USING THE APPLICATION OF THERMOOPTICAL MEASURING METHOD TO INCREASE THE EFFICIENCY AND MINIMIZE THE EMISSIONS OF COAL-FIRED PLANTS

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Outline

- Introduction to Fraunhofer Germany
- Research fields of Fraunhofer ISC
- Increase efficiency and minimize emissions of coal fired plants using TOM
  - Application of Thermo-Optical-Measuring method
  - Optimization of firing process through in-situ characterization of ash/slag behavior and the interaction with environmental material
  - Characterization of wetting on refractory material and corrosion process
  - Analysis of slag components
  - View to degasing process via IR-spectroskopy

Summary
Fraunhofer-Gesellschaft, the largest organization for applied research in Europe

- 67 institutes and independent research units
- More than 23,000 staff
- € 2.3 billion annual research budget totaling
  - Roughly two thirds of this sum is generated through contract research on behalf of industry and publicly funded research projects
  - Roughly one third is contributed by the German federal and Länder governments in the form of base funding
- International cooperation
Fraunhofer Institutes
Part-time R&D-Partners to meet specific industry needs

Max Planck/ Helmholtz/ Universities

Basic research

Technology development & prototypes

Applied R&D

part-time industry partner

Industry and SMEs

part-time Fraunhofer partner

Commercial application

TRL
9
Fraunhofer-Institut für Silicatforschung ISC – Locations
380 Employees (2014)
27.6 Mio € Budget (2014)
approx. 8,800 m² labs and technical space
5 sites centrally located within Germany

Fraunhofer ISC overview – “It’s a material world”

Material-based solutions

Materials Chemistry
- Inorganic Sol-gel-materials
- Hybrid materials
- Barrier coatings
- Particles

Application Technology
- Micro-optics/Electronics
- Specialty glass
- Dental/Micromedicine

Services
- Applied Analytics
- Device Development
- Cultural Heritage

Center for Applied Electrochemistry
- Battery materials and components
- Testing
- Post mortem analysis

Center Smart Materials
- Adaptive Materials
- Sensors
- Energy harvesting

Fraunhofer Center HTL
High temperature lightweight materials, energy efficient heat treatment
Bayreuth

Project Group IWKS
Materials recycling, substitution, and ressource strategies
Alzenau/ Hanau
Fraunhofer ISC
Our core competencies

**Materials**
- Glass/Ceramics/Fibers
- Nanoparticles
- Battery materials
- ORMOCER®s
- Smart materials

**Processing**
- (Wet) Coatings
- Roll-to-Roll
- Clean room
- Pilot plants
- Demonstrators

**Analytics**
- Materials characterization
- Failure analysis
- Quality control
- In situ test equipment

Solutions for industrial partners

MATERIAL SOLUTIONS INSIDE & ON TOP

pictures: Fraunhofer ISC
USING THE APPLICATION OF THERMOOPTICAL MEASURING METHOD TO INCREASE THE EFFICIENCY AND MINIMIZE THE EMISSIONS OF COAL-FIRED PLANTS
Why using TOM for the optimization on coal fired plants?

- Online view to the real process in the lab furnace → boiler
- Monitoring of efficient conditions through the firing process
  - Decrease temperature → Decrease cost
  - Detection of flow behavior of ash/slag to avoid slagging in the boiler and enforce cleaning process
  - Characterization of wetting on refractory material to avoid corrosion process and increase lifetime of the environmental material
  - Analysis of slag components for quality control
  - View to gasification process via IR-spectroskopy to improve CO₂ capture (CCS)

Higher efficiency + less emission + less cost
Application of Thermo-Optical Measuring procedures (TOM)

In-situ optical investigation of slag and ash behaviour

- Continuous monitoring of sample silhouette by CMOS camera during heat treatment up to 2400°C
- Full automatic control of gas atmosphere
- Additional modules for creep, TGA, viscosity and gas analysis (my physical lab in a furnace 😊)

- Dimension change
- Viscosity
- Creep
- Wetting
Application of Thermo-Optical Measuring procedures (TOM)

