THERMAL STABILITY AND MATERIAL BALANCE OF NANOMATERIALS IN WASTE INCINERATION

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Life cycle of products containing nanoparticles

Possibility of NP release into the environmental compartments:
air, water and soil

- Manufacturing of nanoparticles
- processing industry
- Consumer

waste disposal
- recycling
- incineration
- (landfill)
Project overview

basic lab-scale investigations

Nanoparticle release in incineration plants

behaviour of nanoparticles

Thermal waste treatment

• Lab-scale flame
• Tube furnace

• BRENDA
• Hazardous waste incinerator

ProCycle (NanoCare)

Thermoplastic Nanocomposites

Recycling and thermal disposal

• KLEAA
• Lab-scale flame
Mechanistic hypothesis on the behaviour of NP agglomerates in flames

**Agglomerate**

- **Evaporation & Nucleation**
  - Single, small particles
  - Bigger agglomerates
  - Aggregates
  - Sintering

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Institute for Technical Chemistry

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Thermal stability and material balance of nanomaterials in waste incineration
Stability of NP agglomerates in flames

Slit burner (Atomic absorption spectroscopy)

Number concentration

Mobilitätsdurchmesser $d_{\text{ME}}$ [nm]

SiO$_2$

TiO$_2$

CeO$_2$

Mobility diameter $d_{\text{ME}}$ (nm)

Mobility Diameter $d_{\text{ME}}$ (nm)

Thermal stability and material balance of nanomaterials in waste incineration

Propane / Air
Ceria-particles added to a flame

4 g/l CeO$_2$ in deionized water sprayed flow: 440 ml/min
C/O = 0.333
HaB = 430 mm

$v_{\text{cold}} = 8$ cm/s ($T \sim 1167$ °C)
$v_{\text{cold}} = 10$ cm/s ($T \sim 1233$ °C)
$v_{\text{cold}} = 12$ cm/s ($T \sim 1284$ °C)
$v_{\text{cold}} = 14$ cm/s ($T \sim 1348$ °C)
Tracer experiments at BRENDA pilot scale plant

**Pilot scale incineration plant:**
- Rotary kiln with burning camber
- 3.5 MW
- Flue gas flow: 3 000 m³/h
- 4 flue gas measuring points

**Dosing**
- Concentration of CeO₂ suspension: 1 g/l
- Suspension dosing rate: 10 l/h
- Flue gas CeO₂ concentration: 2.5 mg/m³

**Operation**
- Gas firing
- Coal dust firing
ELPI measurement behind boiler with ceria dosing

Gas firing:
- low fly ash concentration
- ceria nanoparticles agglomerate with fly ash

Coal dust firing:
- high fly ash concentration
Ceria tracer-experiments at hazardous waste incineration plant

<table>
<thead>
<tr>
<th>Measurement point</th>
<th>Position</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosing</td>
<td>After burner chamber</td>
<td>max. 1.100 °C</td>
</tr>
<tr>
<td>M1</td>
<td>Boiler pass 4</td>
<td>530 °C - 580 °C</td>
</tr>
<tr>
<td>M2</td>
<td>Behind boiler</td>
<td>300 °C - 350 °C</td>
</tr>
<tr>
<td>M3</td>
<td>Behind electrostatic precipitator</td>
<td>120 °C</td>
</tr>
<tr>
<td>M4</td>
<td>Stack</td>
<td>150 °C</td>
</tr>
</tbody>
</table>
Material balance of the dosed cerium

- Flue gas: < 0.01%
- Ash: 10.6% 3.3%
- Waste water: 71.9%
- Loss: 17.5%
- Total: 100%

- Filtrate: 0.0%
- Filter cake: 79.2%
- Underground landfill
- Purification plant
- Landfill
# Results of current research projects

<table>
<thead>
<tr>
<th>Incineration type</th>
<th>Fuel / Nanoparticle</th>
<th>Tracer Recovery [%]</th>
<th>Tracer at Stack</th>
<th>Bottom ash</th>
<th>Boiler ash</th>
<th>Filtration / Scrubber</th>
<th>Concentration [µg/m³]</th>
<th>Fraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLEAA (KIT) lab-scale fixed bed combustion facility</td>
<td>Thermoplastic Nanocomposite with 2 % TiO₂</td>
<td>99</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt; 0,1</td>
<td>&lt; 0,01</td>
</tr>
<tr>
<td>100 kW wood boiler * (grate)</td>
<td>Wood pellets with 1% TiO₂</td>
<td>approx. 98</td>
<td>without filtration</td>
<td>&lt; 5.000 (boiler outlet)</td>
<td>&lt; 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage sludge incineration plant * ZVK Neu-Ulm (fluidised bed)</td>
<td>sewage sludge 0,8 % TiO₂</td>
<td>approx. 50</td>
<td>approx. 5</td>
<td>&lt; 20</td>
<td>&lt; 0,01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal waste incineration plant* MVA-Schweinfurt (grate)</td>
<td>Municipal waste 1% TiO₂</td>
<td>92</td>
<td>5</td>
<td>0,2</td>
<td>5</td>
<td>5</td>
<td>&lt; 0,01</td>
<td></td>
</tr>
<tr>
<td>Municipal waste incinerater ** MVA-Solothurn (grate)</td>
<td>Municipal waste a) 10 kg CeO₂ b) 1 kg CeO₂</td>
<td>32</td>
<td>7</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
<td>&lt; 0,01</td>
<td></td>
</tr>
<tr>
<td>BREENDA (KIT) 2 MW combustion chamber</td>
<td>coal dust with 25 g/h CeO₂ 6,5 mg/m³</td>
<td>without grate</td>
<td>3</td>
<td>64</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
<td>&lt; 0,01</td>
<td></td>
</tr>
<tr>
<td>Industrial hazardous waste incineration plant</td>
<td>Hazardous waste with 100 g/h CeO₂</td>
<td>without grate</td>
<td>10</td>
<td>72</td>
<td>&lt; 0,1</td>
<td>&lt; 0,01</td>
<td>&lt;</td>
<td></td>
</tr>
</tbody>
</table>

* UBA-Texte 37/2016 (UFOPLAN-Project 3712 33 327)  
** Walser et. al (2012)
Thermal treatment of thermoplastic nanocomposites and toxicological investigations with air/liquid interface
Conclusion

- Ceria is a useful tracer
- Lab-scale experiments in flames show a new particle mode
- Agglomeration of the ceria nanoparticles with fly ash
- Retention of the ceria particles in the flue gas cleaning > 99.99 %
- Recovery of the dosed cerium > 80% by balancing the mass flows
- Quantitative recovery of cerium in the filter cake
Thank you for your attention!

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Measurement techniques

Scanning Mobility Particle Sizer - SMPS

Transmission Electron Microscopy - TEM

Electrical Low Pressure Impactor - ELPI
Particle number concentration at a combustion plant downstream of the boiler

Calculation based on half-value period of coagulation of monodispersed aerosols with $D_p < 500$ nm

Half-value period for coagulation (sec)

concentration range downstream of a boiler

Number concentration (cm$^{-3}$)