Real-time Measurements of Metallic Ash Emissions from Engines

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Real time ash measurements
Outline

• Introduction
  – Why do we care about ash?
  – How do they form
    • Metals in lube oil – typically 0.5% metal, Ca, Zn, Mg,..
    • Wear metals
  – Structure and size
  – Oil consumption pathways

• Method
• Initial engine results
• Calibration experiments
• New issues
• Conclusions
Importance of ash emissions

• Diesel engines - build-up and plugging of DPF
  – Increased pressure drop - eventually
  – Reduction of useful filter life, increased cleaning frequency
• Gasoline engines
  – Deposition in 3-way catalyst leads to poisoning
  – Same issues as diesel if GPF used
  – Solid nanoparticle emissions if GPF not used, especially with metallic additives
• Relationship to engine lube oil consumption mechanisms

Ash distribution in exhaust filter channels (Heibel and Bhargava, 2007)

3-way catalyst poisoning by ash deposits (Franz, et al., 2005)
Particle formation history – 2 s in the life of an engine exhaust aerosol

Particles formed by Diesel combustion carry a strong bipolar charge.

This is where most of the volatile nanoparticles emitted by engines usually form.

There is potential to form solid nanoparticles here if the ratio of ash to carbon is high.

Formation

Carbon formation/oxidation
\( t = 2 \text{ ms}, \ p = 150 \text{ atm.}, \ T = 2500 \text{ K} \)

Ash Condensation
\( t = 10 \text{ ms}, \ p = 20 \text{ atm.}, \ T = 1500 \text{ K} \)

Exit Tailpipe
\( t = 0.5 \text{ s}, \ p = 1 \text{ atm.}, \ T = 600 \text{ K} \)

Sulfate/SOF Nucleation and Growth
\( t = 0.6 \text{ s}, \ p = 1 \text{ atm.}, \ D = 10, \ T = 330 \text{ K} \)

Atmospheric Aging Exposure

Fresh Aerosol over Roadway–Inhalation/Aging
\( t = 2 \text{ s}, \ p = 1 \text{ atm.}, \ D = 1000 \text{ T} = 300 \text{ K} \)

Increasing Time

Engine ash emissions

- Non-combustible fraction of diesel aerosol
- Derived from metallic lube oil additives and engine wear metals
- Metallic particles tend to ‘decorate’ carbonaceous exhaust particles
- But form separate particles at sufficiently high metal to soot ratios

Jung, et al., 2005

Sappok and Wong, 2007
Catalytic stripper measurements - nuclei mode usually volatile but shows nonvolatile (ash) core at light load
4.5 liter Tier 4 offroad diesel engine
Catalytic stripper measurements - nuclei mode usually volatile but shows nonvolatile (ash) core at light load
4.5 LTier 4 offroad diesel engine
Mass and number emissions and standards

These are lines of constant geometric mean diameter (DGN) and a geometric standard deviation ($\sigma_g$) of 1.9.

- DGN = 25 nm
- DGN = 50 nm
- DGN = 100 nm

Euro VI number stnd.

Tier 4 engine data, N > 23 nm

US tier 4 mass stnd.

Euro VI mass stnd.
Mass and number emissions and standards – note the impact of counting all the ash

These are lines of constant geometric mean diameter (DGN) and a geometric standard deviation ($\sigma_g$) of 1.9.

- Tier 4 engine data, N total
- DGN = 25 nm
- DGN = 50 nm
- DGN = 100 nm
- Euro VI number stnd.
- Euro VI mass stnd.
- US tier 4 mass stnd.
Typical engine exhaust particle size distribution by mass, number and surface area

Nuclei Mode - Usually forms from volatile precursors as exhaust dilutes and cools

Accumulation Mode - Usually consists of carbonaceous agglomerates and adsorbed material

Coarse Mode - Usually consists of reentrained accumulation mode particles, crankcase fumes

In some cases this mode may consist of very small particles below the range of conventional instruments, Dp < 10 nm

A solid ash core may exist under some conditions

Most of the ash usually found in decorated particles in these 2 modes

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High temperature oxidation method (HTOM) overview

Oxidize soot and hydrocarbons within high temperature tube furnace

Cooled particles measured using real/near-real time particle instruments

Diesel exhaust or other metallic ash containing aerosol

Stable metal oxides and other refractory metal compounds are formed or survive high temperature tube furnace
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Engine exhaust apparatus

- Engine Exhaust
- Supply Air
- Ejector pump diluter with critical orifice
- Tube Oven (1 LPM)
- Oven Temperature Logger
- CAI Analyzer Raw NO
- Horiba NO Analyzer Dilute NO
- Other instruments, EAD, EEPS
- Vent

