Unraveling DPF Degradation using Chemical Tracers and Opportunities for Extending Filter Life

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Ash Impacts Diesel Particulate Filter Performance

- **Ash Sources**
  - Lubricant additives (Zn, Ca, Mg, S, P)
  - Engine wear, corrosion, trace metals in fuels

After only 33,000 miles 50% of material trapped in DPF is ash.
*Assumes 6 g/L maximum DPF PM load prior to regeneration

1. **LONG Time Scale ( ~ 100’s hours)**
   - Ash build-up process and distribution in DPF

2. **SHORT Time Scale ( ~ minutes)**
   - Changes in exhaust flow and temperature (engine control)
Accurately Simulate Key Oil Consumption Mechanisms

- Each parameter independently variable
- Precise control of quantity and characteristics of ash generated

System Specifications

- Exhaust heat exchangers – counter flow
- Centrifugal blower – backpressure control
- D5.66” x 6” DPF
Cummins ISB used for DPF performance evaluation before and after ash loading tests on accelerated test rig.

**Cummins ISB 300**
- Variable geometry turbocharger
- Cooled EGR
- Common rail fuel injection
- Fully electronically controlled
- Gaseous and PM emissions measurement systems

**DPF Flow Bench**
- Core samples: D1” x 6”
- 200,000 hr$^{-1}$ maximum flow
- 700 °C maximum gas temperature
- Air or simulated exhaust
Ash Deposit Build-Up
Ash Build-Up in the DPF is a Dynamic Process

Ash Accumulation

- 60% of ash layer thickness from first 30% of ash deposits
- Ash preferentially accumulates in end-plugs during later stages of ash build-up

~ 100 μm

~ 0.1 μm

~ 10 μm

L/D > 1,000
Additive Tracers

- All oils formulated to 1% sulfated ash
- Applied in series to same DPF (~ 7 kg of oil each)

<table>
<thead>
<tr>
<th>Order of Application</th>
<th>Ca</th>
<th>Mg</th>
<th>Zn</th>
<th>S</th>
<th>P</th>
<th>Total</th>
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</thead>
<tbody>
<tr>
<td>1 Base + Ca</td>
<td>0.30</td>
<td></td>
<td>0.04</td>
<td></td>
<td></td>
<td>0.33</td>
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<tr>
<td>2 Base + Zn</td>
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<td>0.36</td>
<td>0.69</td>
<td>0.33</td>
<td></td>
<td>1.37</td>
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<tr>
<td>3 Base + Mg</td>
<td>0.21</td>
<td></td>
<td>0.05</td>
<td></td>
<td></td>
<td>0.25</td>
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</tbody>
</table>

DPF Specifications

- Cordierite – D5.66” x 6” 200/12, catalyzed
- Washcoat + Pt-based catalyst

Test Fuel - ULSD (Metals below ICP MDL ~1.0 – 0.05 ppm)
Nearly twice as much ash produced with base oil + ZDDP

- Due to greater proportion of sulfur and phosphorous content

Despite 2X more ZDDP ash, little increase in pressure drop

*Total elemental ash-related additive content
Application of Tracer Produces Stratified Ash Layers

- Average Thickness $\mu m$
- Bulk Ash Distribution
- Tracer Distribution
- Distance from DPF Face [mm]
- DPF Substrate
- Ca Ash
- Zn Ash
- Mg Ash
- Radial Center
- Plug

Graphs showing:
- Bulk Ash Distribution with data points for Ca, Zn, and Mg.
- Tracer Distribution with similar data points.
Ash Plug Evolution Consistent with Tracers

Distance from DPF End [µm]

- Ca Layer
- Zn Layer

Relative Abundance

Ca, Zn, Mg
Impact of Exhaust Conditions on Ash Properties
Exhaust Temperature Significantly Affects Ash Volume

- Large decrease in ash volume for temperatures over 700 °C
  - Reduction in ash weight over temperature ranges less than 10%
  - Typical ash porosities 85% - 95% means large potential to reduce volume

Change in Length [%] = dL/Lo
*Sintering Onset

Competing Effects on ΔP Based on Ash Distribution

Temperature [C]

Field CJ-4: *705 °C
Lab Zn: *800 °C
Lab Ca: *1,260 °C
Lab CJ-4: *940 °C

Lost contact with probes
## Ash Core Sample Investigations of Exhaust Effects

### DPF Specifications
- Cordierite D1” x 6” 200/12, catalyzed

### Lubricant Composition
- All oils formulated to 1% sulfated ash

### DPF Ash-Loaded Core Sample Test Procedure (Duplicate)

1. Evaluate pressure drop response using flow bench with air (ambient)
2. Heat core samples in furnace 1.5 hr (650 C…..1,100 C)
3. Re-evaluate DPF pressure drop response on flow bench (1)

<table>
<thead>
<tr>
<th>DPF</th>
<th>Ash Level</th>
<th>Lubricant</th>
<th>Regeneration</th>
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</thead>
<tbody>
<tr>
<td>Cordierite Catalyzed 200/12</td>
<td>12.5</td>
<td>Commercial CJ-4</td>
<td>Periodic</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td></td>
<td>Continuous</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>Base Oil + ZDDP</td>
<td>Periodic</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Base Oil + Ca</td>
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<tr>
<td></td>
<td>29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Short-Term High Flows have Small Effect on Ash Packing

Relative Change in ΔP Before and After Exposure to High Flow

- DPF pressure drop evaluated on flow bench with air at ambient conditions
- Filters heated to specified temperature for 1.5 hours and allowed to cool prior to test

Effect on ΔP -5% to +15%

Max Flow: 200K hr⁻¹
Elevated Temperatures Exert Large Effect on Ash Packing

30% - 60% Reduction in ΔP with Short-Term Exposure to 900°C

Conditions
Air: 25°C
SV: 50,000 hr⁻¹
Large Reduction in Ash Volume at Elevated Temperatures

- 650°C
- 700°C
- 800°C
- 900°C
- 1,000°C
- 1,100°C

ZDDP

Calcium

CJ-4 (P)

CJ-4 (C)

28 g/L

42 g/L

33 g/L
High Temperatures Cause Ash Layer Cracking/Shrinking

Despite large volume reduction, ash weigh change < 7%
Summary and Conclusions

I. Ash Accumulation and Distribution

- Lubricant additive tracers applied to track evolution of ash deposits
- Increase in DPF pressure drop much greater with Ca and Mg than ZDDP
- Ash preferentially accumulates in plug during later stages of deposition

II. Ash Sensitivity to Exhaust Conditions

- Short-term exposure to high flow rates (200K hr⁻¹) exert little effect on ash packing and DPF pressure drop
- Elevated temperature excursions have the potential to significantly reduce ash-related pressure drop 30% - 60%
- High porosity of ash responsible for large reduction in volume when heated
- Effects on DPF integrity and ash removal require additional investigation
Acknowledgements

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  - Valvoline  - Ford  - Lutek

- MIT Center for Materials Science and Engineering
Ash Plug Formation and Build Up

Front of Plug

- Sulfur
- Calcium
- Zinc
- Phosphorus
- Magnesium

Front of plug mostly Mg

Back of Plug

- Sulfur
- Calcium
- Zinc
- Phosphorus
- Magnesium

- No Mg in back of plug
- Zn and Ca dominant