Penetration of nano-sized metallic fuel additives from diesel vehicles

A. Ulrich, A. Wichser, N.V. Heeb, T. Mosimann, M. Kasper, J. Czerwinski, A. Mayer
Effective reduction of particulates with DPF
Filtration effectivity >99 %

>3 orders of magnitude

1. point

#cm³[dN/dlog(Dp)]

w/o additive
Fe + amine
Fe + amine / DPF
High potential of diesel particle filters
Euro 3 + DPF versus Euro 4 and Euro 5

Alptransit NEAT tunnel (57 km) - the longest rail way tunnel of the world
Soot Reduction at tunnel construction sites due to diesel particle filters (DPF)  

SUVA 2004

![Graph showing soot reduction over time with diesel particle filters.](image-url)

- **760 µg/m³**
- **MAK²**
- **BG²**

1. Maximum working place concentration
2. Background concentration
### Overview DPF Systems with Online Regeneration

<table>
<thead>
<tr>
<th></th>
<th>NO\textsubscript{x}</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuous</strong></td>
<td>SCR</td>
<td>CRT\textsuperscript{®}</td>
</tr>
<tr>
<td></td>
<td>selective catalytic reduction</td>
<td>Continuously regeneration trap</td>
</tr>
<tr>
<td><strong>Discontinuous</strong></td>
<td>NCA</td>
<td>DPF</td>
</tr>
<tr>
<td></td>
<td>NO\textsubscript{x} catalytic adsorption</td>
<td>FBC-DPF: diesel particle filter with fuel borne catalyst</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CSF-DPF: with catalytic coating</td>
</tr>
</tbody>
</table>
Soot combustion dependent on temperature

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**dotted lines w/o catalytic support (additive)**

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1Pierre Macaudiere et al., AFS Conference 2003
Particle Filter System Concepts
Metal catalyzed combustion of collected soot

Fuel borne catalyst

Catalytic coating
Particle Filter System Concepts
Metal catalyzed combustion of collected soot

**Fuel borne catalyst**

- **Addition of metal catalyst to fuel**
  => dosing concept / optimization

- **Catalyst in soot**
  => catalyst in center of particulates
  => higher efficiency of regeneration

- **Shorter regeneration time**
  4 min for 30g of soot (*G. Belot 2003*)

- **Always fresh catalyst**

- **Hazard of penetration**
  additive metals, nanoparticles
  => Increase during regeneration? DPF aging (cracks, ...)?

- **Hazard of precipitation / deposit**
  (homogeneous mixture / mass balance)

**Catalytic coating**

- **No additional metal in fuel**

- **Surface catalyst in coating**
  => direct contact necessary
  => risk of incomplete regeneration

- **Longer regeneration time**
  20 min for 30g of soot (*G. Belot 2003*)

- **Possible aging of the catalyst**

- **Hazard of abrasion lower**
  than penetration (new DPF) => aging?

- **Hazard of accumulation**
  => release; poisoning e.g. sulphur at Pt surfaces
Precipitation of a Fuel Additive
Example for a Mass balance for Cerium -
Total mass per cycle

<table>
<thead>
<tr>
<th>Additive quantity</th>
<th>Cerium</th>
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</thead>
<tbody>
<tr>
<td>Total mass ELPI without trap</td>
<td>2.05 µg</td>
</tr>
<tr>
<td>Total mass ELPI with trap</td>
<td>0.037 µg</td>
</tr>
<tr>
<td>Total mass exhaust gas with trap</td>
<td>15.37 mg</td>
</tr>
<tr>
<td>Total mass exhaust gas with trap</td>
<td>0.27 mg</td>
</tr>
<tr>
<td>Deposition in engine, tank, etc.</td>
<td>457 mg</td>
</tr>
<tr>
<td>Deposition in trap</td>
<td>15.1 mg</td>
</tr>
<tr>
<td>Emitted into ambient</td>
<td>0.27 mg</td>
</tr>
<tr>
<td>Filtration rate in engine</td>
<td>96.7 %</td>
</tr>
<tr>
<td>Filtration rate in trap</td>
<td>98.2 %</td>
</tr>
<tr>
<td><strong>Total filtration rate system</strong></td>
<td><strong>99.94 %</strong></td>
</tr>
<tr>
<td>Emissions factor</td>
<td>0.96 µg/kWh</td>
</tr>
<tr>
<td></td>
<td>0.2 µg/Nm³</td>
</tr>
</tbody>
</table>


Empa, 12th Conference on Combustion Generated Nanoparticles 2008
Release of stored sulphur from Pt coated DPF at $T > 400 \, ^{\circ}C$

- Long term operation at low load conditions (VERT 2000 h operation test, $S < 50$ ppm)
- PM filtration rate: particle No. >98 %, but bad particle mass
- Release time > 30 min

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Set point</th>
<th>n / M</th>
<th>$\Delta m$</th>
<th>$t_s$</th>
<th>$t_e$</th>
<th>Amount of water loss</th>
<th>Cl</th>
<th>NO2</th>
<th>NO3</th>
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<td>2000/530</td>
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<td>481</td>
<td>430</td>
<td>0.8</td>
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<td>&lt;DL</td>
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<td>2000/530</td>
<td>6.1</td>
<td>481</td>
<td>430</td>
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<td>&lt;DL</td>
<td>&lt;DL</td>
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Sulphur Artefacts

