Application of thermochemistry for the prediction of slagging in coal fired boilers


*Lausitz Energie Kraftwerke AG

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Introduction

R&D Project KORRISTENT

KORRISTENT

- **Funding** by BMWi (Federal Ministry for Economic Affairs and Energy) program „Anwendungsorientierte nichtnukleare F&E im 6. Energie-forschungsprogramm“, Förderbereich „Kraftwerkstechnik sowie CO₂-Abscheidung und –speicherung“
- **time:** 01/01/2016 - 31/12/2019
- **project ID:** 03ET7066A

**Cooperation partner**

- TU Bergakademie Freiberg
  - Institute of Energy Process Engineering and Chemical Engineering (IEC)
  - Institute of Analytical Chemistry (IAC)
  - Institute of Ceramic, Glass and Construction Materials (IKGB)
- Lausitz Energie Kraftwerke AG

**Objective**

Development of solutions for reduced slagging of coal fired boilers especially for critical fuels
Introduction

Power station Boxberg

**Issue**
  - 900 MW el., pulverised fuel firing systems, tower type boiler, **blend of RW/NO lignite**
  - **Slagging of boiler wall**, sintered deposits at “Schott” (first horizontal tube bundle heat exchanger)
  - Automated cleaning system (water cannons) keeps slagging manageable
  - **decreasing coal quality in future** requires R&D

**Work plan**
  - Analysing context between coal/ash properties, operation parameters and slagging based on process samples
    - Chemical-mineralogical characterization of process samples (XRF, REM-EDX/WDX + EBSD, XRD, CT)
    - Development and application of ICP-OES with electro-thermal evaporation
    - experimental investigations (impedance spectroscopy, simulation of slagging in drop tube reactor)
  - Modelling via thermochemistry and CFD
  - providing applicable proposal for solution
## Analysis of process samples

### Sample pool

<table>
<thead>
<tr>
<th>Sample period</th>
<th>blend RW/NO</th>
<th>coal</th>
<th>fly ash</th>
<th>wet ash</th>
<th>deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>May/June 2015</td>
<td>50/50...70/30...100/0</td>
<td>-</td>
<td>78</td>
<td>-</td>
<td>1 aluminosilicatic slagged</td>
</tr>
<tr>
<td>October 2015</td>
<td>70/30</td>
<td>42 shift samples</td>
<td>42 shift samples</td>
<td>42 shift samples</td>
<td>-</td>
</tr>
<tr>
<td>December 2015</td>
<td>60/40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1 Fe-dominated</td>
</tr>
<tr>
<td>July 2016</td>
<td>100/0</td>
<td>1 mixed sample</td>
<td>48</td>
<td>103</td>
<td>1 aluminosilicatic slagged (large slagged lumps) + 34 Fe-dominated</td>
</tr>
<tr>
<td>November 2016</td>
<td>0/100</td>
<td>1 mixed sample</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>August 2017</td>
<td>50/50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17 Fe-dominated</td>
</tr>
<tr>
<td>December 2016</td>
<td>100</td>
<td>coals and sediments from opencast mine RW</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Analysis of process samples

Coal (set of 42 shift samples RW/NO 70/30)

<table>
<thead>
<tr>
<th>Oxid</th>
<th>Average Ma.-%</th>
<th>Min. Ma.-%</th>
<th>Max. Ma.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>39,8</td>
<td>30,0</td>
<td>50,2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14,7</td>
<td>7,7</td>
<td>20,1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12,2</td>
<td>7,6</td>
<td>15,3</td>
</tr>
<tr>
<td>CaO</td>
<td>12,2</td>
<td>7,7</td>
<td>15,8</td>
</tr>
<tr>
<td>MgO</td>
<td>2,5</td>
<td>1,8</td>
<td>3,2</td>
</tr>
<tr>
<td>SO₃</td>
<td>16,2</td>
<td>10,4</td>
<td>22,5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0,2</td>
<td>0,2</td>
<td>0,2</td>
</tr>
<tr>
<td>K₂O</td>
<td>1,1</td>
<td>0,6</td>
<td>1,8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1,1</td>
<td>0,7</td>
<td>1,5</td>
</tr>
<tr>
<td>Summe</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Ash content 6–12 Ma.-% raw, B/A = 0,3–0,9
- Quartz, clay minerals and pyrite dominate
- Al, Si, 50% Fe, K, Ti → extraneous ash (70%), sediments
- Ca, Mg, 50% Fe → inherent ash (30%), humates
- Flow temperature in red. atmosphere in average 1330°C

