations using the specially-formulated lubricants showed ash consisting primarily of calcium sulfates to exhibit significantly increased flow resistance as opposed to ash primarily composed of zinc phosphates. Furthermore, ash accumulated along the filter walls was found to be packed approximately 25% denser than ash accumulated in the channel end-plugs. Both lubricant chemistry and the filter's thermal history were correlated to ash packing density and distribution following DPF post-mortem analysis.

In this study, a heavy-duty diesel engine was utilized in conjunction with a rapid lubricant degradation and aftertreatment ash loading system, which has been validated in detail previously against engine-out exhaust and ash accumulated in the field. Results with specially-formulated lubricants containing only calcium-based detergents, only ZDDP additives, and conventional CJ-4 oils were compared utilizing an aging cycle simulating 180,000 miles of on-road use. On-engine DPF performance evaluation, coupled with subsequent filter post-mortem analysis, clearly indicate the manner in which lubricant chemistry and exhaust conditions influence ash properties and DPF performance.

The results of this work demonstrate the effects of individual lubricant additives on the resulting ash properties controlling DPF pressure drop, including ash packing density and permeability. Results will be useful in optimizing the design of the combined engine-aftertreatment-lubricant system for future diesel engines, balancing the requirements of additives for adequate engine protection with the requirements for robust aftertreatment systems.

INTRODUCTION

Diesel particulate filters (DPF) are widely used to significantly reduce engine-out particulate matter (PM) emissions in order to meet ever-tightening PM emissions standards. Aside from carbonaceous soot, diesel PM also contains a small amount of inorganic ash, generally between 0.5% and 1.0% [1]. Over time, and following successive filter regenerations, ash accumulates in the DPF and ultimately limits the filter's useful service life. Ash accumulation in DPFs increases flow restriction through the filter, resulting in increased exhaust backpressure, and negatively impacts vehicle fuel economy. Furthermore, ash build-up also reduces the DPF's soot storage capacity and alters the pressure drop characteristics of the filter to soot accumulation [2, 3].

Investigations of ash composition have identified inorganic additives in diesel engine lubricants as the primary contributors to ash build-up in the DPF, when fuel-borne catalysts are not used [4,5,6]. These additives primarily consist of calcium- and magnesium-based detergents as well as zinc-based anti-wear additives. The most prevalent anti-wear additive used in on-road diesel engine oils is zinc dialkyl-dithio-phosphate (ZDDP), a complex of zinc, phosphorus and sulfur compounds, which also functions as an anti-oxidant. It should be emphasized however, that although broadly categorized above, a large number of variations of

these specific additives exist, and formulations tend to be application-specific and may also vary substantially from manufacturer to manufacturer.

Although it is widely accepted that lubricant additives are the largest contributor to DPF ash, engine wear metals and corrosion products, and trace metals in diesel fuels may also contribute, generally to a lesser extent. The latter source, fuel-borne metals, has recently received increasing attention, particularly in relation to biodiesel fuels, as the possibility exists for these fuels to contain elevated levels of alkali and alkaline earth metals, due to the manufacturing process [7]. Investigations of these secondary ash sources were beyond the scope of this work, which focused on more conventional applications with petroleum-based fuels.

In order to mitigate the problem of lubricant-derived ash accumulation in diesel particulate filters, the CJ-4 oil specification was developed, and limits sulfated ash content to no more than 1.0%. In addition to setting a cap on sulfated ash, the CJ-4 specification places specific chemical limits on the total amount of sulfur and phosphorous in the lubricant [8]. Engine manufacturers have also sought to address the issue through reduced engine oil consumption, and aftertreatment system manufacturers have developed unique means for increasing the ash storage capacity of DPFs [9]. Despite these measures, little is known regarding the effect of individual lubricant additives on DPF performance degradation, and diesel particulate filters still require periodic servicing for ash cleaning.