Gladis, 2010
Engine exhaust measurements: volume weighted size distributions

1.9 L VW TDI engine; 1400 RPM/40 N-m; ULSD fuel

Total exhaust - upstream oven

2009/11/02 - Ash
0.5 μm³/cm³

2009/11/10 - Ash
1.3 μm³/cm³

2009/11/12 - Ash
1.2 μm³/cm³

2009/11/02 - Ash
0.5 μm³/cm³

Gladis, 2010
Transient ash emissions

Gladis, 2010
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Spray calibration system with thermal precipitator for collection of TEM samples

Thermal Precipitator
Lube oil spray results: evaporation and oxidation of specially blended lube oils

Gladis, 2010  Center for Diesel Research
# Lube oil spray results: composition of specially blended lube oils and ash survival fraction

## Oil composition, ppm, mass

<table>
<thead>
<tr>
<th>Base stock</th>
<th>B</th>
<th>Ca</th>
<th>Mg</th>
<th>P</th>
<th>S</th>
<th>Zn</th>
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<td>976</td>
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<td>1008</td>
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<tr>
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<td>1998</td>
<td>1008</td>
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<tr>
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<td>802</td>
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<tr>
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<td>2</td>
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<td>3724</td>
<td>57</td>
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</table>

## Ash compound survival fraction

### Concentration

<table>
<thead>
<tr>
<th>Blend #</th>
<th>Element</th>
<th>Compound</th>
<th>Concentration [ppm]</th>
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<tbody>
<tr>
<td>100A</td>
<td>Ca</td>
<td>CaCO3</td>
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<tr>
<td>101A</td>
<td>Zn</td>
<td>ZnSO4</td>
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<tr>
<td>102A</td>
<td>Ca</td>
<td>CaSO4</td>
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<tr>
<td>103A</td>
<td>Mg</td>
<td>MgCO3</td>
<td>500</td>
</tr>
</tbody>
</table>

### Metallic Volume Fraction

<table>
<thead>
<tr>
<th>Blend #</th>
<th>Element</th>
<th>Compound</th>
<th>Concentration [ppm]</th>
<th>Expected</th>
<th>Measured</th>
<th>Measured/Expected</th>
</tr>
</thead>
<tbody>
<tr>
<td>100A</td>
<td>Ca</td>
<td>CaCO3</td>
<td>3946</td>
<td>2.9E-03</td>
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<tr>
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<td>Zn</td>
<td>ZnSO4</td>
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<tr>
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<td>3724</td>
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<tr>
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<td>Mg</td>
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<td>500</td>
<td>5.3E-04</td>
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<td>1.48</td>
</tr>
</tbody>
</table>

**What happened to the zinc compounds?**
**Why is survival fraction so high for Ca and Mg?**

Gladis, 2010

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Engine lube oil spray TEMs

Ca, Mg
TEMs from engine oil ash, very small particles, leftover from decorated soot
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New setup for transient ash measurements

- Engine
- Dyno
- Dilution Tunnel
- FTIR
- Oven: 1100 °C, 1 lpm
- Gas Analyzer
- MicroSoot
- EEPS
- HEPA
- LFE: 8 lpm
- Dilution Air
- Exhaust
- Intake
- PC
Transient ash measurements during speed ramps at heavy and light loads

[Graph showing MS mass, EEPS V, exhaust temperature, and engine speed over elapsed time.]
Real time black carbon and real time ash show similar time response

• This is reasonable as we expect much of the ash to be decorating soot particles (black carbon)
• But it could also mean that there is carbon breakthrough, incomplete oxidation of particles
• Concentrations of ash downstream of oven are very low so downstream ash measurements are challenging
• Measured carbon breakthrough with LII instrument
Black carbon measured downstream of oven using Artium LII300 during temperature ramp.

Carbon disappears at 1100 SS but a pulse appears during load spike.
Further tests show no carbon breakthrough on load transient
Moving forward

• Carbon breakthrough, interference - solved using 1150 C
• New spray calibration experiments with pure salts
  – CaSO$_4$, MgSO$_4$, ZnSO$_4$, Zn$_3$(PO$_4$)$_3$
  – Zinc compounds show higher losses than Ca, Mg?
• Tests with new oils
• Steady state and transient ash emissions
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Conclusions

- We have developed a method that allows us to measure exhaust ash emissions from engines in near real time.
- Results suggest significant ash emission during engine transients, both up and down in load and speed.
Acknowledgements

- We would like to thank BP and Corning for their support of this work.
- The work was also partially supported by internal funding from the U of M
Questions
Background work

New results, upstream and downstream number concentration, downstream size distribution