→ highly fluctuating coal properties

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formel</th>
<th>Ma.-% coal wf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>10-13</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂(Si₂O₅)(OH)₄</td>
<td>5-11</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₃[(OH)₂</td>
<td>AlSi₃O₁₀]</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>2-5</td>
</tr>
<tr>
<td>Marcasite</td>
<td>FeS₂</td>
<td>max. 0,5</td>
</tr>
<tr>
<td>Anatase</td>
<td>TiO₂</td>
<td>1-2</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄ * 2H₂O</td>
<td>0-3</td>
</tr>
</tbody>
</table>

Base = \( \frac{Na₂O + K₂O + CaO + MgO + Fe₂O₃}{SiO₂ + Al₂O₃ + TiO₂} \)

Acid
Analysis of process samples

Coal (set of 42 shift samples RW/NO 70/30)

- Sediments quartz and clay minerals (kaolinite, illite, muscovite) determine ash content, LHV and B/A
- quartz and kaolinite can be calculated via XRF-Data and stoichiometry (proven by direct measurement via XRD)
Analysis of process samples

Fe-dominated deposit from boiler wall – SEM

- **Fe$_2$O$_3$-Matrix** (layers, formerly melt) with inclusions of alumosilicatic slag and quartz grains
- Intermediate layers from fly ash (unspecific composition)
Analysis of process samples

Fly ash

- Fe$_2$O$_3$ particles
- in large Fe-rich particles FeS-rich centre
- due to particle form formerly liquid
Analysis of process samples

Wet ash and „Schlackestürze“ (large slagged lumps)

- relicts of quartz and clay minerals in recrystallized matrix (pyroxene (\(\text{CaFeSi}_2\text{O}_6\) and \(\text{CaMgSi}_2\text{O}_6\)), anorthite (\(\text{CaAl}_2\text{Si}_2\text{O}_8\)), fayalite (\(\text{Fe}_2[\text{SiO}_4]\)),
- FeS-inclusions
- same composition for aluminosilicatic slagged lumps

Fig.: coarser wet ash

Fig.: Schlackesturz
Analysis of process samples

Mechanism of deposit/slag formation

- formation of FeO-FeS-melt from pyrite
- formation of initial layer on boiler wall, collection of fly ash particles
- mechanism 1: oxidizing of FeO-FeS-melt forms Fe$_2$O$_3$ (see SEM results of Fe-dominated deposits)
- mechanism 2: secondary reaction of FeO-FeS-melt with fly ash particles results in alumosilicatic melt with relicts of quartz and decomposed clay minerals (see SEM results of coarser wet ash and *Schlackestürze*)

→ coarser wet ash fraction corresponds to cleaned slag/deposit from boiler wall
→ definition of slag index: relative amount of wet ash fraction > 9.5 mm

Analysis of process samples

Correlations between slagging and coal properties

- in general a mass balances (coal ash = wet ash + fly ash) is difficult to achieve (Representative samples? Frequency of sampling vs frequency of coal property change? Sampling point before coal distributor!)
  → moving average over two shifts
Analysis of process samples

Correlations between slagging and coal properties

- Salgging ~ heating value
- Salgging ~ 1/ash content
- Salgging ~ 1/(quartz + clay minerals)

![Graph showing correlations between slagging and coal properties.](image)
Analysis of process samples

Correlations between slagging and coal properties

- Slagging ~ B/A
- B/A represents indirectly also other slagging sensitive parameters (ash, quartz+clay, LHV, pyrite)
- B/A connects ash composition with temperature of slag formation ($T_{\text{liq}} = f(B/A)$)

$$\text{Base} = \frac{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$$
Thermochemistry

Basic calculations

• Database: Factsage 7.3 (FToxid; Gtox v2018)
• Calculations in SimuSage (adjustment of T for 100% slag)
• Input:
  • raw coal composition
  • air–fuel ratio = 0.9
  • no flue gas recirculation considered
• validation against AFT (hemisphere temperature at CO/CO₂ 40/60 by vol.) and well established correlation of 
  \( T_{\text{liq}} = f(B/A) \)

Thermochemistry

Basic calculations

• correlation of $T_{\text{liq}} = f(B/A)$ in general visible for both databases
Basic calculations