LUBRICANT CHEMISTRY EFFECTS ON ASH PROPERTIES

While a number of factors influence ash properties and the resulting magnitude of the ash effect on DPF plugging and pressure drop increase, including exhaust conditions, regeneration strategy, DPF thermal history, and ash composition, it is the latter parameter which serves as the focus of this work. Despite much work studying ash effects on DPFs and the recent development of the CJ-4 oil specification, relatively little is known regarding the effect of individual additives on DPF performance, much less the synergistic effects of various combinations of additives in fully-formulated lubricants. Developing an understanding of the manner in which additive chemistry influences ash properties is critical to minimizing the impact of lubricant-derived ash on DPF performance.

A survey of the literature revealed several studies investigating the contribution of lubricant and ash chemistry, in addition to the absolute trapped mass of ash in the filter, to the increase in DPF pressure drop observed with ash accumulation. A 2003 study by Chevron utilized eight different lubricant formulations each containing different levels of boron-based dispersants, ZDDP, and calcium-based

detergents. Lubricant sulfated ash content ranged from 0.42% to 1.9%. DPF ash loading was accelerated by blending the candidate oils in the fuel (5% oil in the fuel by mass). While calcium was observed to be the largest contributor to lubricant sulfated ash content, as measured by ASTM D874-06, DPF pressure drop increase, due to ash accumulation, appeared to be more closely correlated to zinc and phosphorous concentrations in the lubricant than calcium. Interestingly, no boron was found in the DPF, although it was present in the lubricants [10].

In contrast to the Chevron study, a 2005 report by Lubrizol noted that high lubricant phosphorous concentrations were not directly correlated to an increase in DPF pressure drop. This study utilized ten lubricants with various levels of calcium, magnesium, ZDDP, phosphorous, and boron. The authors further noted an interaction between the platinum levels in the DPF and phosphorous in the ash, possibly creating conditions suitable for reducing the ash particles to a sufficiently small size to pass through the DPF pores. Similar to the Chevron study, no boron was observed in the ash deposits accumulated in the particulate filter [11].

A number of studies have attempted to identify and quantify the various lubricant-derived ash components accumulated in the DPF. In general, a large fraction of the ash was found to consist of metallic sulfates and phosphates, with a much smaller contribution of metal oxides. Calcium sulfate is observed to be the predominant lubricant-derived component found in the ash, with concentrations ranging from 59% to 75% of the total ash [4, 12, 13]. The significant differences reported in the Chevron and Lubrizol tests highlight the need for understanding, at a fundamental level, the impact of lubricant chemistry and its resulting influence on ash composition and morphology, which ultimately affects DPF pressure drop.

ASH COMPOSITION AND EFFECT ON PRESSURE DROP

Ultimately the composition and properties of the ash accumulated in the DPF are defined not only by the initial lubricant additive chemistry, but also by the ash formation mechanisms and conditions, such as thermal history, in the DPF. Specifically, ash composition influences the ash packing density and porosity and may also significantly affect the pore sizes of the accumulated ash layer. [Table 1](#) presents a compilation of typical ash constituents and their associated properties.

Table 1. Common ash constituents and properties.

	Density	Molar Mass	Melting Point
	g/cm ³	g/mol	° C
CaSO ₄ *	2.96	136.14	1460
Zn ₂ Mg(PO ₄) ₂	3.60	345.01	***
Zn ₂ (P ₂ O ₇)	3.75	304.10	***
Zn ₃ (PO ₄) ₂	4.00	386.11	900
CaO	3.35	56.08	2572
ZnO	5.61	81.41	1975**
MgO	3.58	40.30	2852
FeO	5.75	71.84	1377
* Anhydrous *** Accurate data unavailable			
** Decomposes			

The pressure drop due to exhaust flow through a porous media (DPF substrate, soot layer, ash layer) is generally the largest contributor to the total filter pressure drop, and can be described using Darcy's Law:

$$\Delta P_{Wall / Ash / Soot} = \left(\frac{\mu}{K_p} \right) \cdot v_w \cdot w \quad (1)$$

where μ is the exhaust gas dynamic viscosity, K_p is the permeability of the porous media, v_w is the gas wall velocity, and w is the layer thickness. In the equation above, inertial effects are neglected, as the Reynolds number for the flow through the porous media is generally much less than unity ($Re \ll 1$) for typical DPF applications [14]. The flow resistance of the porous media is therefore a function of the thickness of the porous layer, as well as its permeability.

