Corrosion of superheater materials under oxyfuel conditions

R. Kull, M. Stein-Brzozowska, G. Scheffknecht, T. Theye
Jörg Maier
Maier@ivd.uni-stuttgart.de
Background Information

• FP6 Project **ENCAP** co-funded by the European Commission

• ENCAP-Topics of IVD-Oxyfuel combustion:
  • Fuel characterisation (burnout, emission formation NO\textsubscript{x}, CO, SO\textsubscript{2}, H\textsubscript{2}S, SO\textsubscript{3} etc.
  • Air and Oxyfuel combustion tests in a 500 kW test facility
    • Fly ash quality, Deposits
    • Material Corrosion
Content of Presentation

• Sampling and Test setup of 500kW Oxyfuel Facility

• R&D topics
  • Characterization of high temperature Deposit (Lausitz lignite)
  • Carbonisation of Sulfates (laboratory tests)
  • Impact of CO$_2$-rich flue gas atmosphere on formation of oxide layer

• Summery & Future Progress
Deposit-Corrosion Probes (air/oxyfuel)

**Un-cooled ceramic**

Temperature controlled

(Alloys 400-750°C)

\[ T_{\text{sample}} = T_{\text{flue gas}} = 650-1000 \, ^\circ\text{C}, \]

\[ T_{\text{exposed}}: 10 \, \text{h} \]
Characterisation of high temperature deposits of Lausitz lignite under Oxyfuel environment

- Formation of sulfates
- Formation of carbonates?
Element Distribution SEM-MAP – Ca, S, Fe

Collected oxy-deposit on an un-cooled mullite tube, 800°C, 10 h exposure
- Close relation between sulfates and carbon on the particle surface
- Carbon content increased by exposure time
Scheme of change in Fe-particle characteristics during oxyfuel-combustion of Lausitz lignite

Fe-particle in deposit

Fe-, O- enriched
Fe$_2$O$_3$ (Hematite),

CO$_2$-rich environment

T$_{\text{deposit}}$: 800°C

Fe-particle in deposit ($t_{\text{exposed}}$: 10 h)

Fe-, O- enriched
Fe$_2$O$_3$ (Hematite),

Ca-, S-, O- enriched
CaSO$_4$

Ca-, S-, O- enriched, C- enriched
CaSO$_4$, Ca-C…
Laboratory tests with respect to carbonatisation of a Ca-Sulfate deposit in a CO₂-rich environment
Laboratory exposure tests

**CO₂-rich**
- SO₂: 0 %
- H₂O: 10 %
- CO₂: 86%
- O₂: 4 %
- Deposit: 1. Ca-Sulfate / 2. none

**CO₂-free**
- SO₂: 0 %
- H₂O: 10 %
- CO₂: 0%, N₂ 86%
- O₂: 4 %
- Deposit: 1. Ca-Sulfate / 2. none
Exposure of austenite with and without Ca-Sulfate deposit in a CO$_2$-rich atmosphere

austenite [Cr] = 20 %
[SO$_2$] = 0 %, [H$_2$O] = 10 %, [CO$_2$] = 86 %, [O$_2$] = 4 %
T = 650°C, Exposure time: 350 h
Element Distribution along Material Cracks

BSE

Fe

Ni

Cr

O

S
Exposure (350 h) of Ca-Sulfate in a CO$_2$-rich and CO$_2$-free (oxidizing) atmosphere
Summary: Carbonatisation of a Ca-Sulfate

-Ca-Sulfate shows a high tendency to form carbonates in an CO₂-rich atmosphere
-carbonatisation of Ca-sulfates enhances the release of Sulphur Components which promotes sulphur corrosion mechanism
Impact of an CO$_2$-rich flue gas atmosphere on the formation of the oxide scale
Formation of Oxide Scale under Air and Oxyfuel
Summary regarding Formation of Oxide Scale

• for austenitic materials: formation of oxide scale in CO₂-rich flue gas environment shows significant differences compared to the CO₂-lean case

• for austenitic materials: enhanced formation of carbides observed

• impact of increased carbide formation on the formation of a protective and mechanically stable oxide scale requires further investigation

• Impact of Cr-content on formation of protective oxide scale (austenits > 20% Cr)
Future activities

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Exposure time</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMV 310N</td>
<td>650 °C</td>
<td>24/350/500h</td>
<td>Air/Oxyfuel</td>
</tr>
<tr>
<td>Sanicro 25</td>
<td>650 °C</td>
<td>24/350/500h</td>
<td>Air/Oxyfuel</td>
</tr>
<tr>
<td>304 HCu</td>
<td>650 °C</td>
<td>24/350/500h</td>
<td>Air/Oxyfuel</td>
</tr>
<tr>
<td>DMV 617</td>
<td>650 °C</td>
<td>24/350/500h</td>
<td>Air/Oxyfuel</td>
</tr>
<tr>
<td></td>
<td>750 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 263</td>
<td>750 °C</td>
<td>24/350/500h</td>
<td>Air/Oxyfuel</td>
</tr>
<tr>
<td>Alloy 740</td>
<td>750 °C</td>
<td>24/350/500h</td>
<td>Air/Oxyfuel</td>
</tr>
</tbody>
</table>

- impact of coal deposits (bituminous, lignite) and synthetic deposits on sulphur enhanced superheater corrosion
- impact of SO$_2$-rich atmosphere on superheater corrosion
Acknowledgment

The experiences and results are mainly generated in the Frame of the already finished FP6 Project ENCAP
This work has been co-funded and supported by European Commission, Utilities, Manufacturers, etc

The national COORETEC-Project “Corrosion and Slagging in High Temperature Power Plants with advanced Materials”
This work has been co-funded and supported by Bundesministerium für Wirtschaft und Technologie (BMWi) under grant number 0327744A, EnBW Kraftwerke AG, E.ON Energie AG, RWE Power AG, Vattenfall Europe Generation AG&Co. KG, Evonik Steag GmbH, Alstom Power Systems GmbH, Hitachi Power Europe GmbH, AZT Risk & Technology GmbH, Salzgitter Mannesmann Stainless Tubes GmbH, Sandvik GmbH, ThyssenKrupp VDM GmbH, V&M Deutschland GmbH.

Many thanks to the co-authors and especially René Kull and Thomas Theye