- Reproducibility of AFT-temperatures for reducing atmosphere 80 K (according to ISO 540: 1995E)
- Robust (simple) prediction of slagging as function of temperature and coal ash composition possible
- Not considered: special role of pyrite, inert amounts of quartz and clay (mullite)
Thermochemistry

Extended Model

• FactSage 7.2, FactPS, Ftoxid, FTmisc

• Input data:
  • fuel analysis of 42 coal samples (LEAG-shift data: ultimate analysis, disulphide, XRF of ash)
  • XRF of wet ash fraction > 9.5 mm (average)

• high degree of freedom (air-fuel ratio, inert components, T – range):
  • modeling FeO-FeS-melt
  • reduce number of free parameters (T, reactive SiO₂-content)
  • apply model on 42 coal samples
1. calculation: pyrite induced melts

Input streams:
- C, H, O, N, S and water of respective coal sample
- Fe content of the ash (Fe₂O₃)
- Combustion air

Parameter variation:
- Air ratio \( \lambda_1 = 0.2; 0.4; 0.6; 0.8; 0.9 \)
- Temperature: \( T = 700 – 1300 ^\circ C \)
- Variation of \( T \) and \( \lambda_1 \) to minimize the difference between the amounts of
  - disulphide in the coal sample and
  - sulphur in the resulting liquid phase

Result:
\( T \) and \( \lambda \) of FeO-FeS-melt formation (ca. 950-1050 °C, \( \lambda = 0.2-0.3 \))
Thermochemistry

Auxiliary calculation

1. auxiliary calculation:
   melting temperature wet ash
   \( T = 700 - 1500 \, ^\circ\text{C} \)

   Input from coal average:
   - C, H, O, N, S
   - \( \lambda_{\text{sec}} = 0.9 \)

2. auxiliary calculation:
   \( \% \text{SO}_2 \) content
   \( T \) from 1. aux. calculation

   Input from coal average:
   - C, H, O, N, S
   - ash
   - \( \lambda_{\text{sec}} = 0.9 \)

Coal sample

1. calculation: Fe-O-S system
   \( T = 700 - 1300 \, ^\circ\text{C} \)
   \( 50 \, \text{K steps} \)
   Input from coal samples:
   - C, H, O, N, S
   - FeO
   - \( \chi_j = 0.2; 0.4; 0.6; 0.8; 0.9 \)
   Result: smallest difference to disulfide content
Thermochemistry

Auxiliary calculation

1. melting temperature of the average slagged wet ash (>9.5mm)

Input:

• C, H, O, N, S and water of the average coal sample
• Ash composition and content of the coarse wet ash fraction > 9,5 mm
• Combustion air $\lambda_{AC1} = 0,9$ (burner belt section)
• Variation of temperature $T = 700 \rightarrow 1500$ °C for 100% slag

Result: melting temperature of the average slagged wet ash

1153°C
Thermochemistry

Auxiliary calculation

2. reactive SiO$_2$ content

Input:

- C, H, O, N, S and water of the average coal sample
- Ash composition of average coal sample
- Combustion air $\lambda_{AC2} = 0.9$
- Temperature: melting temperature from 1. auxiliary calculation
- Variation of the reactive SiO$_2$ amount to minimize the difference between the composition of the coarse wet ash fraction and the liquid phase

Result: reactive SiO$_2$ content of 43 wt. %
Thermochemistry

2. calculation: wet ash/slag

Input:
• 42 shift coal samples
• gaseous and liquid phases from 1. calculation
• Remaining ash components of coal samples (excl. Fe)
• reactive amount SiO₂ content based on 2. auxiliary calculation
• Combustion air \( \lambda_{1+2} = 0.9 \)
• Temperature from 1. auxiliary calculation

Result: amount of slag phase phase determines slagging tendency
Thermochemistry

Calculated slag phase vs Slagging index and Slag incidents
Conclusion

- relations between coal properties and slagging extracted (slagging=f(LHV, quartz, clay, pyrite))
- B/A allows for robust estimation of slagging propensity, whereas slagging ~ B/A within investigated range of composition
- application thermochemistry allows prediction of T-dependent slag formation
- further improvement of thermochemical model by
  - analysis of inert components (quartz, clay in wet ash and fly ash via XRD)
  - improved estimation of temperature (as function of LHV and boiler load)
- practical application of model (or key figure):
  - simplification of model (have to be based on measurable coal and operational parameters)
  - implementation of ETV-ICP-OES as online measurement (multielement analysis, indirectly detection of quartz, clay minerals and pyrite)
Gefördert durch:

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