The permeability of a porous material is determined by the porosity and pore diameter of the material. Various empirical relationships such as that of Rumpf and Gupte as well as Carman-Kozeny have been applied to estimate DPF permeability, for clean and soot loaded filters [15]. The porosity describes the void volume of the porous material and is defined as:

$$\varepsilon = 1 - \frac{\rho_{Packing}}{\rho_{Theoretical}} \quad (2)$$

The packing density, $\rho_{Packing}$, is the measured density of the porous material or powder and the theoretical density, $\rho_{Theoretical}$ is the true density of that material. The theoretical densities of various ash components commonly found in the DPF are listed in Table 1. The packing density of the ash has a direct effect on the volume (layer thickness) and distribution of the accumulated ash in the DPF as well. Soot

permeability may also be expressed as a direct function of the exhaust gas conditions and soot particle geometry. The soot layer permeability is defined as:

$$K_{Soot} = f(\varepsilon) \cdot d_{Primary}^2 \cdot SCF \quad (3)$$

The soot layer permeability is, thus, a direct function of the soot layer porosity and particle size. SCF is the Stokes-Cunningham Factor to account for non-continuum conditions due to the small size of the soot particles [16]. Unlike soot properties, the fundamental mechanisms controlling ash properties are not well-known. However, based on this theoretical framework, it is quite clear that ash composition does exert considerable influence on the properties (permeability, porosity, and packing density) which directly affect DPF pressure drop. The present work aims to explore these effects in more detail.

EXPERIMENTAL SET-UP AND PROCEDURES

The experiments described in this study were conducted under carefully-controlled conditions utilizing conventional lubricants as well as specially formulated diesel engine oils, in order to study the effects of individual additives on ash properties and DPF performance. The DPFs were loaded with ash using an accelerated ash loading system, and DPF performance evaluation followed a set procedure using the Cummins ISB diesel engine and a separate flow bench. A number of analytical techniques were used to measure ash properties and explain the observed differences in filter performance.

ENGINE AND INSTRUMENTATION

The engine used in this study was a pre-production Cummins development engine based on the ISB 300 engine platform. The ISB 300 is a 6 cylinder, 5.9 liter, turbocharged, direct injection diesel engine. The engine is rated at 224 kW (300 hp) at 2500 rpm and 890 N-m (660 ft-lb) at 1600 rpm. The ISB 300 is equipped with a high-pressure common rail fuel injection system, variable geometry turbocharger, and cooled exhaust gas recirculation (EGR). Table 2 provides additional details regarding the engine specifications and geometry.

Table 2. Cummins ISB 300 engine specifications.

Engine Parameter	Description
Model	ISB 300
Maximum Torque	890 N-m @ 1600 rpm
Maximum Power	224 kW @ 2500 rpm
Cylinders	in-line 6
Displaced Volume	5.9 liters
Combustion System	direct injection, 4-stroke
Injection System	common rail
Aspiration	variable geometry turbocharger and intercooler

ASH LOADING SYSTEM

The accelerated ash loading and aftertreatment aging system was designed to load a conventional D5.66" (14.38 cm) × 6" (15.24 cm) DPF to 40 g/l of ash in slightly under 100 hours. A simplified schematic of the test system is shown in [Figure 1](#), and additional details are presented in [Figure A-1](#) in the [Appendix](#). Use of the accelerated loading system in conjunction with the Cummins ISB enables the feed-gas particulate and ash characteristics to be carefully controlled and monitored. The accelerated ash loading system further allows for control and acceleration of specific oil consumption mechanisms, enabling the simulation of engine-out ash and PM as closely as possible.