Condensation

A. Ulrich et al., 11. ETH Conference on Combustion Generated Nanoparticles 2007
A. Mayer, A. Ulrich et al., SAE 2008-01-0332
Release time for stored SOx artefacts
Results for DPF 7

- Release time > 30 Min
- Higher T promotes release

A. Ulrich et al., 11. ETH Conference on Combustion Generated Nanoparticles 2007
A. Mayer, A. Ulrich et al., SAE 2008-01-0332
Release of stored sulphur from Pt coated DPF at high Temperature long term accumulation at low load conditions

![Graph showing mass in mg for different sample IDs (V23 to V30)]

A. Ulrich et al., 11. ETH Conference on Combustion Generated Nanoparticles 2007
A. Mayer, A. Ulrich et al., SAE 2008-01-0332
Particle Filter System Concepts
Metal catalyzed combustion of collected soot

Fuel borne catalyst

- Addition of metal catalyst to fuel => dosing concept / optimization
- Catalyst in soot => catalyst in center of particulates => higher efficiency of regeneration
- Shorter regeneration time
  4 min for 30g of soot (G. Belot 2003)
- Always fresh catalyst
- Hazard of penetration additive metals, nanoparticles => Increase during regeneration? DPF aging (cracks, ...)?
- Hazard of precipitation / deposit (homogeneous mixture / mass balance)

Catalytic coating

- No additional metal in fuel
- Surface catalyst in coating => direct contact necessary => risk of incomplete regeneration
- Longer regeneration time
  20 min for 30g of soot (G. Belot 2003)
- Possible aging of the catalyst
- Hazard of abrasion lower than penetration (new DPF) => aging?
- Hazard of accumulation => release; poisoning e.g. sulphur at Pt surfaces
VERT Procedures

**Swiss National Standard**

**SNR 277205**

- VSET: Possible formation of
  - toxic secondary emissions
  - penetration of FBC metals
  - abrasion of metallic coating

- **VFT2**: long term behaviour

**Materials Science & Technology**

*Empa, 12th Conference on Combustion Generated Nanoparticles 2008*
ISO 8178/4 C1-cycle for construction site engines

Load

Torque

RPM

Idling

Intermediate RPM

100 %

100 %

75 %

50 %

10 %

0.15

0.15

0.15

0.15

0.10

0.10

0.10

0.10

N. Heeb, EMPA Report 167985

Empa, 12th Conference on Combustion Generated Nanoparticles 2008
VERT
Sampling Procedures

Swiss National Standard
SNR 277205
Principle of Electrical Low Pressure Impactor

ELPI
### Specification of ELPI impactor

<table>
<thead>
<tr>
<th>Stage</th>
<th>Dso% [µm]</th>
<th>Di [µm]</th>
<th>Number min [1/cm³]</th>
<th>Mass min [µg/m³]</th>
<th>Mass max [mg/m³]</th>
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<tr>
<td>12</td>
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<td>8.00E+03</td>
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<td>0.042</td>
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<td>0.005</td>
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</tr>
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</table>
Analysis
Filter Samples

eg. ELPI Filter

Sample Digestion Using Microwave

SEM/EDX

ICP-OES

ICP-MS
Characteristics of Plasma Mass Spectrometry
ICP-MS

- Fast multielement technique 75 elements in 2 min.
- High sensitivity ppb to ppt levels (µg/L - ng/L)
- Large dynamic working range
- Fast scan => transient signals
- Resolution
  quadrupol-ICP-MS ~ 0.7 amu
  high resolution ICP-MS ~ 0.001 amu
Comparison of sensitivity and dynamic working range for different analytical techniques

X-ray techniques (XRF, PIXE, etc)
Types of fuel additives (FBC)
Nanoparticulate (additive fuel suspension)
versus organo-metallic additives (additive fuel mixture)

Iron doped ceria

Ferrocene

Ce/Fe core

$\sim 6 \text{ nm}$

$100 \text{ nm}$
Effect of a metal additive on soot combustion

- dotted lines w/o additive
- solid line with Ce additive
- Pt coating

*Pierre Macaudiere et al., AFS Conference 2003
*K. Ogyu et al., 2006-01-1526
Effect of fuel additives on size distribution

Standard Diesel
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS
Effect of fuel additives on size distribution

Standard Diesel + 5 ppm Ceria Regeneration Additive

100 kW TDI Diesel Engine, 1400 rpm / 50 % Torque, SMPS
Effect of fuel additives on size distribution

Standard Diesel + 10 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS
Effect of fuel additives on size distribution

Standard Diesel + 20 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS

Particle Number Conc.
\[ \text{dN/dlog(Dp)} \text{[cm}^{-3}\text{]} \]

- Standard
- Add. 5 ppm
- Add. 10 ppm
- Add. 20 ppm
Effect of fuel additives on size distribution