THE TOM - PRINCIPLE

- optical axis
- light source
- CMOS-camera
- PC
- balance
- gas analysis/viscosity
- IR/GC
- load
- force
- furnace window

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Application of Thermo-Optical Measuring procedures (TOM)
Application of Thermo-Optical Measuring procedures (TOM)

- Sample size up to 60 mm $\varnothing$
- Temperature range RT – 2400°C
- Resolution ca. 0.3 µm
- Detection of: Sample height, width, area, curvature, contact angle

![Diagram showing the thermal expansion of Al$_2$O$_3$](image)

**CTE of Al$_2$O$_3$**

Thermal expansion of Al$_2$O$_3$

- TOMMI
- Literature data
Application of Thermo-Optical Measuring procedures (TOM)

- Investigation of oxide, non oxide ceramics and powder metals
- In situ measurement of sintering kinetics and warping
- Detection of high temperature reactions
- Investigation of wetting and infiltration processes
- Determination of thermophysical data

Wetting of SiO₂

Infiltration of Si to Carbon
Application of Thermo-Optical Measuring procedures (TOM) on various coal, ashes and slag

- TOM-AC at the IEC (Department of Energy Process Engineering and Chemical Engineering) in use to optimize firing process in the boiler and determine slag behaviour
- Investigations on various coal and biomass ashes within the projects Virtuhcon and DER (density, wetting behaviour, surface tension, degasing, interaction with refractory, …)
- Detection of high temperature reactions
- Experimental investigation of surface tension:

![Images showing slag wetting at different temperatures: -1204 °C, -1309 °C, -1355 °C, -1383 °C]

View to slag wetting at high temperatures
Slag-refractory interactions – TOM-AC

Investigation of wetting behavior

- new developed refractories of different ceramic systems
- test with different ashes/slags (acid, intermediate, basic)
- experimental conditions:
  - up to 1450 °C
  - 10 K/min
  - reducing atmosphere (5 vol.-% H2 in Ar)

\[
\frac{A}{B} = \frac{\text{acid}}{\text{base}} = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}} \quad \text{(Gew.-%)}
\]

\[
T_{kr} = 1385.44 + 74.1 \cdot \frac{A}{B}
\]

Investigation of slag flow behaviour at refractory walls
(entrained flow gasifier)

Aim: validation experiments for numerical simulation

- Observed Phenomena: diffusion of slag into refractory and transition into gas phase (deposition at windows) test with different ashes/slags (acid, intermediate, basic)

- Experimental setup:
  - 3-component slag (Al2O3 - 10 at.%, CaO - 45 at.%, SiO2 - 45 at.%),
  - melting point 1275°C
  - maximum temperature 1300°C, inert conditions (N2 purge gas)

Pictures at different temperatures

-900°C
-1275°C
-1300°C
-1250°C (cooling)
Detection of slag viscosity at high temperatures using Maximum-Bubble-Pressure method

- Ashing and slagging of samples
- Surface detection
- Measurement of Maximum Bubble Pressure
- Derive Density via Subtraction of Pressures

\[ \rho_{1,2} = \frac{\bar{p}_{1,max} - \bar{p}_{2,max}}{g \cdot (h_1 - h_2)} \]

\( \bar{p}_{1,max}, \bar{p}_{2,max}, \bar{p}_{3,max} \) - Derived pressures

Surface Position = -104,665 mm
Detection of slag viscosity at high temperatures using Maximum-Bubble-Pressure method

Lusatian brown coal slag $T=1450 \, ^\circ\text{C}$

Pressures [Pa] vs. Time [min]

- **Calculation of total Bubble Pressure**
  
  $p_\sigma = \bar{p}_{1,\text{max}} - \bar{\rho} g (h_{\text{Oberfläche}} - h_1)$

- **Calculation of surface tension**
  
  $\sigma_H = \frac{p_\sigma \cdot r_{\text{Kap}}}{2}$

- **...if bubbles are hemispherical**
  
  $\sigma_{\text{Schrö}} = \frac{p_\sigma \cdot r_{\text{Kap}}}{2} \left[ 1 - \frac{2}{3} \left( \frac{r_{\text{Kap}} \cdot \rho \cdot g}{p_\sigma} \right) - \frac{1}{6} \left( \frac{r_{\text{Kap}} \cdot \rho \cdot g}{p_\sigma} \right)^2 \right]$  