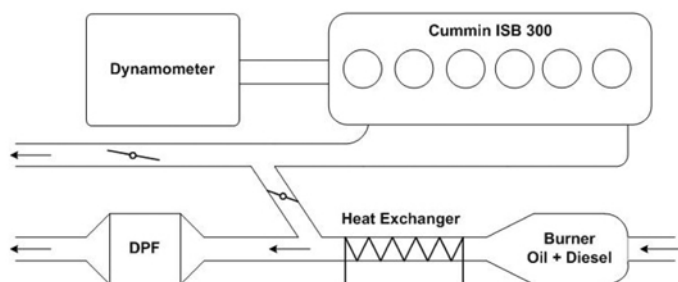


Figure 1. Experimental set-up showing accelerated ash loading system mounted beside Cummins ISB test bed.

The accelerated ash loading system, described above, has been validated in previous studies. Work by the authors reported in 2008 showed a detailed comparison between engine-out ash and PM characteristics from the Cummins ISB (composition, size distribution, and morphology) with the characteristics of the ash and particulate matter produced using the accelerated loading system. No significant differences other than increased exhaust ash levels with the accelerated ash loading system were noted [17]. More recent work presented a comparison of DPFs aged in the laboratory using the accelerated ash loading system with filters subjected to 180,000 miles of on-road fleet testing using CJ-4 oils. Ash packing density, distribution, and composition were quite similar for both the laboratory and field-aged filters [3].

The accelerated ash loading system is composed of a diesel burner and custom combustion chamber. A secondary air-assisted oil injector mounted on top of the combustion chamber allows for precise control of lubricant introduction into the combustor. Oil flow to the injector is supplied by a computer controlled constant volume pump. Fully-formulated lubricants, base oils, and individual additives can be introduced into the combustor using this system. [Table 3](#) presents the system's operating specifications and [Figure A-1](#) in the [Appendix](#) depicts the system lay-out.

Table 3. Accelerated ash loading system specifications.

System Parameter	Description
Fuel Consumption	1.5 - 7.6 l/h
Oil Consumption	0.94 - 9.4 ml/min
Injection Pressure	700 - 1400 kPa
Air Flow	266 - 1130 slpm
DPF Inlet Temperature	200 - 800 °C

A heat exchanger mounted downstream of the combustor provides additional control over exhaust temperature, independent of the burner settings, allowing for online DPF regeneration. In this manner DPF inlet temperatures can easily be controlled between 200 °C and 800 °C.

A junction following the heat exchanger outlet connects the Cummins exhaust system to the accelerated ash loading rig. A portion of the ISB's exhaust can be routed to the ash loading system, providing a realistic exhaust composition (gaseous and PM). Further, a centrifugal blower mounted downstream of the DPF test section provides additional control over exhaust gas flow rates through the particulate filter during the accelerated ash loading cycle. Typical space velocities for DPF loading and regeneration ranged from 15,000 hr⁻¹ to 25,000 hr⁻¹ depending on operating conditions. With the burner switched off, the test set-up functions as a flow bench with airflow through the DPF varied using the blower.

TEST MATRIX AND PROCEDURES

The fuels and lubricants were subjected to a detailed elemental analysis to accurately quantify additive composition and to account for the presence of any trace elements in the fuel. An SAE 15W-40 commercially available CJ-4 diesel engine oil was used in this study along with two specially formulated lubricants. These lubricants consisted of a group II base oil containing only a ZDDP additive, and a group II base oil containing only a calcium detergent. All of the oils were blended to the 1.0% sulfated ash level. The elemental composition of the lubricants, and base oil, is listed in [Table 4](#).

Table 4. Lubricant elemental composition. *Value supplied by manufacturer.

Lubricant	ASTM D5185					
	B	Ca	Mg	P	Zn	S
	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
CJ-4	586	1388	355	985	1226	3200*
Base Oil	1	<1	<1	8	<1	60
Base Oil + Ca	3	2928	5	2	<1	609
Base Oil + ZDDP	1	<1	<1	2530	2612	6901

Both the Cummins ISB and the diesel burner on the accelerated ash loading system were fueled with an ultra-low sulfur diesel (ULSD, 15 ppm S) fuel. In order to rule out metals in the fuels contributing to the DPF ash, the test fuels were periodically analyzed to monitor the trace metals content. All trace elements in the diesel fuel were below the minimum detectable limits of the analysis (ASTM D5185).