Standard Diesel + 35 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS

Particle Number Conc. $dN/d\log(Dp)[cm^{-3}]$

- Standard
- Add. 5 ppm
- Add. 10 ppm
- Add. 20 ppm
- Add. 35 ppm
Effect of fuel additives on size distribution

Standard Diesel + 35 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS

![Graph showing the effect of fuel additives on size distribution. The graph plots particle number concentration (dN/dlog{Dp}) against mobility diameter (nm). The x-axis represents mobility diameter ranging from 10 to 1000 nm, with a logarithmic scale. The y-axis represents particle number concentration ranging from 1.00E+05 to 1.00E+09, also on a logarithmic scale. Two curves are shown: one for standard diesel and another for diesel with 35 ppm Ceria Regeneration Additive. The graph indicates a reduction in particle number concentration for the additive case.]
Effect of fuel additives on size distribution
5 ppm Fe + 31 ppm C8 amine // 5 ppm Fe + 5 ppm Cu regeneration additives

1. point
Effect of fuel additives on size distribution
iron/amine and iron/copper regeneration additive

5. point

- w/o additive
- Fe+amine
- Fe + Cu

#/cm³ [dN/dlog(Dp)]

mobility diameter [nm]
Effective retention for FBC in the DPF
Fe/amine additive

Fe penetration <0.8%
emission factor 1.6 µg/Nm³
Effective retention for FBC in the DPF
Filtration effectiveness >99%

penetration, 1. point

Fe penetration <0.8%
emission factor 1.6 \( \mu \)g/Nm\(^3\)
Effective retention for FBC in the DPF

Fe/Cu additive

Cu penetration <0.1%
emission factor 0.29 μg/Nm³

W/o additive
Fe + Cu
Fe + Cu / DPF

# / cm³ [dN/dlog(Dp)]

mobility diameter [nm]
Effective retention for FBC in the DPF
Fe/Cu additive

Cu penetration <0.1% emission factor 0.29 µg/Nm³
Potential of DPF to reduce toxic components e.g. PAHs / Toxicity

Talk N.V. Heeb

D. Wenger et al., Environ. Sci. Technol. 42(8); 2008; 2992-2998.
Metall emissions determined by XRF

Oxidation catalyst (OC) versus DPF with OC

Effect of metallic fuel additives on formation of secondary emissions e.g. Dioxin with Cu

N.V. Heeb et al., ETH Conference on Combustion Generated Nanoparticles 2007
Is there a difference in penetration of FBC during regeneration phase compared to loading phase?
Relative enhancement of emissions during DPF regeneration phase for a Fe/Cu additive

![Graph showing relative emission of regeneration versus load phase for Fe and Cu additive during DPF regeneration. The graph illustrates the element and size dependent increase of penetration during regeneration phase, depending on loading status of the DPF.]
Loading versus Regeneration phase

Ceria Regeneration Additive – Possible Penetration of the Additive Metal Ce

![Graph showing concentration of Ce (sampling raw gas) and Ce (gravimetric filter) with and without regeneration.]
Loading versus Regeneration

Ceria Regeneration Additive – Possible Release of Stored Metals e.g. Zn

<table>
<thead>
<tr>
<th>Concentration [mg/km]</th>
<th>without regeneration</th>
<th>with regeneration</th>
<th>weighted average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (sampling raw gas)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn (gravimetric filter)</td>
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</tr>
</tbody>
</table>
Loading versus Regeneration
Ceria Regeneration Additive – Possible Release of Stored Metals e.g. Ca
Advantages and Disadvantages of DPF

- High filtration efficiency for particle (> 99 % can be achieved)
- Reduction of toxic and carcinogenic components e.g. PAHs, metals
- Hazard of formation of secondary emission
  Cu (e.g. FBC) supports Dioxin formation, Pt coating tends to sulphur accumulation
- Possible deposition of FBC in the engine (precipitation)
- Fuel additive can change size distribution of emission
- Enhanced penetration of FBC during regeneration phase
  depending on the loading status of the DPF
  (penetration of catalytic metal additive and release of stored metals)
- Contribution of penetration during regeneration is low when short regeneration time is taken into account
  (if DPF ageing effects further increase needs to be checked)
Outlook – Further Investigations

- Localization of additive deposition (engine, exhaust pipe, CVS)
- Does an “initial deposition phenomenon exists? (later release?)
- Long-term stability of additive fuel mixtures (Influence of additive and fuel composition, homogeneity of mixture, temperature stability)
- Influence of lubricants
- Further investigations on the DPF operation conditions loading and regeneration phases (fuel additives, coating)
- Retaining of metals in the DPF (possible release during regeneration?)
- Storage and release effects (e.g. sulphur)
- Long-term behaviour of DPF on penetration or abrasion (aging)
- Comparison of different concepts (DPF + FBC; coated DPF)
Acknowledgements

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- T. Mosimann, A. Hess, M. Kasper (ELPI, SMPS)
  Matter Engineering
- A. Wichser, U. Gfeller, N.V. Heeb, P. Schmid
  (Analysis) Empa
- A. Mayer (Coordination)
- BAFU, SUVA, Industry Partners (Finance)
Thank you for your attention

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