- **...using the Schrödinger correction**

  $\bar{\rho} = 2990 \, \frac{\text{kg}}{\text{m}^3}$

  $\sigma_H = 0,444 \, \frac{\text{J}}{\text{m}^2}$

  $\sigma_{\text{Schrö}} = 0,442* \, \frac{\text{J}}{\text{m}^2}$

*confirmed magnitude with values from Slag atlas [Allibert et al 1995] (typical range: 0,3 - 0,7 J/m²)
Investigation of the release of volatiles

Release of volatile ash components:

- temperature of degasing and degasing intensity
- pretest for other high temperature investigations within sensitive devices (prevention of over boiling, spattering)
Slag-compound analysis (1)

SEM – analysis with EDX

- analysis of heterogeneous slag compounds embedded with EPO
- 4 different locations on polished cross section
- additional analysis of IR- spectra of slag at high temperature (>1600°C)

SEM with 4-point EDX
## Slag-compound analysis (2)

**SEM – analysis with EDX**

### Table of Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Gewichts%</th>
<th>Gewichts% σ</th>
<th>Atom%</th>
<th>Komponentenn%</th>
<th>Formel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kohlenstoff</td>
<td>0.157</td>
<td>0.657</td>
<td>0.292</td>
<td>0.577</td>
<td>CO2</td>
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<td>Natrium</td>
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<td>1.944</td>
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<td>Aluminium</td>
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<td>Silizium</td>
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<td>Phosphor</td>
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<td>0.059</td>
<td>1.038</td>
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<td>Chlor</td>
<td>0.719</td>
<td>0.033</td>
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<tr>
<td>Kalium</td>
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<tr>
<td>Sauerstoff</td>
<td>43.017</td>
<td>0.685</td>
<td>59.921</td>
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</table>

![Graph showing SEM analysis](image)
### Slag-compound analysis (2)

**SEM – analysis with EDX**

<table>
<thead>
<tr>
<th>Element</th>
<th>Gewichts%</th>
<th>Gewichts% σ</th>
<th>Atom%</th>
<th>Komponenten %</th>
<th>Formel</th>
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</thead>
<tbody>
<tr>
<td>Kohlenstoff</td>
<td>3.658</td>
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<td>Sauerstoff</td>
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### Slag-compound analysis (3)

SEM – analysis with EDX

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<tr>
<th>Element</th>
<th>Gewichts%</th>
<th>Gewichts% σ</th>
<th>Atom%</th>
<th>Komponenten %</th>
<th>Formel</th>
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<td>Aluminium</td>
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<td>Silizium</td>
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<td>Schwefel</td>
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<td>Chlor</td>
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<td>0.035</td>
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<td>Kalzium</td>
<td>2.265</td>
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<td>0.891</td>
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<td>Eisen</td>
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<td>Kupfer</td>
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<td>0.128</td>
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<td>Sauerstoff</td>
<td>66.911</td>
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### Slag-compound analysis (4)

#### SEM – analysis with EDX

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<tr>
<th>Element</th>
<th>Gewichts%</th>
<th>Gewichts% σ</th>
<th>Atom%</th>
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</tbody>
</table>
Slag-compound analysis

IR-Spectra analysis

- IR-analysis of heterogeneous slag compounds during melting-degassing at high temperature (>1600°C) first steps…

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Transmission [a.u.]
Wellenzahl [cm⁻¹]

Different bonds/double bonds of Si, C, O, H
Summary

- Versatile tool for investigation of heating processes up to 1750°C/2400°C to help to understand how to increase efficiency of coal firing process and minimize emissions
- In situ measurement of sintering, shrinkage and warping of various coal, ashes and slag
- Determination of creep, mass change, wetting and crack properties
- Determination of viscosity character of melts, slag
Acknowledgement

Thank you for your kind attention!