The cordierite diesel particulate filters used in this study measured D5.66" (14.38 cm) × 6" (15.24 cm) giving a total DPF volume of 2.47 liters with a cell geometry of 200 cells/in.² (31 cells/cm²) and wall thickness of 0.012 in. (0.30mm). All of the filters were coated with a platinum catalyst and washcoat. Aside from instrumentation with several thermocouples, the locations of which are shown in [Figure A-1](#) of the [Appendix](#), the DPFs were not altered in any way.

The test procedure was designed to minimize test variability and allow for careful control and monitoring of ash composition and exhaust conditions. All DPF performance evaluation was conducted using either the Cummins ISB or the flow bench. The accelerated ash loading system was only used to load the particulate filters with ash. The combined effects of soot and ash on DPF pressure drop were also studied. In this case, the filters were loaded to a predetermined ash level using the accelerated ash loading system, and subsequent soot loading was accomplished using only the Cummins ISB. Due to the small filter volume, only a portion of the exhaust from the engine was diverted to flow through the DPF when the engine was used.

Initially all of the DPFs were subjected to a degreening cycle using the burner with no oil injection to expose the filters to a series of high temperature cycles. Supplementary exhaust from the Cummins ISB was also used to load the filter with soot. Following complete DPF regeneration, the filter was weighed hot to determine its clean weight. The balance used to weigh the DPF has a 12 kg maximum capacity with 0.2 g resolution. All DPF ash and soot loading reported in this work was determined by weighing the DPF hot to eliminate error due to condensed water in the filter. DPF internal temperatures at the time of weighing were around 200 °C.

Following filter degreening, the basic test procedure is as follows:

1. DPF pressure drop performance characterization using the Cummins ISB for soot loading to 6 g/l.
2. Flow bench tests to measure pressure-drop at various stages of DPF soot loading.
3. Complete DPF regeneration using burner system.
4. Ash loading using the accelerated loading system with periodic DPF regeneration.
5. Flow bench tests to measure pressure-drop over a range of space velocities at various stages of DPF ash loading.

The test procedure described above was repeated a number of times (steps 1-5) with each filter to evaluate the effect of ash and soot loading on DPF pressure-drop for various soot and ash levels.

The specifics of the ash loading procedure used in this study were previously described in detail in [\[2, 3\]](#). All of the DPFs were subjected to periodic regeneration. Typical soot loading conditions were at a filter inlet temperature of 250 °C for one hour followed by filter regeneration at an inlet temperature of 620 °C for 15 minutes. The loading and regeneration cycles were repeated over the course of the ash loading protocol.

The maximum specific DPF ash load achieved in this study was 42 g/l. This level of ash accumulation is estimated to be equivalent to roughly 240,000 miles (386,000 km) or 5,960 hours of DPF operation. This estimate is based on the following assumptions for a typical medium heavy-duty diesel engine: 15 g/hr average oil consumption [\[18\]](#), 40 mi/hr (64 km/hr) average speed, and a full sized particulate filter volume of 12 liters. In some cases different levels of ash loading were desired, with correspondingly different on-road equivalent distance/hours.

Unless otherwise noted, all of the pressure-drop data presented in this work was acquired from the flow bench measurements using air at ambient conditions. Use of the flow bench provides more repeatable flow conditions for each test. Following ash loading and performance evaluation, all of the filters were subjected to a detailed post-mortem analysis.

FILTER POST-MORTEM ANALYSIS

For the post-mortem analysis, each DPF was axially sectioned into two equal and symmetric halves. One half of the filter was preserved for future testing and analysis, while the other half was further sectioned into a number of smaller samples. [Figure 2](#) depicts the location of the DPF samples.

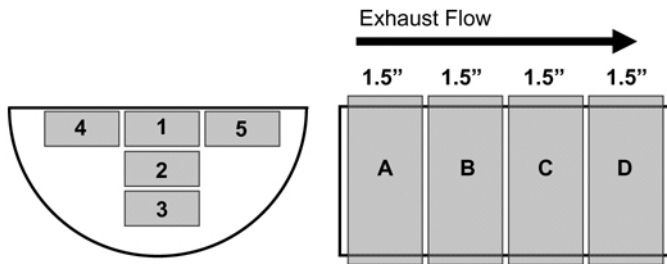


Figure 2. DPF sample locations used for post-mortem analysis.

One filter half section was further divided into four 1.5 inch (3.8 cm) long sections axially. The axial sections were subdivided into five samples corresponding to the different radial positions labeled in Figure 2. Each DPF sample consisted of approximately 140 to 180 individual cells. In this manner, twenty core samples were obtained from each filter allowing for determination of ash properties' variation in both the axial and radial directions in the DPF. The following measurements were taken for each DPF core sample:

- Ash layer thickness or plug dimensions depending on the ash distribution in the sample. This information was used to compute ash volume.
- Ash mass used in combination with the ash volume measurements to compute ash packing density.

The measurements listed above provide ash layer thickness profiles, ash packing density profiles, and ash distributional information for the ash accumulated in the DPF. Select ash samples from each filter were further subjected to compositional analysis via X-ray diffraction (XRD) as well as microscopy analysis via SEM-EDX. Ash volume and packing density measurements for each individual ash core sample followed a set procedure developed in-house.

For ash samples originating near the front or middle section of the DPF, the ash was mostly distributed in a thin layer along the channel walls. The front and back of each ash sample was imaged, and the ash layer thickness measured directly from the images using commercially available image processing software. Two ash layer thickness measurements were made per channel on each side of the filter sample. Figure 3 depicts a close-up view of a typical filter sample and the ash layer thickness measurement.

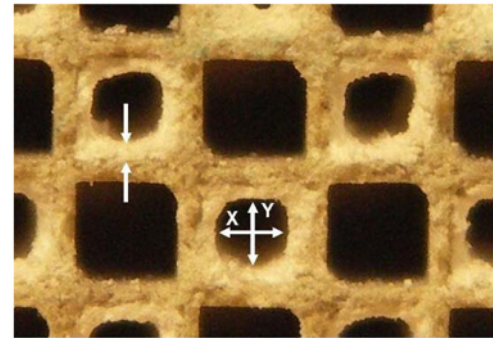


Figure 3. Close-up view of ash thickness measurements for the ash deposited along the DPF channel walls.

By measuring ash layer thickness at the front and back of each sample, the thickness profile over the 1.5 inch (3.8 cm) sample length was readily determined. For DPF samples from the back of the DPF, the ash tended to be primarily accumulated in plugs completely filling the channel. In these cases, the ash volume was computed from the known channel dimensions and sample length. The ash layer thickness and end-plug measurements for each sample were then combined to reconstruct the ash distribution profiles inside the entire filter.

EXPERIMENTAL RESULTS

The effect of individual lubricant additives on DPF pressure drop, due to ash accumulation alone, is shown in Figure 4. The figure shows the pressure drop trends for three DPFs loaded with 28 g/l to 42 g/l of ash, determined by periodically weighing the filters, using three different lubricant formulations. The pressure drop data shown in Figure 4 was recorded following complete DPF regeneration, ensuring that only ash and no soot remained in the filter. DPF regeneration was determined to be complete following exposure to filter inlet temperatures of at least 625 °C for 20 minutes using the diesel burner. Considering the use of catalyzed DPFs in this work, verification of filter pressure drop stability, and the absence of any soot found in the DPFs as part of the post-mortem analysis confirms the data shown in Figure 4 reflects only the ash effect on DPF pressure drop. While all of the lubricants were formulated to a 1.0% sulfated ash level; the specific composition of the lubricant additive packages varied considerably and was listed in Table 4.